FINAL REPORT

Characterization of Residues from the Detonation of Insensitive Munitions

SERDP Project ER-2219

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14. ABSTRACT

Live-fire training is a critical component in the training regimen of militaries. Training with munitions will involve the use of energetic materials. Unfortunately, many energetic compounds are toxic or harmful to the environment and human health. The US Army Cold Regions Research and Engineering Laboratory and Defence Research and Development Canada–Valcartier have developed methods through SERDP and ESTCP programs that enable the reproducible estimation of energetic residues mass DEPOSITION for many commonly used weapon systems. Multi-increment sampling on snow has proven to be the most reproducible method for energetics residues characterization research.

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Table of Contents

List of Tables

List of Figures

ABSTRACT: Live-fire training is a critical component in the training regimen of militaries. Training with munitions will involve the use of energetic materials. Unfortunately, many energetic compounds are toxic or harmful to the environment and human health. The US Army Cold Regions Research and Engineering Laboratory and Defence Research and Development Canada–Valcartier have developed methods through SERDP and ESTCP programs that enable the reproducible estimation of energetic residues mass DEPOSITION for many commonly used weapon systems. Multi-increment sampling on snow has proven to be the most reproducible method for energetics residues characterization research. SERDP Project ER-2219 is focused on three areas: determining mass DEPOSITION and dissolution of insensitive high-explosive compounds from the detonation of insensitive munitions being integrated into US stockpiles, development of analytical methods for insensitive high explosive formulations, and assessing the robustness of the current life cycle environmental assessment process (LCEA) for munitions with respect to the use of these munitions. Four insensitive high-explosive formulations have been tested: PAX-21, PAX-48, IMX-101, and IMX-104. The PAX-21 research indicated significant DEPOSITION of ammonium perchlorate, and the use of these munitions is now restricted. Detonation of IMX-101 and IMX-104 rounds resulted in high residues DEPOSITION of NTO and NQ, both highly soluble compounds. Very high DEPOSITION rates of NTO and NQ from the IMX-101 practice rounds has led to a re-eveluation of the explosive load for these rounds. Combustion products, used in the LCEA process to determine the impact of training with munitions, were compared to DEPOSITION mass for C4 blocks, with a finding that combustion products, when measured, account for only about 7% of the energetics residues from a detonation. In Canada, various configurations of C4 as well as shaped charge donor charges were tested to efficiently blow in place a PAX-48 filled IM 120-mm tank round. The objective was to identify a set-up that would lead to an acceptable deposition rate. Also, the deposition rates of two IM formulations were conducted, as a comparison with the NTO/DNAN family IM formulations. The ER-2219 research has had critical, far-reaching effects on the insensitive munitions community.

Key Words

Insensitive munitions, insensitive high explosives, detonation residues, PAX-21, PAX-48, IMX-101, IMX-104, Ammonium Perchlorate, combustion products, life-cycle environmental assessment, international research

List of Acronyms

AcN	Acetonitrile (a solvent)
AP	Ammonium Perchlorate (a strong oxidizer that can be an explosive)
ARDEC	US Army Armament Research, Development, and Engineering Center
ATF	US Bureau of Alcohol, Tobacco, Firearms, and Explosives
BIP	Blow in place
BRI	Biotechnology Research Institute (National Research Council of Canada)
C4	Composition 4 (a conventional high explosive formulation)
Comp-B	Composition B (a conventional high explosive formulation)
CRREL	US Army Cold Regions Research and Engineering Laboratory
DNAN	2,4-Dinitroanisole (an IHE compound)
DRDC	Defence Research and Development Canada – Valcartier
EFP	Explosively-formed projectile (a munition disposal device)
EOD	Explosive ordnance disposal
EPA	US Environmental Protection Agency
ERDC	US Army Engineer Research and Development Center
GC-μECD	Gas Chromatography-micro Electron Capture Detector
GC-MS	Gas Chromatography-Mass Spectrometer
HE	High explosive (such as TNT and Comp-B)
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (Octogen: an HE compound)
HPLC-ESI/MS	High-performance liquid chromatograph with electrospray ionization – mass spectrometer (an analytical chemistry instrument)
HPLC-UV	High-performance liquid chromatograph with ultraviolet detector
HTBP	Hydroxyl-terminated polybutadiene (an energetic binder and propellant)
IHE	Insensitive high explosive
ITP / IDA	Inside The Plume or Inside the demarcated Deposition Area (Detonation residues surface deposition area)
IMX	Insensitive Munitions eXplosive
MI	Multi Increment® (a sampling method developed for surface characterization)
NQ	Nitroguanadine (a propellant compound used in IHE formulations)
NRMRL	National Risk Management Research Laboratory (EPA)
NTO	3-nitro-1,2,4-triazol-5-one (an IHE compound)
OTP / ODA	Outside The Plume / Outside the Deposition Area (Annular detonation residues surface deposition area(s) surrounding the ITP/IDA area)
PAX	Picatinny Arsenal Explosive (a family of IHE formulations)
PBX	Plastic-bonded explosives
RDX	1,3,5-trinitro-1,3,5-triazine (Hexogen, an HE compound)
RTA	Range and training areas
SPE	Solid-phase extraction (a sample preparation technique)
TATB	2,4,6-triamino-1,3,5- trinitrobenzene (an IHE compound)
TNT	Trinitrotoluene (an HE compound)
UHPLC-MS	Ultra-high-pressure liquid chromatograph – mass spectrometer
UXO	Unexploded ordnance item

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Principal investigators for the project are Drs. Sonia Thiboutot, and Guy Ampleman of Defence Research and Development Canada – Valcartier (DRDC); Michael Walsh, Marianne Walsh, and Dr. Susan Taylor of the Cold Regions Research and Engineering Laboratory (CRREL); and Dr. Brian Gullett of the Environmental Protection Agency. Principal scientific staff in addition to those listed above include Charles Ramsey of Envirostat, Matthew Bigl and Dr. Samuel Beal of CRREL, Dr. Johanna Aurell of the University of Dayton Research Institute, and Drs. Emmanuela Diaz, Sylvie Brochu, and Patrick Brousseau of DRDC. Technical contributors included Annie Gagnon, André Marois, and Annie Martinet of DRDC; Karen Foley, Nancy Perron, Arthur Gelvin, Stephanie Saari, Gary Larsen, Marc Beede, Andrew Bernier, Jordan Hodge, and Ann Staples of CRREL; and William Mitchell, William Squire, and Dale Greenwell of the US EPA.

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Both teams wish to thank SERDP for their continued support for this research. We have published over 30 journal articles for ER-1481 and ER-2219, demonstrating the significance and importance of the research.

Many thanks to all those on our project who assisted in our field tests and in the laboratories, helping to make this project a very productive success.

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Final Report

SERDP Project ER-2219

Characterization of Residues from the Detonation of Insensitive Munitions

INTRODUCTION

Live-fire training is a critical component in the training regimen of a military. Training with combat weapon systems involves the use of munitions that, in most cases, contain energetic materials. Unfortunately, some energetic compounds are toxic or harmful to human health and upon accumulation on training areas, may represent a threat to the environment or to human health. Accumulation of detonation residues containing these compounds on a range can lead to dissolution from the explosive matrix and contamination of surface and groundwater. To determine the loading of a training range with these compounds of concern, it is necessary to derive the deposition mass rates on a per-round basis for these weapon systems. The US Army Cold Regions Research and Engineering Laboratory (CRREL) and Defence Research and Development Canada–Valcartier (DRDC) have developed methods through SERDP and ESTCP programs over the last 10 years that enable us to reproducibly estimate energetic residues mass deposition from many commonly-used weapon systems. Residues masses can be estimated for most common live-fire training operations, such as firing, propellant disposal, engineering training, and detonation of live rounds **[1] [2]**. Multi-increment® sampling on snow is powerful and the most reproducible method we have found for determining mass residues rates and is used in this research **[3]**. SERDP Project ER-2219 is focused on determining mass deposition and dissolution of insensitive high-explosive compounds from the detonation of insensitive munitions(IM) being integrated into US stockpiles **[4]**.

This final report describes research conducted in the US and Canada on analytical methods developed for the new insensitive high explosive (IHE) compounds, energetics residues mass from detonation testing on IM, the efficiency of shaped-charges and demolitions blocks on IM, dissolution tests conducted on post-detonation IHE compounds from various formulations, field comparisons between depositional residues and estimates of airborne contaminant mass based on aerial plume sampling, and a comparative test between command detonation systems for IM developed by CRREL and the US Armaments Research, Development, and Engineering Center. As much of the research described in this document can be found in published peer-reviewed journal articles, many details are not included.

OBJECTIVES

The overarching objectives for this project were to provide the IM and range sustainability research community with reproducible data that can be used in determining the detonation efficiency of various munitions containing IHE and to generate an empirical database that can be used in predicting contaminant loading of training ranges.

Analytical method development is the backbone of the project. The objective of this task was to develop methods that will allow the detection and quantification of IHE compounds from aqueous and solid residues resulting from the detonation of various IM formulations.

The quantification of post-detonation IHE residues from various training scenarios was the main objective of the project. The mass of residues resulting from high-order (HI), low-order (LO), blow-in-place (BIP), close-proximity, and shaped-charge detonation of rounds were estimated to fulfill this

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[1] Multi-Increment® is the trademark of Envirostat, Inc.

objective. Originally, the target formulation was IMX-104. Since the initiation of the project, the list of formulations has been expanded to include PAX-21, PAX-48, and IMX-101.

The characterization of post-detonation particles was the third objective of the project. This objective had two parts: the physical characterization of the larger particles resulting from low-order detonations and disposal operations (size, mass, and constituent distribution) and the dissolution of compounds from the formulation matrix (drip and submersion dissolution).

The fourth objective was to **provide other SERDP IM projects with post-detonation particles** of the various formulations on an as-needed and as-available basis.

The fifth objective covered **an examination of the current Life-Cycle Environmental Assessment (LCEA) process and a determination of the appropriateness of estimating detonation residues based on gaseous combustion products**. This objective was an add-on task to the original project.

A sixth objective, the **testing on IMX-101 rounds**, was not fully met because of extenuating circumstances beyond the control of the project PIs. This objective was also a white-paper add-on task.

In addition to the SERDP objectives, we conducted **comparative command-detonation residues characterization** tests, comparing the residues mass characterization results derived from using the CRREL-developed command detonation fuzing system to one developed by the US Army Armaments Research, Development, and Engineering Center (ARDEC). These tests were conducted on behalf of ARDEC to verify the results initially obtained by CRREL.

Finally, as with all SERDP projects, **dissemination of the research findings** is an important objective. This has been accomplished through peer-reviewed journal articles, formal (reviewed) test reports, contributions to the workgroup on emerging contaminants as a subject matter expert on insensitive munitions residues, presentations to the munitions community, and participation in multinational technology transfer, including NATO research task groups on range characterization. Moreover, technology transfer of the methods developed through SERDP for determining detonation efficiencies has occurred in 2015 and 2017, with the participation by the UK and Finland in the field trials. Both countries are implementing multi-increment sampling and Finland is initiating a munitions characterization research program as a result of their participation..

TECHNICAL APPROACH

Analytical Methods

The current literature on analytical methods for the explosive components of IM was reviewed. Conventional energetic constituents, hexogen (RDX), octogen (HMX), nitroguanadine (NQ), already have well-established analytical methods, many of them developed at CRREL under previous SERDP projects. For the newer IHE compounds, dinitroanisole (DNAN) and nitrotriazolone (NTO), most methods have been developed for lab-scale analysis of pure substances for industrial hygiene purposes, not for environmental applications. **Table 1** contains a list of analytes of interest for the project.

We focused on method development for the High-Pressure Liquid Chromatograph-Ultra-Violet Detector (HPLC-UV), a common analytical chemistry instrument. We took a two-pronged approach to the development of the analytical methods for IHEs. For compounds with currently established but inadequate methods, we did developmental research on mixed and higher-concentration samples using the stated methods to determine if they can be adapted to our needs. For those compounds without methods and for the new IM formulations, we did a product and literature search to determine which columns or solid-phase extraction cartridges held the most promise. Extensive testing was done on the formulation residues using the chromatographic supplies most likely to fit our needs. Recovery of analytes was measured against commercial and lab-constructed standards to determine the efficiency of the system. Recovery times were also measured in an effort to develop the most time-efficient method, knowing we would have many hundreds of sample to analyze over the life of the project. Methods have been optimized for the analysis of PAX-21, PAX-48, IMX-101, and IMX-104 and their constituent compounds in water and detonation residues [5].

Table 1: Compounds of interest in tested IM formulations

Analyte	Type of Compound	Typical Use	IHE Formulation	Method
RDX	Nitramine	High explosive	PAX-21, IMX-104	EPA 8330B [6]
HMX[(a)]	Nitramine	High explosive	PAX-21, IMX-104	EPA 8330B [6]
NQ	Nitramine	Propellant	IMX-101	CRREL [7]
AP	Inorganic salt	Oxidizer**[(b)]**	PAX-21	EPA 6850[(c)][8]
DNAN	Nitroaromatic	Energetic binder	PAX-21, IMX-101, IMX-104	CRREL [9]
NTO	Nitrotriazole	High explosive	IMX-101, IMX-104	CRREL [5]

[(a)] HMX is a manufacturing impurity often found in RDX. It is also a component of booster and supplemental charges.

[(b)] Ammonium Perchlorate (AP) is considered an explosive in particle sizes <15μm [8]

[(c)] Method modified by CRREL to analyze higher concentrations

Residues Mass Estimates: US Tests

Six series of trials have been conducted in the US on munitions containing PAX-21 (2012), IMX-104 (2013, 2014, 2015 (2), and 2017), and IMX-101 (2014 and 2017) (**Table 2**). The trials were composed of three core tests: High-order detonations using a command detonation system employing a fuze simulator (all tests), low-order detonations using the CRREL command-detonation fuzing system (2012, 2013, and 2014), and blow-in-place (BIP) detonations using a single block or two blocks of C4 explosive (2012, 2013, and 2014). The high-order and BIP tests were conducted on snow-covered ice (2012-14, 2017) or a clear ice surface (2015 for IMX-104 rounds and 2017 for IMX-101 rounds). The low-order tests were conducted on a clean ice surface.

Table 2: US Munitions tested to date – SERDP ER-2219

Munition	IHE Filler	Year	Filler Mass[(a)]	Components	References
60-mm	PAX-21	2012	358 g	RDX, DNAN, AP	[9] [10]
	IMX-104	2013	339 g	RDX, DNAN, NTO	[11]
		2017			
81-mm	IMX-104	2013	807 g	RDX, DNAN, NTO	[11]
		2014			[12]
		2015			
		2017			[13]
155-mm	IMX-101	2014	1100 g	DNAN, NTO, NQ	[12]
		2017			[13]

[(a)]Does not include energetics used in the fuze simulator booster cup or the supplemental charges

For high- and low-order detonation tests conducted from 2012 through 2015, the CRREL fuze simulators (CFS) containing various quantities of C4 explosive were used to initiate detonation **(Fig. 1)**. These simulators were previously tested on 81-mm Comp-B (Composition B) mortar rounds **[14]**.

Residues mass and constituents were the same for the Comp-B live-fire and command-detonation tests. For the IM trials, several rounds were detonated prior to the tests with varying amounts of C4 in the booster cups of the fuze simulators to determine the correct fuze simulator booster mass for high and low order detonations. In 2017, a command detonation fuze simulator was designed by ARDEC (AFS) using a modified standard-issue fuze with the original fuze booster pellet during testing. The objective of the AFS was to more closely mimic the performance of a live-fired round.

a) Simulator with C4 booster charge　　b) Installing simulator in fuze well

Figure 1. Fuze simulator for initiating high- and low-order detonations

For the PAX-21 trials, we used an EFP (explosively-formed penetrator) device to conduct disposal tests. Between 57 g and 230 g of C4 was used to drive the EFPs. For the IMX-104 trials, a standard shaped-charge was used for the disposal tests. For these and the BIP tests, either a fuze or a fuze simulator with C4 was installed in the rounds. One to two blocks of C4 in various configurations were used to initiate the rounds for the BIP tests. Because of restrictions on describing EOD operations, the BIP test setups cannot be discussed in this report.

For high- and low-order detonations, the rounds were oriented nose up on snow or ice. For the 2012 PAX-21 and 2017 IMX mortar tests, the tail assemblies were attached to the cartridges with the initiator charge (Charge 0) remaining inside the tail. The external propellant charges were removed **(Fig. 2a)**. For the 2013 – 2015 IMX-104 tests, the tail assemblies were not shipped with the rounds. For high- and low-order detonations, the base of the mortar bodies was screwed into an aluminum plate **(Fig. 2b)**. For both IMX-101 155-mm practice round high-order detonation tests, the projectiles were aligned vertically, base plate down. All BIP, shaped charge, and EFP tests were conducted with the rounds oriented horizontally on ice **(Fig. 2c)**.

a) PAX-21 High order　　b) IMX-104 Low order　　c) PAX-21 BIP (EFP)

Figure 2. IM detonation test setups

The residues from both the high-order and BIP detonation tests were fine grained (<0.1 mm). To efficiently collect a representative sample of the residues, detonations were conducted on snow or ice. Research conducted through 2014 and in 2017 followed the same basic protocol as outlined by Walsh et al. [3]. Surface samples (10- x 10- x 2.5-cm deep) of the residues were collected in triplicate in the demarcated deposition areas and single or triplicate samples were collected from a 0-3 m annulus outside the IDA. A 3-6 m ODA sample was also collected and 2.5-cm deep “subsurface” increments were collected below 20- x 20- x 2.5-cm deep cleared locations throughout the IDA for randomly chosen detonations. In 2015, a total lack of snow at the test site provided an opportunity to collect a “whole population” sample of a high-order detonation. Three rounds were detonated high-order using the CRREL fuze simulator and a C4 booster charge based on previous research [11] [12]. The extent of the visible residues for two of the detonations was demarcated with a global positioning system (Trimble Pathfinder Pro-XH ±10 cm accuracy). All the residues were then swept up and bagged for later processing and analyses (Fig. 3).

Samples were processed in a small lab located on Ft. Richardson, which allowed shipping only dried filters containing the soot fraction of the residues and the extracted and concentrated aqueous portions of the samples back to the CRREL analytical lab in NH. For NTO, NQ, and AP, the concentrations in the aqueous fractions were high enough that extractions were not necessary. Filtrate aliquots (40 mL) were shipped to CRREL for direct analyses of these compounds. Analyses were conducted on an HPLC-UV or UHPLC-MS. Confirmation of some analyses were conducted on a GC-MS if concentrations were low of interferences were suspected. Outside analyses of the AP samples were conducted on an HPLC-ESI/MS.

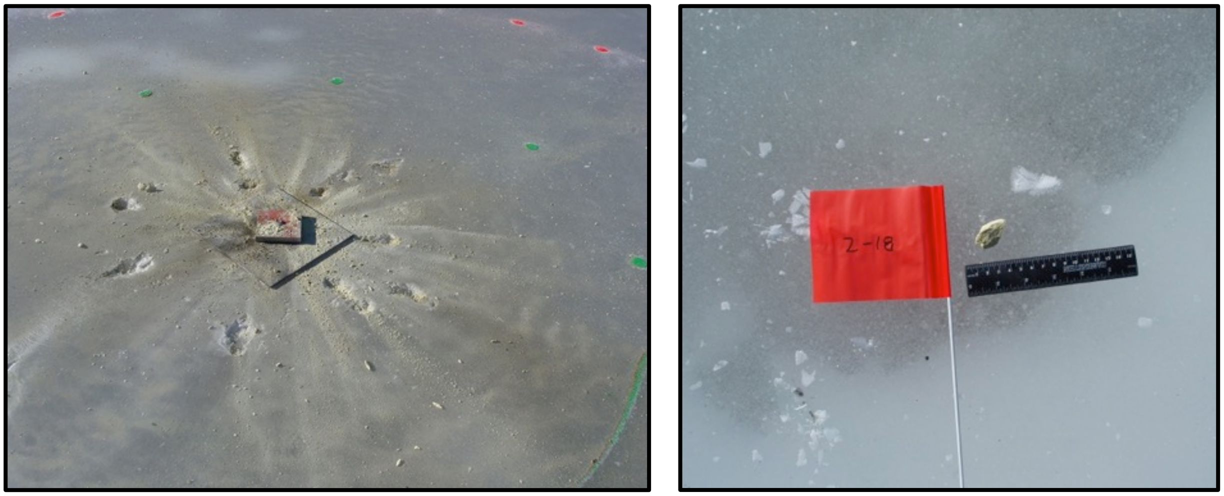

a. HI Resides depositions on ice (black areas are residues)　　b. Sweeping up residues

Figure 3. High-order detonation residues on ice

Particle Characterization: US Tests

IHE Particles were collected following the field detonation of munitions. The particles scattered by these field tests were measured in a variety of ways. Through 2014, particles from low-order, shaped-charge, and EFP detonation of fuzed rounds were sized and massed. From these data, size distributions were constructed that provided information on how the explosive breaks apart when detonated. Small quantities of post-detonation particles were returned to the lab where they were imaged using optical microscopy, Raman spectroscopy, and micro-computed tomography (µCT) to learn the sizes, shapes, and 3-D distributions of the constituent compounds of the various formulations. Some of the particles were also used in drip dissolution tests to understand how quickly these formulations dissolve [15] [16]. We were able to image particles in various states of dissolution using optical microscopy and µCT. The imaging and dissolution results are described in the SERDP ER-2221 Interim Report (Donstova/Taylor).

In 2015, we took advantage of the lack of snow at the test area and the resulting large expanses of clear ice to simulate high-order, low-order, and partial detonations of IMX-104 rounds to determine the spatial distribution of particles. The cold temperature and dry ice allowed the efficient collection of the particles. Sizing and massing of the larger particles (cm size) occurred in the field. Mid-sized particles (mm to cm size) were collected from the ice surface and sized and weighed in the lab on post. The location of these particles was recorded using a GPS. Material on the ice was swept up from meter-wide annuli surrounding the detonation points and bagged according to the distance from the detonation. Smaller particles (<mm sized) were picked out of the bagged material in the lab on post **(Fig. 4)**.

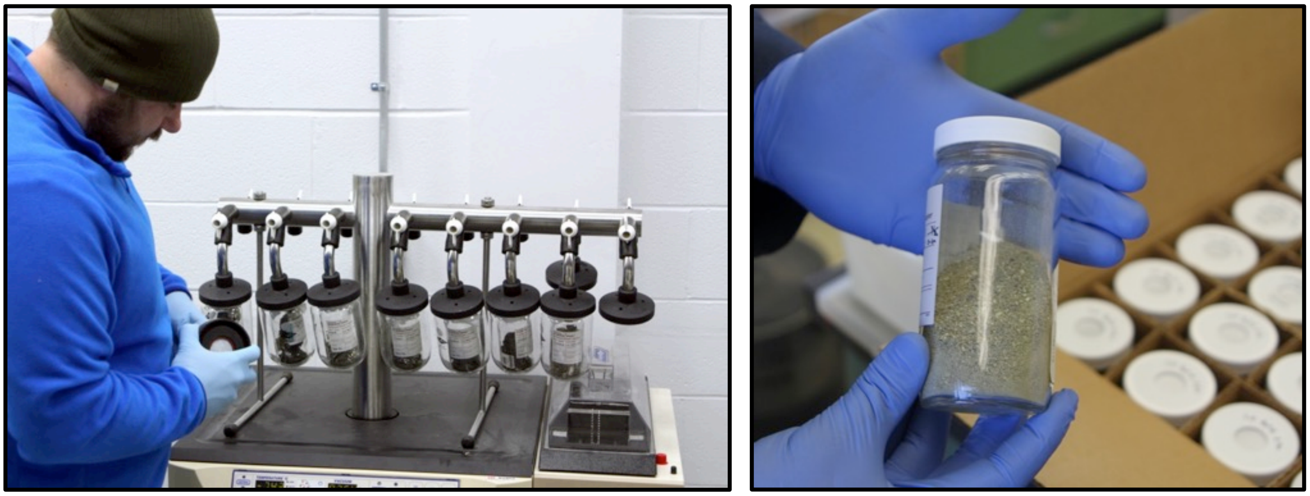


a. Low-order detonation residues b. Ejected particles on ice

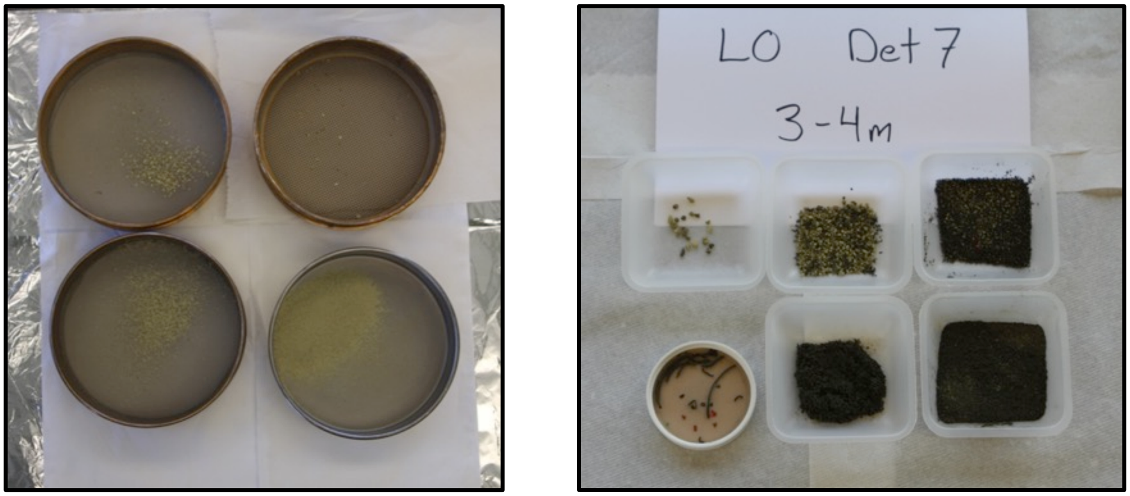
c. Field measurement of particles d. Removing particles from swept areas

Figure 4. Collection of low-order post-detonation particles and chunks in Alaska

The remainder of the swept samples was kept frozen and shipped to the CRREL lab in NH, where they were desiccated in batches in a VirTis Freezemobile 12XL desiccator to remove the ice debris from the detonation residues. The particles were then sieved, binned, and weighed to derive an estimate of the mass, particle size distribution, and number of particles **(Fig. 5)**.



a. Setting samples up on freeze drier b. Particles from one sample



c. Sieved sample d. Binned particles from one annular ring swept sample

Figure 5. Freeze-drying swept samples to extract post-detonation particles

Life Cycle Environmental Assessment: US Tests

Two tests were conducted in 2015 to assess the efficacy of determining energetics residues resulting from a detonation by interpreting air-monitoring sensors for gaseous combustion products. The first test entailed exposing the aerial sampling systems to five co-located detonations of two blocks of C4 (520 g RDX/HMX per block). The second tests entailed exposing the systems to two co-located detonations of a single 81-mm IMX-104 mortar round. The EPA Quality Assurance Project Plan (QAPP) can be found in **Appendix B**.

Two systems were used to collect air samples. The first system was a pair of remote-controlled “flyers”, air-monitoring systems mounted on a cable suspended over the detonation points. These systems are designed to traverse through the aerial detonation plume to ensure they collect a sectional sample **(Fig. 6)**. However, equipment problems resulted in the flyers being statically suspended on the cables for the tests. Each flyer contains C/CO_2 sensors and an 81-mm square quartz fiber filter. Air is pulled through the quartz filter at 1200 L/min. In addition to the flyers, a suite of air sensors was suspended from a small hexacopter unmanned aerial system (UAS) from the University of Alaska, Fairbanks, which was flown through the plume. The purpose of testing this system was to determine if a UAS could be used to estimate energetics in a detonation plume. Energetics estimations based on the combustion products detected by both systems were compared to both the surface residues (on snow) and residues captured on the 81-mm square filters on the two stationary air monitoring systems (flyers) based downwind from the detonation points.

Figure 6. Flyers suspended on cables downwind from C4 detonation point

The filters were labeled as indicated in **Table 3**. After sample collection, each filter was wrapped in aluminum foil and a plastic bag and placed in a freezer. The filters were stored frozen until they were shipped overnight in a cooler with Blue Ice to the CRREL laboratory in Hanover, NH. Upon receipt, they were placed in a freezer until they were processed for analysis of energetics.

Table 3. LCEA Test Sample List

Sample ID	Sample Date	Matrix	Remarks	RDX Mass (µg)*
BS-Qfilter-020715	02/07/15	Background	Flyer #1, Outside lab building, ~3 hr sampling	<d, <d
PS-C4-Qfilter-OR-021115-01	02/11/15	C4	Flyer #1, ~0.06 g Carbon	0.14, 0.13
PS-C4-Qfilter-WI-021115-02	02/11/15	C4	Flyer #2, ~0.06 g Carbon	0.25, 0.20
PS-81-Qfilter-OR-021315-01	02/13/15	81mm	Flyer #1	<d, <d
PS-81-Qfilter-WI-021315-02	02/13/15	81mm	Flyer #2	<d, <d

Energetics were extracted from the filters using acetonitrile. First, each filter was placed in a wide-mouth 500-mL jar, then 10 mL aliquots of acetonitrile were added until the filter was immersed in solvent. Fifty milliliters of solvent were needed. The jars containing the filters and solvent were placed on a platform shaker and rotated at 175 rpm for 18 hours. The filter extracts were analyzed by Gas Chromatography-Micro Electron Capture Detector (GC-µECD) using US EPA Method 8095: Explosives by Gas Chromatography [17]. Extracts were also analyzed by US EPA Method 8330B: Nitroaromatics, Nitramines and Nitrate Esters by HPLC [6].

GC-µECD

The acetonitrile filter extracts were filtered through Millipore Millex-FH (PTFE 0.45 µm) filter units and transferred to autosampler vials that were then placed into an Agilent 7693 Series autosampler tray. A 1-µL aliquot of each extract was directly injected into the Agilent 7890A purged packed inlet port (250°C) containing a deactivated Restek Uniliner (Catalog #20964). The primary determinations were conducted on a 6-m × 0.53-mm-ID RTX®-TNT fused-silica column that has a 1.5-µm-thick film of a proprietary Crossbond phase. The GC oven was temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 250°C. The carrier gas was hydrogen at 1.4 psi inlet pressure. The µECD detector temperature was 290°C; the makeup gas was nitrogen at 45 mL/min.

Extracts were also analyzed using an RTX®-TNT2 confirmation column on an HP6890A gas chromatograph equipped with a splitless injector. The injection port liner was a deactivated Restek Uniliner (Catalog #20336). Column dimensions were 6-m X 0.53-mm-ID with a 1.5-µm film thickness. The GC oven was temperature-programmed as follows: 130°C for 1 min, 10°C /min ramp to 160°C, 30°C /min ramp to 270. The carrier gas was hydrogen at 1.6-psi inlet pressure. The µECD temperature was 275°C and the make up gas was nitrogen at 60 mL/min.

HPLC-UV

Extracts are mixed 1/3 v/v with water and filtered through Millipore Millex-FH filter units prior to injection (100 µL) into the HPLC-UV. The output from the UV detector was monitored at two wavelengths: 230 nm (optimal for RDX) and 295 nm (optimal for DNAN). The chromatographic separation was achieved on a 15-cm × 3.9-mm (4-µm) NovaPak C-8 column maintained at 28°C and eluted with 15:85 isopropanol/ water (v/v) at 1.4 mL/min.

Calibration Standards

RDX concentrations were estimated from peak height measurements and compared to a commercial (Restek Corp.) single analyte standard. In addition, a multi-component mix (8095 Calibration Mix A containing HMX, RDX, TNT, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,3,5-TNB, 2-Am-4,6-DNT, 4-Am-2,6-DNT, and tetryl) was analyzed for verification. DNAN concentrations were estimated based on a calibration solution prepared from reference material obtained from the manufacturer BAE Systems (Kingsport, TN). Standards were prepared at 2, 20, and 100 µg/L.

In addition to the field work, foreign and domestic LCEAs were reviewed to determine post-detonation residues were being adequately address. A total of six LCEAs, the most recent being for the PAX-21 rounds, were reviewed.

Residues Mass Estimates: Canadian Tests

In Canada, an insensitive explosive named GIM (Green Insensitive Munitions) was developed and patented by DRDC-Valcartier **[18]**. This new explosive is a melt cast formulation where TNT in the molten state is used as an organic solvent to dissolve and incorporate into the formulation an energetic copolyurethane thermoplastic elastomer also developed and patented by DRDC Valcartier **[19].** The copolyurethane is giving the insensitive character to the formulation. Another Plastic Bonded insensitive eXplosive (PBX) formulation based on Hydroxyl Terminated Polybutadiene cured to get a thermoset matrix surrounding HMX was also tested to compare with the GIM explosive. PBX formulations are presently fielded in France and also very popular in the U.S. Navy. A representative formulation of this family of IM formulation was adapted by DRDC Valcartier and was named CX-85.

In order to evaluate the Canadian formulations and to compare with the US insensitive formulations PAX and IMX, deposition rates evaluation for GIM and CX-85 was performed in February 2012 using snow cover, as in the US trials **[1 - 3]**. Twelve 105-mm munitions were prepared by Mr. Brousseau and his team, six filled with GIM and six with CX-85. The deposition rates for the munitions were evaluated for two scenarios; normal functioning (HO) and BIP. Large ice blocks were used to minimize the risk of penetrating the soil profile underlying the snow, thus minimizing the risk of cross-contamination **(Fig. 7).** For the high-order tests, the noses of the 105-mm munitions were filled with C-4 (20 g) under a plastic cap screwed on the nose. A detonation cord was placed in contact with the C-4 through an aperture in the plastic cap and a detonator was placed in contact with the det cord two feet away. Prior to detonation, the rounds were placed vertically on the ice block. For the BIP scenario, the noses of the munitions were closed with a screw cap and a block of C-4 was fixed to the side of the 105-mm munitions. Three GIM and CX-85 munitions were used with the normal functioning set-up while three were used with the BIP set-up. A total of twelve detonations were performed.

Canada has recently purchased 120-mm IMHE tank cartridges developed by Nammo and produced by General Dynamics Ordnance and Tactical Systems - Canada (GD-OTS-C). The IMHE filling is one of the new IM melt-cast formulations developed by ARDEC. In light of DRDC's expertise within our SERDP ER-2219 involvement, Director General Land Equipment Program Management (DGLEPM) or namely the Directorate Armament Sustainment Program Management (DASPM) and Director Land Equipment Program Staff (DLEPS) tasked DRDC to measure the deposition rates of 120-mm IM rounds in both high order (HO and blow in place (BIP) scenarios. In order to assess 120-mm components DR, 120-mm rounds were provided to DRDC Valcartier by DSAPM through GD-OTS Canada. Ten rounds were detonated in 2014, six in 2015, seven in 2016, and six in 2017. The IM explosive formulation used in these 120-mm rounds is named PAX-48 and is based on DNAN, NTO and HMX. The information related to the respective percentage of each ingredient and on the total mass of energetics per round was provided to DRDC and cannot be released here. The rounds tested were prepared by the Explosive Ordnance Disposal (EOD) team to mimic the detonation of a regular round or a BIP operation as described in the experimental section. The pictures and descriptions of the BIP set-ups cannot be released in this report, as it is considered as Control Goods sensitive information, but it can be released to specific US recipients, upon formal request to Dr. Thiboutot, as upon an acceptable controlled-goods mean of transfer of information.

Experimental Section

Trials were conducted at the Defence Research and Development Canada (DRDC) Valcartier test site located on the Valcartier RTA, and followed the protocol developed by Walsh et al. **[3]**. The tests were conducted in two windows: in February 2014 over a period of four days and in February 2015 over a period of two days. This was achieved in collaboration with the Munitions Experimental Test Center Valcartier and CRREL. It involved EOD personnel responsible for the explosive initiations and detonations. The deposition trials were conducted during the winters of 2014, 2015, 2016, and 2017 at the Defence Research and Development Canada (DRDC)-Valcartier Research Center test site located on the Canadian Forces Base Valcartier RTA. The tests were conducted in four events: Ten rounds were detonated in February 2014 over a period of four days, six in February 2015 over a period of two days, seven in March 2016 over a period of three days, and six rounds in march 2017 over one day. All trials were achieved in close collaboration with the Munitions Experimental Test Center Valcartier (METC) and involved EOD personnel responsible for the explosive initiations and detonations. In 2016 and 2017, Defence Construction Canada (DCC) was also actively involved for project management and sub-contracting field work.

In 2014, the weather conditions were average for February, with light winds and temperatures between -18 to -8 ^{o} C with a snow cover of 0.9 meter deep. Freezing rain occurred prior the trial and led to a solid snow pack, favourable to the deposition trial. In 2015, the weather conditions were similar, with an overcast sky and temperatures around -10^{o}C with a snow cover of 0.7 m deep. In 2016, the weather was a challenge, with unusual high temperatures in February and little snow on the soil surface. Early March snowfall allowed the trial to be held in mid-March, with a snow pack of approximately 0.5 m deep, considered as the minimal thickness for such work. The temperatures were also at their acceptable limits, and varied between -5 and -1^{o} C, with an overcast sky. In 2017, high snow falls prior to our test allowed a deep pack of snow (1.3m) and perfect weather conditions with an overcast sky and -14^{o} C, with no wind.

For all four trials, prior to detonations, one to six field blanks were collected in the areas where the detonations would later be performed in order to assess the explosive background contamination In 2014, ten detonation points (DP) were selected using sufficient distances (around 70 m) between the DPs along two access roads. All locations were selected similarly in 2015-2017. Walking trails were created using snowshoes to reach the DP to ensure EOD safety, and large ice blocks (50 x 100 x 25 cm, see **Fig. 7**) were placed at the DP to minimize the penetration of the detonation into the soil profile, thus avoiding cross-contamination coming from the soil underneath.

Figure 7. Ice blocks used for the trial

Detonation initiations

The 120-mm rounds were placed on the ice blocks and detonated using the following scenarios. Please note that further details related with the detonation scenarios were provided to DoD and SERDP but involve controlled goods material that cannot be published openly.

- High Order set-up

In order to mimic HI detonation, C4 plastic explosive was packed inside the nose of the round to completely fill the cavity left for the fuse and was covered by a nose plug to ensure confinement. The detonator was inserted in the middle of the nose plug in a hole designed in the plug. The detonator was wired for electric initiation. In order to assess the reproducibility of our set-up and the validity of our results, five replicates of the HI were done.

- BIP set-ups using C4

In the BIP scenario, the nose of the round was closed using a plug to mimic a UXO and bring a certain confinement that would be representative of a fuzed UXO. Four BIP set-ups were studied involving C4 in various configurations. Based on the limited availability of 120 mm rounds, between three and four replicates were done using each set-up. For the sake of this report, we will refer to donor charge C4 configuration A to D.

- BIP set-ups using shaped charges

The results obtained for the C4 set-ups indicated deposition rates of concern of the insensitive constituents. In 2015, in order to study alternative BIP methods and with the objective of reducing the deposition rates, three types of commercially available shaped charges were investigated as donor charges in a few configurations. Commercially available shaped charges, produced by SAAB Bofors Dynamics Switzerland Ltd, referred to as the SM-EOD suite, were used and will be described later on in this section. Two calibers of the Bofors shaped charges were used in this study, the SM-EOD 33 and the SM-EOD 67, with respective diameters of 33 and 67 mm. A third type of shaped charge was extracted from an 84-mm Karl Gustav shoulder-fired antitank weapon to investigte if a larger shaped charge would decrease the BIP DR. Detailed information on the BIP set-ups has been provided to DoD and SERDP upon acceptable Controlled-goods information exchange.

Sample collection, processing and analytical methods

Following detonation, as soon as the EOD personnel cleared the sites, the outline of the residues deposition areas were visually demarcated by walking around the perceived terminus of the residues. This area was designated as the Inside the Deposition Area (IDA). The outline was traced using a global positioning system (GPS) and the deposition area was integrated. An annulus of approximately 2-m wide was then walked around the border of the IDA. This area was designated as the Outside of the Deposition Area (ODA). **Figure 8** illustrates the visual deposition pattern of one of the detonations. Precautions were taken to avoid bringing cross-contamination between the depositions by washing the snowshoes and the sampling gear using clean snow and wipes.

Figure 8. 120-mm detonation residues showing whole deposition area

Once the areas were demarcated, two person teams sampled the IDA areas by collecting three field replicates of composite samples using the method described by Walsh *et al.* **[3]**. In our study, one person was dedicated to collect the ODA residues in two replicate. Surface snow samples (10- x 10- x 2.5-cm deep) were collected using specifically designed spoons. Around 100 increments were collected using the Multi-increment[1] sampling (MIS) random systematic approach inside the IDAs **(Fig. 9)**, while around 60 increments were collected in ODAs. The number of increments was adapted to statistically represent the whole IDA area and large composite snow samples were built using this strategy. The exact amount of increments was recorded to allow the calculation of the IDA rate in function of the surface area collected.

Figure 9. 120-mm residues deposition after sampling was conducted

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Snow samples were brought back to the laboratory and kept frozen at -20^{o}C until processing. Before melting the snow samples, the snow was transferred to clean polyethylene bags to avoid potential cross-contamination (**Figs. 10, 11**). Samples were processed by melting the snow overnight at room temperature, and the melted water was filtrated using 45µ glass microfiber filters 90 mm Whatman Cat No 1820-090 to remove the solid soot residues (**Fig. 12**).

Figure 10. Transferring snow sample to a clean bag prior to melting overnight

Figure 11. Melting the snow sample

Figure 12. Sample filtration

Whenever the samples clogged in the filtration process, filters were changed. All filters used for the same sample were combined, air-dried away from light in clean 125-mL amber glass jars (**Fig. 13**) and extracted using 40 ml of acetonitrile overnight using a shaker table. The aqueous portion was combined in a large jar, carefully homogenized through vigorous mixing and then measured as shown in **Figure 14**. Two aliquots were poured into 500-ml amber glass bottles for subsequent analysis for HMX, RDX, and DNAN. In addition, two 40-ml aliquots were poured in 125-ml amber glass jars for analysis of NTO.

In 2014, for fifteen samples, three 500-ml amber glass bottles and three 40-ml aliquots were decanted, and one sample out of three were sent to the Biotechnology Research Institute (BRI) for inter-laboratory confirmation. This was done because it was the first time that DNAN and NTO were extracted and analysed at DRDC. Solid-phase extractions (SPEs) were performed on the 500-ml aliquots for future analyses of HMX, RDX, and DNAN (**Fig. 15**). The aliquots were concentrated at 100:1 in acetonitrile

(AcN) during the extraction of the analytes from the Waters Porapak RDX SPE cartridge, since the volume was reduced from 500 to 5 ml. Sample preparation followed EPA Test Method for Solid Waste (SW-846) Method 8330B (US EPA 2006) [6]. All glassware used in the process were carefully washed with water and soap, and then rinsed three times using de-ionized Type-1 reagent grade water (18 MΩ-cm) (Fig. 16). Laboratory blanks were included in the process to ensure its effectiveness. A series of laboratory control samples, consisting of reagent grade water (18 MΩ-cm) spiked at various concentrations of energetics within the calibration curves of the target analytes were run to determine their recovery.

Figure 13. Filters combined and dried in amber glass containers

Fig. 14. Measuring the aqueous phase volume

Fig. 15. Desorption from Waters Porapak RDX SPE

Figure 16. Glassware cleaning process

Analyses on the solvent extracts were conducted using two analytical chromatographic methods. The extracts were analyzed for DNAN, RDX and HMX by High Pressure Liquid Chromatography (HPLC) with a photodiode array detector, on a Supelcosil LC-18, 250 x 3mm x 5µm column and a mixture of water and methanol (50%) as the eluent and using an external calibration curve between 0.05 and 10 mg/L. The detection limit in the sample extracts was 0.05 mg/L for the three compounds, which is equivalent to 0.0005 mg/L in the aqueous samples that were pre-concentrated by a factor of 100 using SPE. When no detectable levels of the analytes were obtained, extracts were re-analyzed using a gas chromatographic (GC) method on a DB-1 column of 7.4 m, with a nominal diameter of 530 µm and a nominal film thickness of 1 µm and, also using a secondary column as a DB-200 of 5.9m, with nominal diameter of 530 µm and a nominal film thickness of 1 µm. The inlet was a cool-on column injector used with hydrogen in a constant flow mode. The columns were coupled to electron capture detectors (µECD) and an external calibration curve was used between 0.1 ng/ml and 20 ng/ml. The GC method led to a detection limit of 0.01 ng/ml equivalent to 0.0001ng/ml in the aqueous samples that were pre-concentrated.

NTO was analyzed following a method developed by Marianne Walsh from CRREL. Samples were injected using a matrix of 1:3 water:AcN. For the aqueous melted snow samples, 1 mL of the aqueous sample was mixed with 3 mL AcN. For the filtered soot extracts, 1 mL of the AcN extract was mixed with 2 mL of AcN and 1 mL of reagent grade water. The method involved a modular system from Thermo Scientific composed of a Spectra-System Model P4000 pump, a Spectra System UV2000 dual wavelength UV/VS absorbance detector set at 315 nm, and a Spectra System AS300 autosampler. The column was a 100 x 3 mm (3 µm) Hypercarb from Thermo Scientific eluted with 0.6 mL/min of 25:75 (v/v) water/AcN with 0.1% trifluoroacetic acid (Fisher HB9813-4) at 30°C. The calibration range for NTO was from 0.02 to 10 mg/L and the estimated detection limit was 0.02 mg/L.

Calibration standards for RDX, HMX and NQ were prepared from commercial solutions obtained from Accustandard. Calibration standards for DNAN and NTO were from solid reference materials from GD-OTS Canada. Replicate stock solutions at 1000 mg/L were prepared in AcN for all analytes. The calibrated range for the UV detector was from 0.02 to 10 mg/L for RDX, HMX, and DNAN and 0.002 to 10 mg/L for NTO.

Shaped-charge efficiencies

DRDC investigated the use of commercially available shaped-charges to develop an efficient, safe, clean, and simple method to blow-in-place both conventional and insensitive munitions in a summer trial in 2013. SAAB Bofors Switzerland manufactures shaped charges for destruction and demining activities, referred to as SM-EOD system, until late 2012 [20]. They created a range of Explosive Ordnance Disposal (EOD) products known as the SM-EOD family. SM-EOD products can be deployed for military use, providing a precision shaped-charge jet with no need for contact with the target. The SM-EOD charge comes with its own lightweight adjustable tripod or support rods that allow the charge to be aimed against a specific point on the UXO. The stand-off distance from the target can be from a few millimeters up to 10 m depending of the size of unit selected. SM-EOD charges can be used for the destruction of all types of unexploded ordnance, from 5 g – 1000 kg, especially where physical contact is not possible. The operational concept is that the high shaped-charge jet velocity perforates the suspect target case and either causes a low order reaction or initiates detonation of the explosive charge. An experienced operator has the ability to select a disposal mode that meets the circumstances, and a user's manual is provided that provides guidance to trigger the desired reactions. These tools were assessed by the U.S. Institute for Defense Analysis for the US military [21].

In this summer trial, the shaped charges' subjective efficiencies were tested against in service ammunition and 105-mm artillery projectiles filled with IMX-104 provided by General Dynamics Ordnance and Tactical Systems-Canada (GD-OTS Canada). The ultimate objective was to validate if the shaped-charges would cause better BIP outcomes, both for high and low order reactions and how they would react against IM rounds. The low order detonations will not be discussed here, as this objective was for Canadian EOD needs only. No detonation residues were collected in this trial, which was conducted in the summer on a sandy surface.

Two types of SM-EOD shaped-charges were acquired and tested: the SM-EOD 20 (11 g of pressed RDX) and the SM-EOD 33 (57 g of pressed RDX). Both systems are shown in Figure 17. These systems were selected based on their flexibility and safety features. All systems come with a tripod that allows triggering high or low order reactions by varying the stand-off distances between the UXO and the shaped-charge and the location where the jet hits it. In a follow-up test, a shaped-charge was extracted from a Carl Gustav 84-mm shoulder-fired rocket. The objective was to test the effectiveness of a larger shaped-charge than the 33-mm SM-EOD 33.

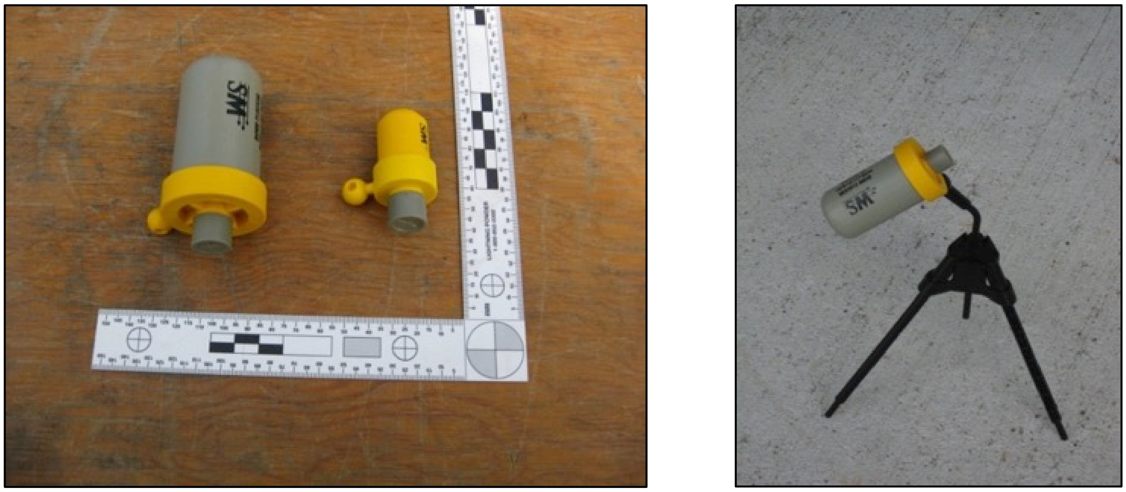

Figure 17. Shaped-charges: SM-EOD 33, SM-EOD 20 and SM-EOD 33 with the tripod.

The trial was carried out at the demolition site of DRDC Valcartier and was conducted from 3 to 12 July 2012 and from 23 July to 2 August 2012. A detonation arena was constructed using concrete blocks to avoid the dispersion of the explosive filling when a low order occurred. The SM-EOD charges were used in various configurations on the following munitions items: C13 hand grenade, 40 mm rifle grenade, 60-mm mortar projectile, 66-mm rocket warhead, 81 mm mortar projectile, 84 mm Carl Gustav rocket warhead, 105-mm howitzer HE projectile, 155-mm howitzer HE projectile, and 105-mm IM projectile (Fig. 18). Munitions were placed on the surface or were buried in the ground. The shaped-charges were placed over the munition and aimed at different locations to obtain either low-order or high-order detonations. The stand-off distances and angles of attack between the shaped-charges and the UXO were varied. After the detonations, an ammunition technician confirmed the type of the detonation, based on the detonation behavior and remains. After each test and depending of the results, the scientific authority made some corrections on the aiming point and orientation to get the desired result. All larger metallic and energetic materials debris were picked up after each detonation for disposal and the remaining energetic material on the surface soil was burned in place using a propane burner.

Figure 18. 105-mm IM projectile filled with IMX-104 (without fuse)

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RESULTS

Analytical Methods

CRREL conducted research on analytical methods for several IHE compounds in water and in solid form. Methods were developed for PAX-21 residues on an ultra-high-pressure liquid chromatograph – mass spectrometer (UHPLC-MS) on various test columns. Solid-phase extraction was also investigated for DNAN and NTO, two IHE compounds recently incorporated into explosive formulations. A method for perchlorate analysis on the UHPLC-MS was also developed, enabling us to verify results obtained from analyses conducted for the PAX-21 tests by two commercial labs. An analysis method for NTO in IMX-104 and IMX-101 was developed in cooperation with the US Army Public Health Command that is reliable and reproducible **[22, 23]**. Methods for all IHE compounds in the three IM formulations have been achieved, although there may be more efficient methods for analyses. A new chromatography column was used IMX-101 that cuts the run time significantly **[5]**. Results have been published.

Mass Deposition

Mass deposition is reported for high-order and blow-in-place detonations and are indicative of the detonation efficiencies of the explosive formulation as well as the energetic compounds that make up these formulations. Mass depositions for the low-order detonations are also reported and are illustrative of the large variability inherent in low-order dets. Low-order detonation residue mass estimates are useful in verifying that low-order detonations actually occurred, not always an easy assessment. More detailed data for 2012 –15 can be found in the SERDP ER-2219 Interim Reports 1 & 2 **[4].**

US Tests

Samples were analyzed for one or more of the following energetic compounds, depending of the explosive formulation, donor or shaped charge, and the booster and supplemental charges: RDX, HMX, DNAN, NTO, NQ, and AP. Results will be presented chronologically and according to the type of detonation. Quality assurance results will also be presented.

2012 – High-order and BIP Detonations (PAX-21)

The PAX-21 tests resulted in significant findings. The efficiencies of the organic components of the IHE filler were high for the high-order detonations and acceptable for the BIP detonations **(Table 4)**. However, the results for the AP component were a matter of concern. The 85% efficiency of the AP during the high-order detonation would indicate low-order magnitude consumption (75% to 99.9%). Over 98% of the AP was recovered from the aqueous portion of the sample. For the BIPs, we had only the aqueous portion of the sample to analyze. From this, 38% of the perchlorate remained after detonation. The high AP mass residues quantity indicates only partial detonation of the compound.

Table 4: Results of PAX-21 detonation tests

Detonation Operation	Energetic Compound	Estimated Mass[b]	Percent of original mass
High-order	RDX	7.1 mg	0.007%
	DNAN	9.2 mg	0.006%
	AP	14,000 mg	15%
BIP[a]	RDX	870 mg	0.1%
	DNAN	740 mg	0.6%
	AP	33,000 mg	38%

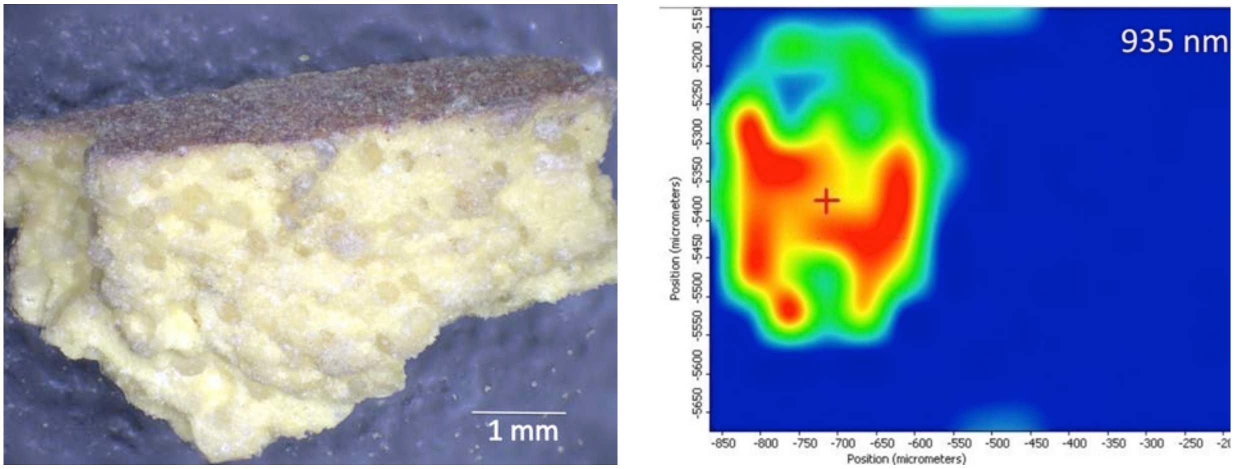
References: **[9] [10]**

[a] BIP data for aqueous fraction of samples only

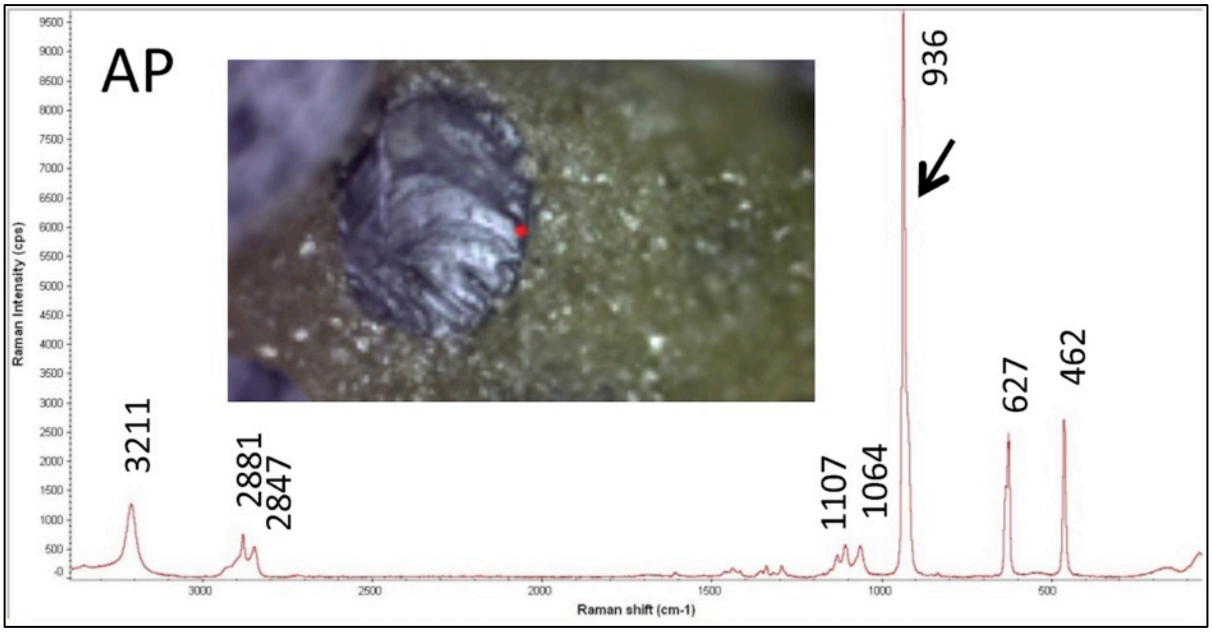
[b] Estimate of post-detonation residues mass

IDA sizes for both the high-order and BIP detonations were calculated. The mean areas were 330 m^2 for both the high-order and BIP tests. An area of 250 m^2 was sampled outside the demarcated residues deposition areas (ODAs). Only two ODAs had detectable levels of organic explosives and the values are below the reporting limits. No ODAs were analyzed for AP.

Photomicroscopy of the particles depicted large (>200µm) AP crystals within the PAX-21 matrix, confirmed by Raman spectroscopy (Figure 19) [9]. Dissolution tests and follow-up µCT scanning of particles are covered in the ER-2221 Interim Report.



a. PAX-21 chunk with translucent AP crystals b. Raman image of AP crystal (+) in matrix



c. Raman spectrograph of AP crystal (gray) in PAX-21 particle (dull yellow)

Figure 19. Images and Raman spectrum of AP crystals in PAX-21 particle (Taylor and Ringelberg)

2012 – Low-order Detonations (PAX-21)

Particle sizes for the post-detonation residues for the low-order tests are depicted in Figure 20. Size distributions for the single-compound filler TNT and the multi-component filler Comp-B are also plotted for comparison. Comparison with the single-compound filler TNT and the multi-component filler Comp-B can be made from the graph. The slopes for PAX-21 and Comp-B are very similar, indicating similar disaggregation kinetics during detonation. The particle sizes for PAX-21 run smaller than for Comp-B. Both PAX-21 and Comp B differ significantly from TNT.

Size and mass measurements conducted on particles collected from the EFT detonations are depicted in Table 5. For each test, the mass of the 10 largest chunks was measured and the remainder of the particles massed by bin size. Only particles large enough to pick up by hand (≈0.5 mm or larger) were massed. All tests produced low-order detonations as evidenced by the percentage of the original fill that was scattered and recovered as residue (0.1 – 25%). This range is larger than the 11% residual mass remaining from BIPs using the fuze simulator.

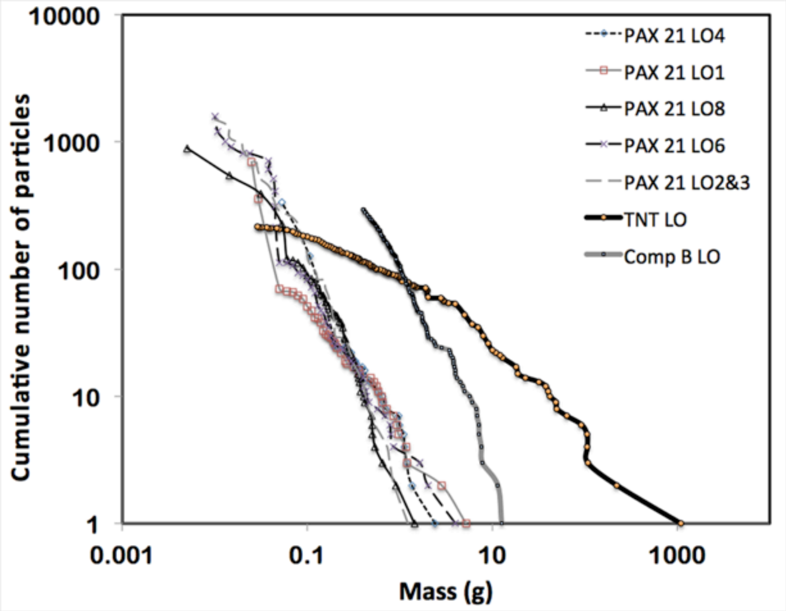


Figure 20. Post-detonation particle size distributions (S. Taylor, CRREL) [9]

Table 5. Shaped-charge BIP residues characterization for PAX-21 [15]

Particle Number	S1 (57 g C4)(a) Dimensions (cm) 1	2	3	Mass (g)	S2 (110 g C4) Dimensions (cm) 1	2	3	Mass (g)	S3-S5 (110/170/230 g C4)(b) Dimensions (cm) 1	2	3	Mass (g)
1	1.4	0.9	0.6	0.57	2.1	1.5	0.9	2.17	4.2	3.0	2.0	15.0
2	1.0	0.8	0.6	0.52	1.5	1.0	0.5	0.72	3.0	2.0	1.0	4.36
3	1.1	0.9	0.5	0.50	1.8	1.1	0.5	0.62	3.5	1.5	1.0	4.31
4	1.2	0.9	0.5	0.43	1.7	1.2	0.5	0.59	2.0	1.2	1.4	3.12
5	1.0	0.6	0.5	0.43	1.5	0.4	0.4	0.46	2.0	1.2	1.7	2.83
6	1.2	0.6	0.4	0.37	1.8	0.7	0.6	0.45	1.5	1.5	1.0	2.80
7	1.3	0.8	0.3	0.36	1.0	0.8	0.5	0.42	2.1	1.8	0.8	2.74
8	1.2	1.1	0.2	0.35	1.1	0.9	0.6	0.38	1.8	1.5	0.9	2.49
9	1.2	0.9	0.5	0.34	1.0	1.0	0.4	0.33	2.5	1.0	1.1	2.31
10	0.7	0.5	0.4	0.20	0.9	0.8	0.7	0.32	2.5	1.5	0.9	2.16
Average	1.1	0.8	0.5	**0.41**	1.4	0.9	0.6	**0.65**	2.5	1.6	1.2	**4.21**
Total				**4.1**				**6.5**				**42.1**
Bin Masses												
Coarse (≥ 1mm)				4.1				6.5				89
Medium				—				—				78
Fine (≤ 0.1 mm)				27				14				43
Total				32				21				210
% of Original PAX-21 Mass:				**9%**				**6%**				**20%(c)**

(a) Mass of C4 in shaped-charge device

(b) Three rounds were detonated simultaneously using different C4 charges

(c) Average for the three rounds.

2013 – High Order and BIP Detonations (IMX-104)

The IMX-104 tests also resulted in significant findings. The efficiencies of the RDX and DNAN components once again were quite high, approaching those of conventional munitions performance for the high order detonations and the 60-mm BIPs (Table 6). However, the BIPs for the 81s did not go as well. One round almost failed to detonate, with over 98% of the NTO, 47% of the DNAN, and 11% of the RDX not reacting (BIP 4). The detonation IDA was 28% smaller than the average of the other six IDAs in the test. The snow surface on the BIP 4 IDA was yellow, and the yellow had started to seep into the snow pack as we were sampling. Two other rounds had abnormally high ODA mass for all three components but are counted in the means.

Table 6: Results of IMX-104 detonation tests [11]

Detonation Operation	Munition	Energetic Compound	Estimated Mass(b)	Percent of original mass
High-order	60-mm	RDX	4.5 mg	0.006%
		DNAN	5.3 mg	0.005%
		NTO	2,200 mg	1.2%
	81-mm	RDX	16 mg	0.01%
		DNAN	27 mg	0.01%
		NTO	1,900 mg	0.4%
BIP	60-mm	RDX	8,300 mg	1.4%
		DNAN	20,000 mg	19%
		NTO	89,000 mg	50%
	81-mm(a)	RDX	11,000 mg	1.6%
		DNAN	29,000 mg	11%
		NTO	193,000 mg	45%

(a) BIP data does not include BIP 4, which did not function properly
(b) Estimate of post-detonation residues mass

One round (BIP 7) misfired and was detonated half an hour after the other six. The resultant IDA (900 m^2) was 50% larger than the next largest 81-mm BIP test IDA. Detonation IDA data is given in Table 7.

Table 7: IMX-104 Detonation IDA areas [11]

Detonation Operation	Munition	Sampling Unit	Area (m^2)
High-order	60-mm	IDA	250
		ODA	200
	81-mm	IDA	350
		ODA	230
BIP	60-mm	IDA	580
		ODA	300
	81-mm(a)	IDA	590
		ODA	310

(a) BIP data does not include BIP 4, which functioned improperly, and BIP 7, which occurred under different climatic conditions.

2013 – Low-Order Detonations (IMX-104)

We measured the size distribution of IMX-104 pieces collected from the LO detonations and plot these in Fig. 21. The same TNT and Comp B distributions shown in Fig. 20 are also plotted here to help in comparing the data. As was found for PAX-21, the slopes of the IMX-104 distributions are similar to the slope of the Comp B distribution, another multicomponent explosive. The IMX-104 pieces differ from the PAX-21 in scattering larger chunks (PAX-21 pieces are all less than 10g whereas some IMX-104 pieces are close to 100g).

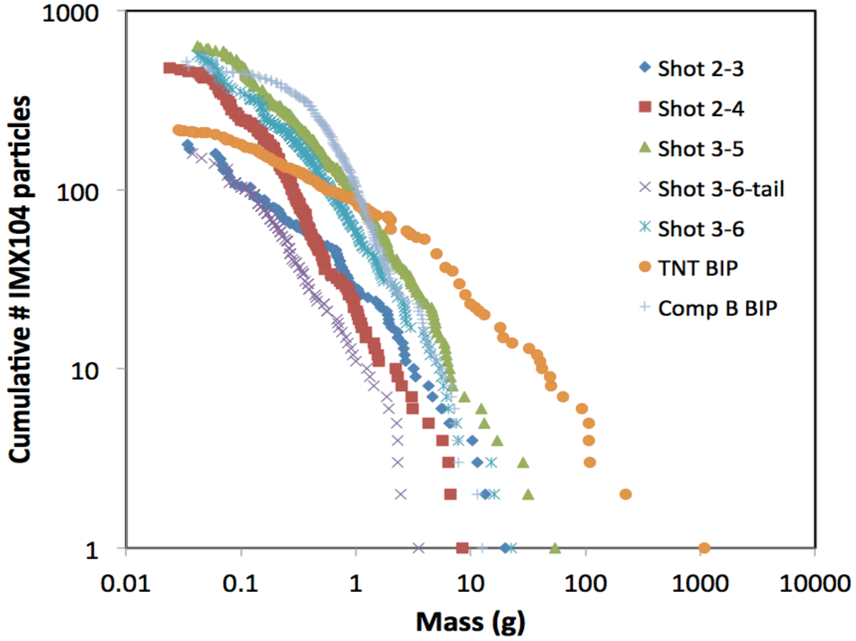


Figure 21. Particle size distributions for LO detonations of IMX104 rounds (S. Taylor, CRREL)

We again had an IHE compound that was inefficient during the detonation process. NTO was found at levels much higher than for DNAN and RDX **(Table 6)**. The high solubility of NTO also resulted in 99% of the compound recovered from the aqueous portion of the melted snow samples for both detonation operations. We conducted drip dissolution tests on post-detonation particles recovered from the field and they displayed significant dissolution of the NTO from the IMX matrix after very little exposure **(Fig. 22)**. Because of the high solubility of the NTO component, we measured the pH of the filtrate portion of the field detonation samples as well as the drip dissolution runoff.

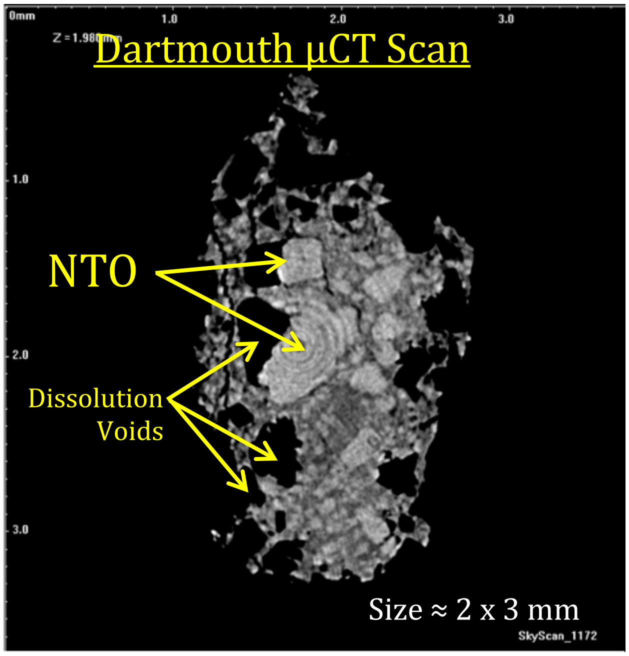


Figure 22. µCT scan of an IMX-104 detonation particle after exposure to 8 mL of water (S.Taylor)

Because NTO is known to be quite acidic in solution, we measured the pH of the aqueous portion of the field detonation samples. The pH of these samples was between 3 and 4, indicating high NTO concentrations and a lack of buffering from the environment or other IHE components.

2014 – High-order Detonations (IMX-101 and IMX-104)

Results of the high-order detonation residues analyses extrapolated over their respective sampling units and totaled for each test are presented in **Table 8**. Where appropriate, the IDA, ODA, and subsurface results are combined to derive the mass estimate for the IDAs. The overall mean detonation efficiency (consumption) of the RDX/HMX for the two types of rounds and the DNAN for the 81s was >99.995%, indicative of high-order detonations. This also indicates the efficient detonation of the supplemental charges, which are composed of 50% HMX / 45% TATB for the 81s and 92% HMX for the 155s. For the NTO, however, the mean detonation efficiencies were 99.87% for the 81-mm rounds and 93.4% for the 155-mm rounds. The NQ detonation efficiency was only 69%.

Table 8. Mean high-order detonation IM deposition results

Munition/ Booster	IDA Area (m^2)	ODA 0-3 (m^2)	ODA 0-6 (m^2)	Analyte[a]	Est. Total Mass[b] (g)	Depositional Mass Range (g)	% of Original Analyte Mass[c]
81 mm	670.	340.	340.	DNAN	0.008	0.0017 – 0.023	0.003%
(IMX-104)				RDX & HMX	0.008	<0.0004 – 0.015	0.005%
18g C4				NTO	0.54	0.37 – 0.70	0.13%
155 mm	320.	280.	290.	DNAN	2.4	0.12 – 5.3	0.49%
(IMX-101)				RDX & HMX	0.012	<0.0004 – 0.035	0.007%
50g C4				NTO	15.	7.3 – 27.	6.6%
				NQ	130.	86. – 180.	31%

(a) RDX includes some HMX as well (<9% of original mass)
(b) Mean of the combined IDA, ODA, and subsurface estimated masses
(c) Based on mid-range value of formulation specifications.

The 81-mm rounds detonated very close to high order, an improvement over the results seen in 2013 (**Table 9**) [11, 12]. A Student t-Test was conducted to determine if there is a significant difference (95% confidence level) between mean total estimated detonation residues mass for the 2013 and 2014 tests. Data from the analysis is given in **Table 10 and Figure 23**. The mean difference between the groups is -1.40 with six degrees of freedom. The t value is -4.9 with a probability of 0.0018, which signifies a difference in mean values.

Table 9. Means of 81-mm IMX-104 HI detonation residues: Effect of varying booster charge

Year (Booster Charge)	NTO (g)	DNAN (g)	RDX & HMX[a] (g)	Overall Efficiency[b]
2013 (12 g)	1.9	0.027	0.016	99.77%
2014 (18 g)	0.54	0.008	0.008	99.93%

(a) RDX includes some HMX as well (<9% of original mass)
(b) Based on initial mass of 842 g for the 12-g booster tests and 848 g for the 18-g booster test

Table 10. Student t-Test for significance of difference between means of 2013 and 2014 tests

Statistic	Group 1 (2013)	Group 2 (2014)
Count	7	5
Mean	1.96	0.555
Variance	0.529	0.0295
Std. Deviation	0.727	0.172
Std. Error	0.275	0.0768

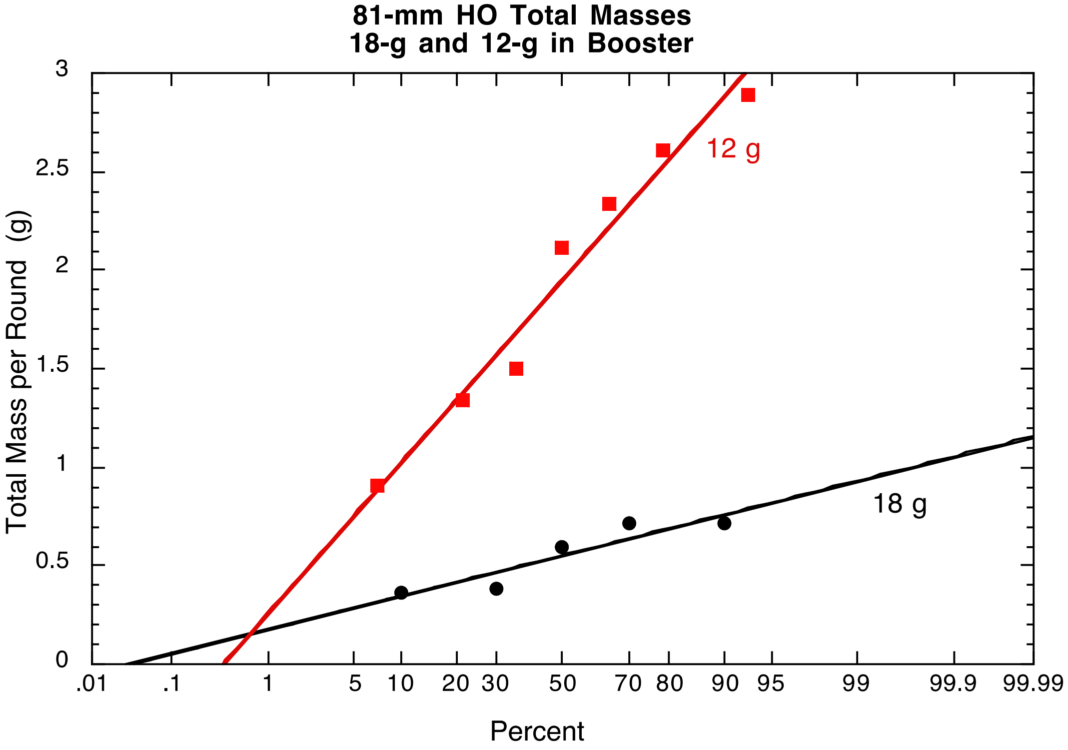


Figure 23. Normal probability plot of detonation residues for 2013 and 2014 HI detonation tests. The linear orientation of the data is consistent with normally distributed data.

The results for the 155-mm rounds indicate they are less efficient, with gram quantities of NTO, NQ, and DNAN residues per detonation. The residues deposition rate for the detonation tests varying the booster charge masses are given in **Table 11**. The values for the single-detonation 20-, 40-, 50-, and 60-g detonations are compared to the mean of the range of values (n=7) for the 50 g tests from **Table 8.** The 40-g booster load appears to be insufficient for these tests. The gain in overall efficiency from increasing the booster charge from 50 g to 60 g for the 155-mm round is minimal and likely insignificant as there is overlap between the 60-g data and the range of the 50-g component values. This indicates that a 50-g booster load was sufficient for the high-order detonation tests. The 20-, 30-, and 33-g booster load tests were much more inefficient than the 40-g test.

Table 11. Comparison of 155-mm IMX-101 HI detonation test results: Effect of varying booster charge

Booster Charge (C4)	NTO (g)	DNAN (g)	NQ (g)	Total HE Load (g)	Overall Efficiency
20 g	—	—	—	1270	76%
40 g	40.	5.9	170.	1280	83%
50 g	15.	0.28	120.	1290	89%
50 g[(a)]	15.	2.4	130.	1290	89%
60 g	14.	0.66	120.	1300	90%

(a) Mean (n=7) residues values from Table 3

The average residues IDA sizes were 670 m^2 for the 81-mm detonations and 320 m^2 for 155-mm HI detonations with a 50-g booster charge. The ODAs averaged 340 m^2 for the 81s, 51% of the IDA areas. For the 155s, the ODAs averaged 280 m^2, 88% of the original IDA areas. ODA residues averaged 0.30% of the total estimated mean residues mass for the 81-mm BIP detonations. For the 155s, ODAs averaged 1.2% of the total estimated mean residues mass. The goal for ODAs is <3% of the total estimated mean surface residues. Subsurface residues were 0.28% of the total estimated mean surface residues for the 81s (n=1) and 1.2% for the 155s (n=3). The goal set by CRREL for subsurface residues recovery is <1.5% of the total estimated mean mass of the surface residues. One subsurface sample was taken at the end of a partially sunny sampling day to ensure we were capturing the worst case for melting and diffusion of the residues into the snow. Several sunny days with temperatures near freezing drove this sampling strategy. A map of the detonation IDAs and their layout within the test area can be found in **Figure 24**.

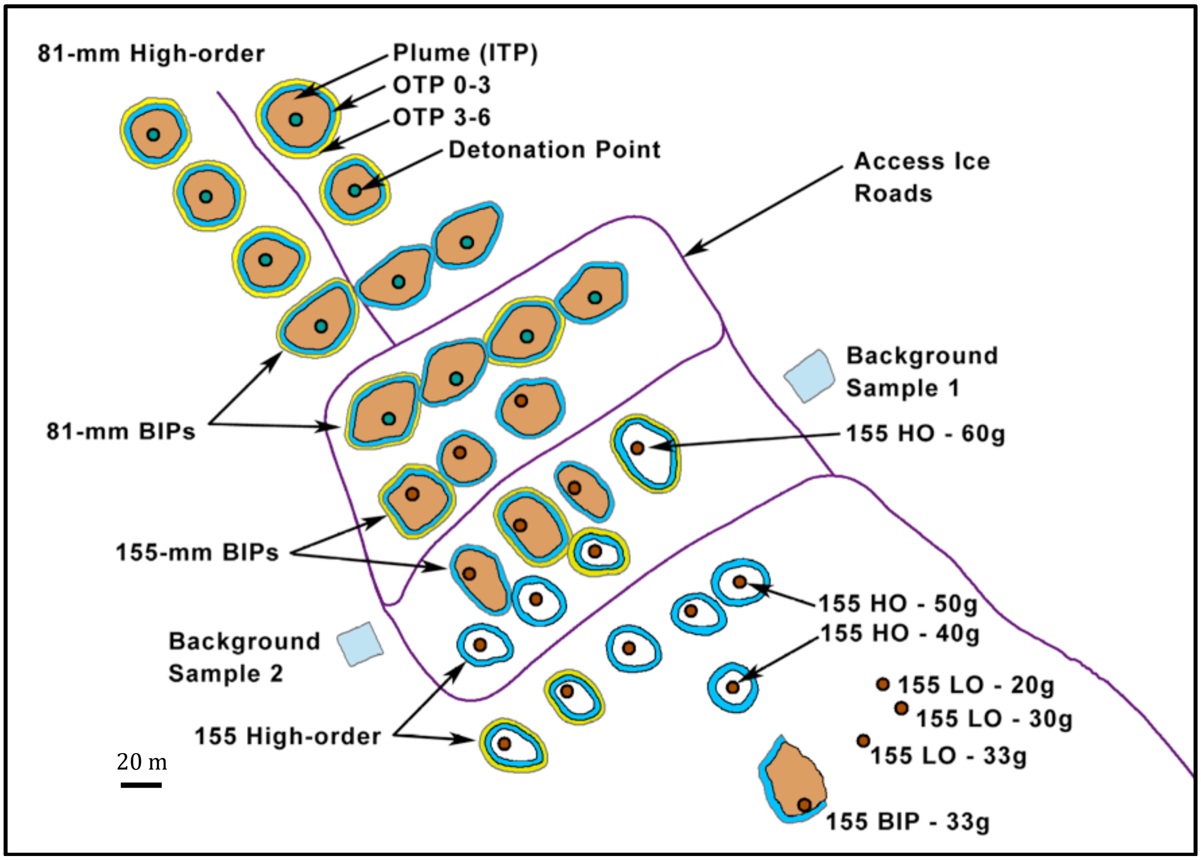


Figure 24. Test layout and mapped detonation IDAs: 2014

Figure 24 illustrates some important aspects of the detonation tests. The background samples bracket the locations of the tests and were sampled prior to any detonation test. The ice pad, where the low-order tests occurred, is located in the area of the LO shots in the lower right. Access roads on the ice are demarcated in purple. The shape of the high-order detonations, annular circles, indicates little or no wind, ideal wind conditions for the tests. The 81-mm BIPs indicate a similar lack of wind, with the elongation attributable to the horizontal orientation of the rounds prior to detonation. The 155 BIP-33g IDA best illustrates the elongated IDA shape from a detonation that occurs with a slight wind. There is some overlap with the ODA-3-6 areas on some of the IDAs, indicating that spacing between the IDAs should have been about 5 m greater for some detonations. The residue recovered from the ODA 3-6 areas was very small, however, indicating that the overall impact of the few areas of overlap should not be detrimental to the overall estimation of residues for the affected IDAs. IDA and IDA component areas for all the March 2014 tests are given in **Table 12**.

Table 12. Deposition areas for test shots: High order tests

Test (Booster mass)	IDA (m^2)	ODA 0-3m (m^2)	ODA 3-6m (m^2)
155 mm HI Pre-test(a)			
30g Booster	140	—	—
33g Booster	310	—	—
40g Booster	280	330	290
50g Booster	390	310	310
60g Booster	670	360	310
155 mm HI Test (50g)			
Shot 1	280	290	—
Shot 2	380	270	300
Shot 3	280	240	250
Shot 4	350	260	290
Shot 5	330	260	—
Shot 6	370	300	—
Shot 7	250	220	320
Mean	320	260	290
81 mm HI Test (18g)			
Shot 1	650	350	380
Shot 2	650	330	320
Shot 3	580	330	320
Shot 4	890	370	410
Shot 5	580	310	300
Mean	670	340	340

(a) Shots conducted to determine best booster charge mass for high-order detonations and to generate particles

2014 – BIP Detonations (IMX-104)

Results of the BIP detonation residues analyses extrapolated over their respective sampling units and totaled for each test are presented in **Table 13**. Where appropriate, the IDA, ODA, and subsurface results are combined to derive the mass estimate for the IDAs. The overall mean efficiencies for the compounds RDX/HMX and DNAN were >95% for the tests, an efficiency indicating a good BIP detonation. For the NTO, however, the mean detonation efficiencies were only around 90%. The NQ detonation efficiency was much lower, ≈ 75%, indicating an inefficient detonation of that compound.

The 81-mm rounds detonated significantly more efficiently than in 2013, with no overlap between the mean values between the 2013 test and the 2014 test (**Table 14, Figure 25**). The residues deposition rates for the detonation tests varying the number of C4 charges are given in **Table 15**. There is overlap in the data for RDX and NQ and very little separation in the data for NTO. The data do not support using more than one folded C4 block for disposing of this type of round.

Table 13. Mean BIP detonation IM deposition results

Munition/ Booster/ C4	IDA Area (m^2)	ODA: 0-3 (m^2)	ODA: 0-6 (m^2)	Analyte[a]	Est. Total Mass[b] (g)	Depositional Mass Range (g)	% Original Analyte Mass[c]
81 mm (IMX-104) 12g C4 1-Folded	820	340	290	DNAN	5.0	2.7 – 7.3	2.0%
				RDX & HMX	2.1	0.98 – 3.1	0.31%
				NTO	45.	32. – 65.	11%
155 mm (IMX-101) 33g C4 1-Folded	930	330[d]	270[d]	DNAN	36.	—	7.6%
				RDX & HMX	0.006	—	0.001%
				NTO	34.	—	15%
				NQ	190.	—	44%
155 mm (IMX-101) 50g C4 1-Folded	620	310	320	DNAN	5.3	3.6 – 6.4	1.1%
				RDX & HMX	0.021	0.003 – 0.038	0.003%
				NTO	15.	13. – 17.	6.6%
				NQ	100.	91. – 120.	24%
155 mm (IMX-101) 50g C4 2-Folded	670	290	300	DNAN	21.	15. – 27.	4.3%
				RDX & HMX	0.046	0.014 – 0.11	0.004%
				NTO	24.	18. – 26.	10%
				NQ	100.	84. – 120.	25%

[a] RDX includes some HMX as well (<9% of original mass)
[b] Mean of the combined IDA, ODA, and subsurface estimated masses
[c] Based on mid-range value of formulation specifications. Donor block(s) included.
[d] ODAs for 33g BIP are partial. The ODAs intersected the cleared ice pad.

Table 14. Mean mass deposition estimates from 81-mm IMX-104 BIP detonation test results: Effect of changing the donor charge configuration

Year (Donor Charge Configuration)	NTO (g)	DNAN (g)	RDX & HMX[a] (g)	Overall Efficiency[b]
2013 (Axial – Flat)	190.	29.	11.	83%
2014 (Axial – Folded)	45.	5.0	2.1	96%

[a] RDX includes up to 9% HMX
[b] Includes donor block

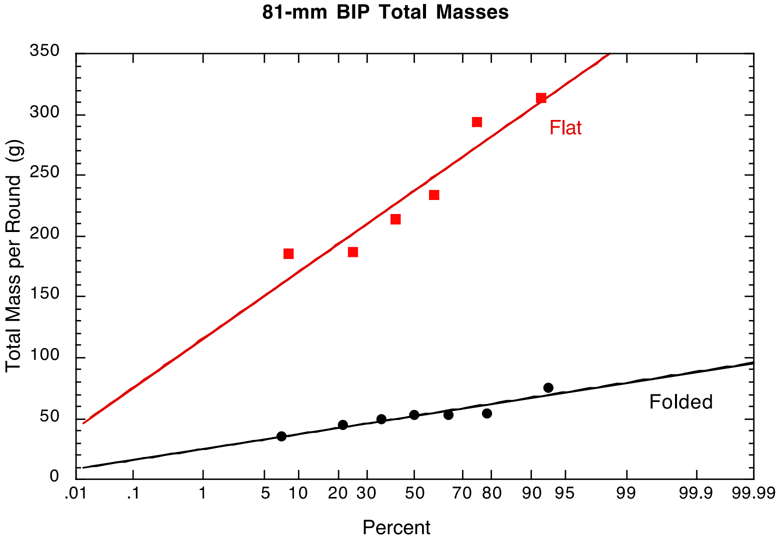


Figure 25. Normal probability plot for 2013 and 2014 BIP detonation test estimated total residues. The linear orientation of the data is consistent with normally distributed data.

Table 15. Comparison of 155-mm IMX-101 BIP detonation test results: Effect of varying the number of C4 donor charges

Donor Charges	NTO (g)	DNAN (g)	NQ (g)	RDX/ HMX (g)	Overall Efficiency[a]
1 Charge[b]	15.	5.3	100.	0.021	91%
2 Charges[c]	24.	21.	100.	0.046	89%

[a] Does not include donor block(s)
[b] Folded and placed axially over fuze booster and supplemental charge
[a] Folded and placed axially and diametrically opposed over fuze booster and supplemental charge

The residues IDA sizes were larger for the BIPs than for the HI detonations, which is typical **[2]**. The average residues IDA sizes were 820 m^2 for the 81-mm BIPs and 640 m^2 for 155-mm BIPs with a 50-g booster charge **(Table 16)**. The combined mean IDA areas for the two series of 50-g BIP are very close: 1250 m^2 vs. 1260 m^2. The 33-g booster charge BIP test was conducted on a day with mild wind, which resulted in a larger IDA area than for the other 155-mm tests. The ODAs averaged 340 m^2 for the 81-mm BIPs, 41% of the IDA areas. For the 155s, the ODAs averaged 300 m^2, 47% of the original IDA areas. ODA residues averaged 0.12% of the total estimated mean residues mass for the 81-mm BIP detonations. For the 155s, ODAs averaged 2.2% of the total estimated mean residues mass. Subsurface residues were quite low for both tests, with subsurface residues estimated at 0.60% of the estimated mean total surface residues for the 81s (n=1) and 0.89% for the 155s (n=2). The goal for subsurface residues recovery is <1.5%.

Table 16. Deposition areas for BIP tests

Test	IDA (m^2)	ODA 0-3m (m^2)	ODA 3-6m (m^2)
81 mm BIP Test			
Shot 1	900	350	270
Shot 2	830	290	—
Shot 3	810	300	320
Shot 4	750	350	—
Shot 5	840	360	280
Shot 6	820	360	—
Shot 7	780	330	—
Means	820	330	290
155 mm BIP Test			
33 g / 1 Block[a]	930	330	270
155 mm BIP Test			
50 g / 1 Block			
Shot 1	640	310	—
Shot 2	730	360	—
Shot 3	500	260	320
Means	620	310	320
50 g / 2 Blocks			
Shot 1	700	300	300
Shot 2	570	250	—
Shot 3	740	330	—
Means	670	290	300
50-g Means	650	300	310

[a] Partial ODAs done on 33-g BIP test

2014 – Fate and Transport (IMX-104 & IMX-101)

Determining the fate and transport of the residues was not an objective of this test. However, initial dissolution rates of the residues in water can be derived from the behavior of the IHE constituent compounds during sample processing. During melting and filtering of the snow samples containing the detonation residues, the components separated differentially between the two fractions (solid and aqueous) based on their solubility in water (**Table 17**). NTO and NQ rapidly dissolved out of the solid phase into the aqueous portion, whereas the DNAN and RDX/HMX were more equally partitioned. This rapid dissolution occurred as the samples melted over a period of less than 24 hours. The sample temperatures were <4°C. This behavior has been observed with particles collected from previous IM detonation tests and exposed to environmental precipitation **[16]**. Dissolution of compounds during melt was the same in 2015.

Table 17. Percent of recovered IHE residues compounds found in aqueous portion of processed samples

Test	HMX	DNAN	RDX	NTO	NQ	# Samples
81-mm BIPs	33%	50%	60%	99%	—	21
155-mm HOs	ID[(a)]	36%	ID[(a)]	99%	98%	27
155-mm BIPs	ID[(a)]	55%	ID[(a)]	99%	98%	25

[(a)] Analyte intermittently detected at very low concentrations near detection limits

2014 – Particle Size Distribution

Three tests were conducted to obtain particulate residues >0.5 mm in size of IMX-101 from a low order detonation of the M1122 155-mm practice round. The first two detonations were conducted with 30- and 33-g booster loads in the fuze simulators. These detonations resulted in a scattering of fine (<0.5-mm) particles over areas of 140 m^2 and 310 m^2 respectively that quickly dissolved into the thin water layer on the surface of the ice pad **(Figure 26)**. The particles were too small for the purpose of the test.

Figure 26. Detonation residues from a M1122 IMX-101 round with a 33-g C4 fuze booster load. Greenish-yellow material on ice surface is dissolved IMX.

The third round was detonated with a fuze simulator containing 20 g of C4 (the normal fuze booster contains 28 g of Composition A5). This detonation yielded a better array of particles, the mass of which added up to 24% of the explosive load, indicating a low-order detonation (75% to 99.99% efficiency). Particle size analyses show comparable particle distributions to other multi-component explosive formulations, both insensitive and conventional **(Figure 27)**. The IMX-101 and -104 formulations track very closely and are similar to PAX-21 and Comp-B. TNT is a single-component formulation and behaves quite differently. There were a very large number of small particles for the detonation tests conducted in 2015, more so than in previous IM tests. This is due to our new swept-surface collection process, which enables the collection of the smaller post-detonation particles. These small particles have a high surface area to mass ratios, which will have a significant effect on dissolutions kinetics [15, 16]. Imaging of the particles from the March tests have not been completed at the time of this report.

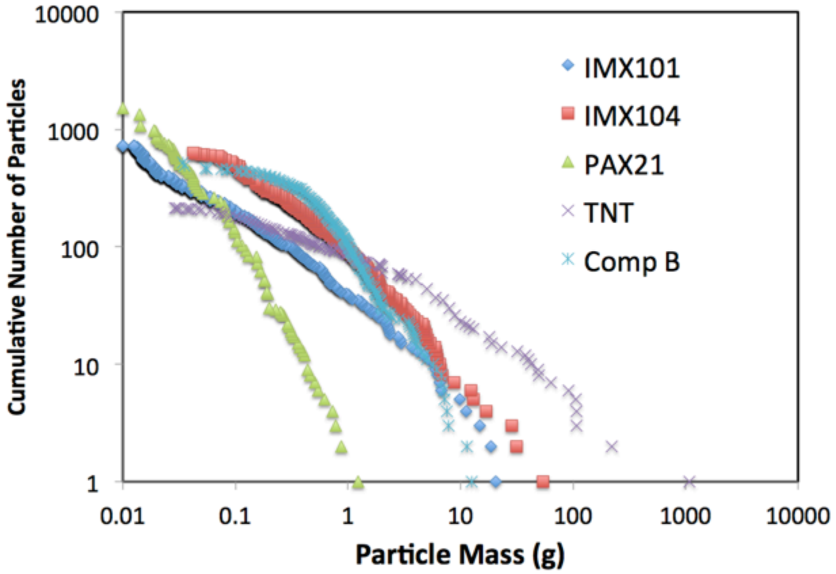


Figure 27. Comparative particle mass distribution for low-order detonations

2015 – High-order Detonations (IMX-104)

Results of the high-order whole population swept samples from detonations conducted in March on ice and for two rounds detonated on snow at the same location (co-located dets) in February for the LCEA tests are presented in Table 18. Also included are the results of one of the March low-order detonations, for which we also swept up all the residues to get an estimation of the residues mass and efficiency.

Table 18. Mean detonation IM deposition results: IMX-104 rounds

Munition/ Booster	Detonation Description	Number of Shots	IDA Area (m^2)	Analyte[(a)]	Est. Total Mass[(b)] (g)	% of Original Analyte Mass[c]
81 mm (IMX-104) 18g C4	High order (Ice Surface) 2 IDAs	2	460.	RDX & HMX	0.004	0.0025%
				DNAN	0.017	0.0065%
				NTO	0.72	0.17%
	High Order (Snow Surface) Co-located dets	2	617	RDX & HMX	0.004	0.0025%
				DNAN	0.013	0.005%
				NTO	1.2	0.27%
	Low order	1	280	RDX & HMX	8.8	5.4%
				DNAN	17	6.7%
				NTO	140	33%

(a) RDX includes some HMX as well (<9% of original mass)
(b) Mean of the estimated masses of the two high-order detonations
(c) Based on mid-range value of formulation specifications.

The overall mean detonation efficiency (consumption) of the RDX/HMX and the DNAN for the high-order detonation tests was >99.995%, indicative of high-order detonations. This also indicates the efficient detonation of the supplemental charges, which are composed of 50% HMX. For the NTO, however, the mean detonation efficiency was 99.83%, more indicative of a low-order detonation, which, by our definition, has a detonation efficiency of 75% to 99.99%. The overall detonation efficiency for the energetics for the high-order detonations was 99.92%, very close to a high order detonation.

The results for LO-1 indicate a low-order detonation, with analyte detonation efficiencies of less than 95% and an overall detonation efficiency of 80%. RDX and HMX are not separated out in **Table 18** because HMX is a manufacturing product of RDX and is found in the C4 booster charge along with RDX. The IDAs were outlined visually and walked with a GPS unit to derive the area for the three detonations. These data are compared to data obtained from sampling of residues on snow in the **Discussion** section of this test report.

As with previous IMX-104 testing, the percentage of the analytes recovered in the aqueous portion of the samples varies widely. Because of the volume of the collected samples, each detonation sample consisted of several parts. Analytical results were combined to derive a final mass estimate. For NTO, the aqueous portion contained over 99% of the analyte. For the 11 high-order (HI) detonation samples analyzed (five for HI-1 and six for HI-3), the range in values was 99.7% to 99.99%, with an average of 99.88% of the NTO in the aqueous portion of the filtered sample. For the low-order detonation (LO-1), the range of values for the six samples was 99.991% to 99.998%, with an average of 99.995% of the NTO in the aqueous portion of the filtered sample. For RDX/HMX, the portion of the analyte recovered from the aqueous portion of the processed samples was 15% for the LO detonation and 60% for the HI detonations. The results for DNAN were 34% and 3.6% respectively for the LO and HI detonations. The residues resident time in the 0°C water was variable, depending on when melt for the sample was initiated. Equilibrium was likely not reached for the DNAN, RDX, and HMX, thus the high variances.

2015 – Spatial Distribution of Particles (IMX-104)

Spatial distribution of the particles is rather complex and will be presented in several manners. A breakdown of the total estimated number of particles binned by mass is the typical method for presenting these data in the past. We will also present the data as a function of distance from the detonation point with no reference to angular orientation. Finally, we will map the spatial distribution of the larger particles for the low-order and partial detonations.

Seven attempts were made to detonate rounds low order. Three rounds detonated low order, two partial detonations occurred, and for two rounds, only the fuze simulators detonated, leaving the rounds essentially intact. Images of the undisturbed remains of the rounds for the latter two types of detonations are presented in **Figure 28**. Residues from all the rounds were collected and the estimated detonation efficiencies are presented in **Table 19.** The results reported in the table are based on the mass of residues collected following the detonations. Supporting evidence of the type of detonation that occurred includes fragmentation extent of the body of the round, filler remaining in the body of the round, and impact on the steel mounting plate on which the detonation was set up. All these indicators agreed along with the residues mass estimates on the type of detonation that occurred for the test.

a) Low-order detonation: Note base of body still in plate and large amount of fine particles

b) Partial detonation: Note large section of body to right of detonation plate

Figure 28. Aftermath of low-order and partial detonations of the 81-mm rounds

Table 19. Detonation results for spatial distribution of particles tests

Detonation	Shot	Booster (g)	Result	Recovered Residues (%) (a)	Overall Efficiency(b)
LO-1	3	9	Low order	20%	80%
LO-2	4	7	Partial Detonation	30%	20%(d)
LO-3	4	7	Low order	6%(e)	94%
LO-4	5	7	Dud (Fuze only)	2%(c)	0.9%
LO-5	5	7	Dud (Fuze only)	0.7%(c)	0.9%
LO-6	6	8	Partial Detonation	27%(c)	20%(d)
LO-7	6	8	Low order	31%	69%

(a) Percent of original mass (recovered as particles.

(b) For partial detonations, filler in the round is estimated. For duds, only booster charge detonated.

(c) Includes only particles recovered outside body of round. Total energetics remaining is in 99% range.

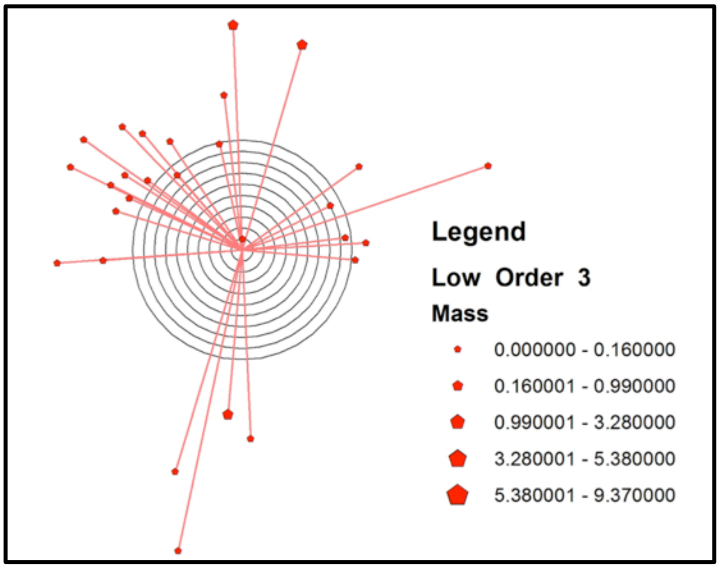
(d) Estimate based on recovered residues plus estimate of remaining explosive filler in body of round.

(e) Includes estimate of residues in samples lost during desiccation process.

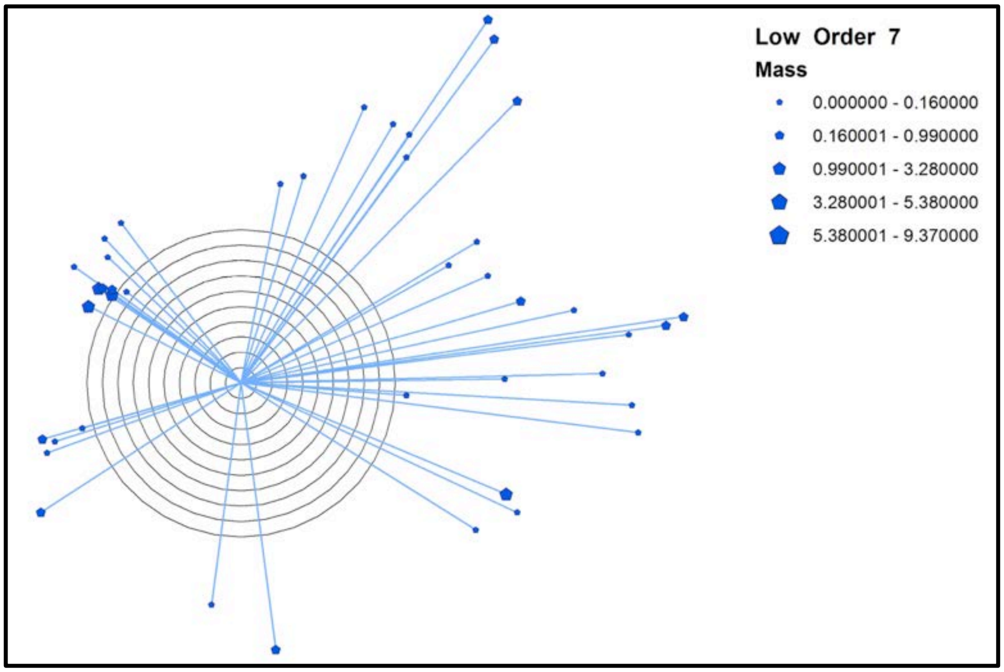
Low-order detonations

Particles from the two low-order detonations were collected differently. For LO-3, the larger particles were collected for the “rings” (1-m annuli) prior to sweeping. The rings were then swept separately and bagged for the initial particle separation and characterization at the field lab on JBER, with the remaining ring material freeze-dried and the particles characterized at the Hanover lab. Larger ejected particles were spatially logged and characterized in the field. For LO-7, only a few particles were collected from the rings prior to sweeping.

Past observations of live-fire low order detonations of rounds has indicated that the distribution of particles is not uniform around the detonation point. The spatial mapping of the larger particles (>1 mm) from the two low-order detonations that occurred during testing confirms these observations **(Figure 29)**. For LO-3, 20 of the 28 (70%) of the largest particles recovered lie in approximately the top half of the dispersal area. The mass of particles is similarly divided, with 3.9 g of the total mass of 4.2 g found in the upper half of the detonation as shown in **Figure 29a**. . For LO-7, the dispersal pattern is similar to that of LO-3, with 38 of 42 (90%) of the largest particles collected from the half of the dispersion area to the upper right of the detonation point. The mass distribution is 16 g vs. 5.4 g, three quarters of the mass deposited in the northeast half of the dispersal area. In both cases, there are large gaps within the dispersal patterns along with areas of concentrated particles.



a. LO-3 large particle distribution



b. LO-7 large particle distribution

Figure 29. Distribution of particles from low-order detonations LO-3 and LO-7

The particles that were swept up for analysis within the annular rings that extended out 10 m from the point of detonation accounted for the majority of the particles and mass recovered following detonation. For LO-3, 49 g of the 53 g recovered as residues from the detonation (92%) was in the swept annuli (rings), as were over 99.99% of the estimated 5.9 million particles. For LO-7, 270g of the 300 g of the recovered energetics (90%) were in the swept rings. We analyzed the radial and mass distributions of the particles for both low-order detonations. Results are given in **Tables 20 and 21**. No corrections were made to the data for the swept samples lost on the freeze drier for the 3-, 4-, and 5-m annuli for LO-3.

Table 20: Particle distribution statistics for low-order detonations (by size bin)

	LO-3			LO-7		
Bin Size Range (mm)	Percent of Total	Total in Bin(s)	Rank	Percent of Total	Total in Bin(s)	Rank
Particle Distribution		**680,000**			**5,900,000**	
>9.5 mm	0%	0	6	0.0004%	25	6
4.75 – 9.5 mm	0.001%	9	5	0.002%	140	5
2.0 – 4.75 mm	0.08%	570	4	0.02%	1400	4
1.0 – 2.0 mm	0.4%	2,800	3	0.2%	10,000	3
0.5 – 1.0 mm	2%	13,000	2	2%	110,000	2
<0.5 mm	98%	660,000	1	98%	5,800,000	1
Mass Distribution		**38**			**300 g**	
>9.5 mm	0%	0 g	6	21%	63 g	2
4.75 – 9.5 mm	3.2%	1.2 g	5	11%	32 g	6
2.0 – 4.75 mm	27%	10 g	3	12%	37 g	4
1.0 – 2.0 mm	25%	9.5 g	2	16%	47 g	3
0.5 – 1.0 mm	19%	7.4 g	4	12%	37 g	5
<0.5 mm	26%	9.9 g	1	28%	84 g	1

Table 21: Particle distribution statistics for low-order detonations (by distance)

	LO-3			LO-7		
Radial Distribution	Percent of Total	Total in Ring(s)	Rank	Percent of Total	Total in Ring(s)	Rank
Particle Distribution		**680,000**			**5,900,000**	
0-2 m	22%	149,000	2	7.9%	470,000	8
2-3 m	13%	88,000	4	23%	1,400,000	1
3-4 m*	.023%	150	8	15%	860,000	2
4-5 m*	.02%	140	9	12%	710,000	3
5-6 m*	.029%	200	7	9.3%	530,000	5
6-7 m	26%	170,000	1	10%	610,000	4
7-8 m	12%	84,000	5	8.1%	475,000	7
8-9 m	11%	73,000	6	9.1%	530,000	6
9-10 m	16%	110,000	3	4.6%	280,000	9
>10 m	0.003%	24	10	0.0005%	29	10
Mass Distribution		**38**			**300 g**	
0-2 m	10%	3.9 g	7	15%	44 g	1
2-3 m	11%	4.2 g	5	9.4%	29 g	6
3-4 m*	3.5%	1.3 g	9	12%	38 g	3
4-5 m*	3.1%	1.2 g	10	10%	31 g	4
5-6 m*	4.3%	1.7 g	8	13%	39 g	2
6-7 m	18%	6.9 g	1	8.8%	27 g	7
7-8 m	13%	5.1 g	3	8.4%	25 g	8
8-9 m	10%	4.0 g	6	7.8%	24 g	9
9-10 m	15%	5.8 g	2	5.3%	16 g	10
>10 m	11%	4.2 g	4	10%	30 g	5

*Note: particles for these three annuli were lost when the sample melted in the desiccator. Based on other results, approximately 5 g of material was contained in each sample.

The mean particle mass for both detonations is quite small: 0.00006 g for LO-3 and 0.00005 g for LO-7. The mean particle size is <0.5mm in its largest dimension with an estimated mass of 0.00004 g. This is reflective of the overwhelming number of particles recovered using the freeze drying method for the 1-m annuli extending out 10 m from the point of detonation, most of which were <0.5 mm. Had we not lost the samples from the three annuli of LO-3, the mean masses would likely have been the same. There were very few larger particles (>5 mm) for either of the detonations.

Partial detonations

Particles from the two partial detonations were collected and the rings swept (see Low-order detonations above) to determine particle dispersion characteristics. The collected particles made up only a small portion of the undetonated explosive filler, the majority of which remained in the body of the rounds (**Figure 30**). For both LO-2 and LO-6, about 50% of the filler remained in the rounds after detonation.

Figure 30. Partial detonation (LO-6) showing filler remaining in body of round

For LO-2, 41 of the 61 (67%) largest particles recovered lie in the southwest half of the dispersal area (**Figure 31a**). The mass of particles is approximately equal in both halves of the dispersal area (≈25g). There is no discernable pattern of large particle dispersion outside the annuli for LO-6 (**Figure 31b**).

The particles that were swept up for analysis within the annular rings that extended out 10 m from the point of detonation accounted for the majority of the particles and mass recovered following detonation. For LO-2, 430 g of the 450 g recovered as residues from the detonation (96%) were recovered from within a 10-m radius of the detonation, as were over 99.99% of the estimated 14 million particles. For LO-6, 298 g of the 300 g of the recovered energetics (99.3%) were in the rings. We analyzed the radial and mass distributions of the particles for both low-order detonations. Results are given in **Tables 22 and 23**. Note that for these tables, the mass remaining in the body of the round following partial detonation totaled around 500g. Both bodies were recovered within 3 m of the detonation point.

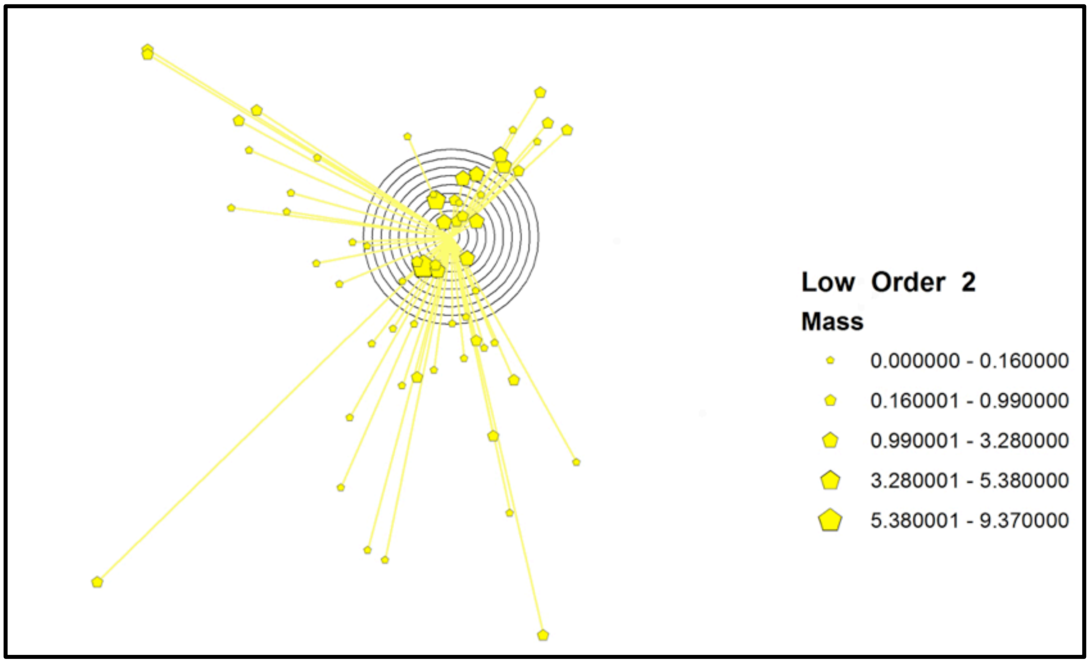
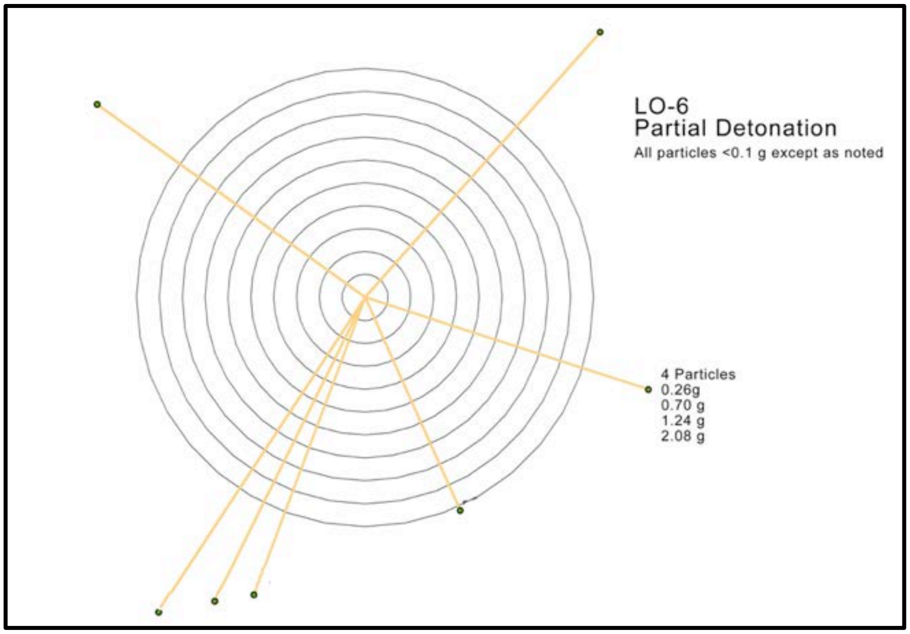


Figure 31a. LO-2 large particle distribution



b. LO-6 particles outside swept annuli

Figure 31. Distribution of particles from partial detonations LO-2 and L0-6

Table 22: Particle distribution statistics for partial detonations (by distance)

Radial Distribution	LO-2 % of Total	Total in Ring(s)	Rank	LO-6 % of Total	Total in Ring(s)	Rank
Particle Distribution		14,000,000			2,200,000	
0-2 m	43%	5,900,000	1	46%	950,000	1
2-3 m	19%	2,700,000	3	15%	330,000	1
3-4 m	20%	2,800,000	2	14%	300,000	2
4-5 m	5.9%	810,000	4	14%	300,000	3
5-6 m	2.5%	340,000	6	2.9%	63,000	5

6-7 m	2.3%	320,000	7	6.2%	130,000	4
7-8 m	1.6%	220,000	9	1.8%	38,000	7
8-9 m	2.9%	400,000	5	0%	0	6
9-10 m	2.2%	290,000	8	0%	0	9
>10 m	0.0003%	42	10	0.0004%	8	10
Mass Distribution		450			300 g	
0-2 m	46%	210 g	1	35%	105 g	1
2-3 m	14%	64g	3	24%	71 g	3
3-4 m	15%	66 g	2	25%	75 g	2
4-5 m	6.8%	30 g	4	7.6%	23 g	4
5-6 m	3.6%	16 g	5	6.2%	19 g	5
6-7 m	3.0%	13g	7	1.1%	3.4 g	6
7-8 m	2.9%	13 g	8	0.5%	1.4 g	8
8-9 m	3.1%	14 g	6	0.0%	0 g	9
9-10 m	2.3%	10 g	10	0.0%	0 g	10
>10 m	2.7%	12 g	9	0.6%	1.6 g	7

*Note: particles for these three annuli were lost when the sample melted in the desiccator. Based on other results, approximately 5 g of material was contained in each sample.

Table 23: Particle distribution statistics for partial detonations (by size bin)

Bin Size Range (mm)	LO-2 % of Total	Total in Bin(s)	Rank	LO-6 % of Total	Total in Bin(s)	Rank
Particle Distribution		14,000,000			2,200,000	
>9.5 mm	0.0001%	13	6	0.002%	36	6
4.75 – 9.5 mm	0.001%	140	5	0.007%	140	5
2.0 – 4.75 mm	0.01%	1,600	4	0.03%	570	4
1.0 – 2.0 mm	0.1%	18,000	3	0.1%	2,500	3
0.5 – 1.0 mm	1%	160,000	2	2%	40,000	2
<0.5 mm	99%	13,000,000	1	98%	2,100,000	1
Mass Distribution		450 g			300 g	
>9.5 mm	4.8%	21 g	6	12%	35 g	5
4.75 – 9.5 mm	7.7%	35 g	5	19%	58 g	2
2.0 – 4.75 mm	16%	72 g	2	26%	77 g	1
1.0 – 2.0 mm	11%	50 g	4	18%	53 g	3
0.5 – 1.0 mm	15%	68 g	3	16%	48 g	4
<0.5 mm	45%	200 g	1	10%	31 g	6

Once again, the mean particle mass for both detonations is quite small: 0.00003 g for LO-2 and 0.0001 g for LO-6. The mean particle size is <0.5mm in its largest dimension with an estimated mass of 0.00004 g. The small (<0.5 mm) particles recovered using the freeze drying method for the 1-m annuli extending out 8 m from the point of detonation accounted for the small mean and median particle sizes. There were more of the larger particles (>5 mm) for both detonations than was seen for the low-order detonations, and these chunks made up 13% and 31% of the total mass of the residues even though they made up less than 0.01% of the particles.

Duds

Particles from the two duds (fuze detonation only) were collected for characterization. All were recovered within 2 m of the detonation point. The round was intact, although the fuze had blown out. Particles came from the upper portion of the explosive filler near the fuze well. **Table 24** displays data from the detonation residue characterizations.

Table 24: Particle distribution statistics for duds

Detonation Sieve Size	Mass (g)	Percent of Total	Number of Particles	Percent of Total	Mass/Particle
LO-4	17		385		0.04
9.51 mm	4.8	28%	2	1%	2.4
4.75 mm	8.4	50%	25	6%	0.33
2.0 mm	3.0	18%	50	13%	0.061
1.0 mm	0.1	1%	100	26%	0.001
0.5 mm	0.5	3%	208	54%	0.0025
LO-5	5.9		150		0.04
9.51 mm	0	0%	0	0%	0
4.75 mm	4.0	67%	20	13%	0.20
2.0 mm	1.7	29%	50	33%	0.034
1.0 mm	0.2	3%	60	40%	0.0032
0.5 mm	0.05	1%	20	13%	0.0025

2015 – High-order Particle Characterization (IMX-104)

The blast wave and fragmentation from the detonations of HI-1 and HI-2 resulted in a loss of several of the sampling pans set out to collect particles. For HI-1, the first three rings of pans were destroyed by the detonation, and for HI-2, the first two rings were also destroyed. After freeze drying the samples collected from the pans, the remaining particles were too small to sieve and the mass too little to weigh. In addition, there was much debris mixed in with the energetics residues, making separation difficult. However, some particles have been separated and photographed **(Figure 32)**. The particles in these images are all well below 1 mm in their longest dimension. We are still in the process of characterizing the particles at the time of this report.

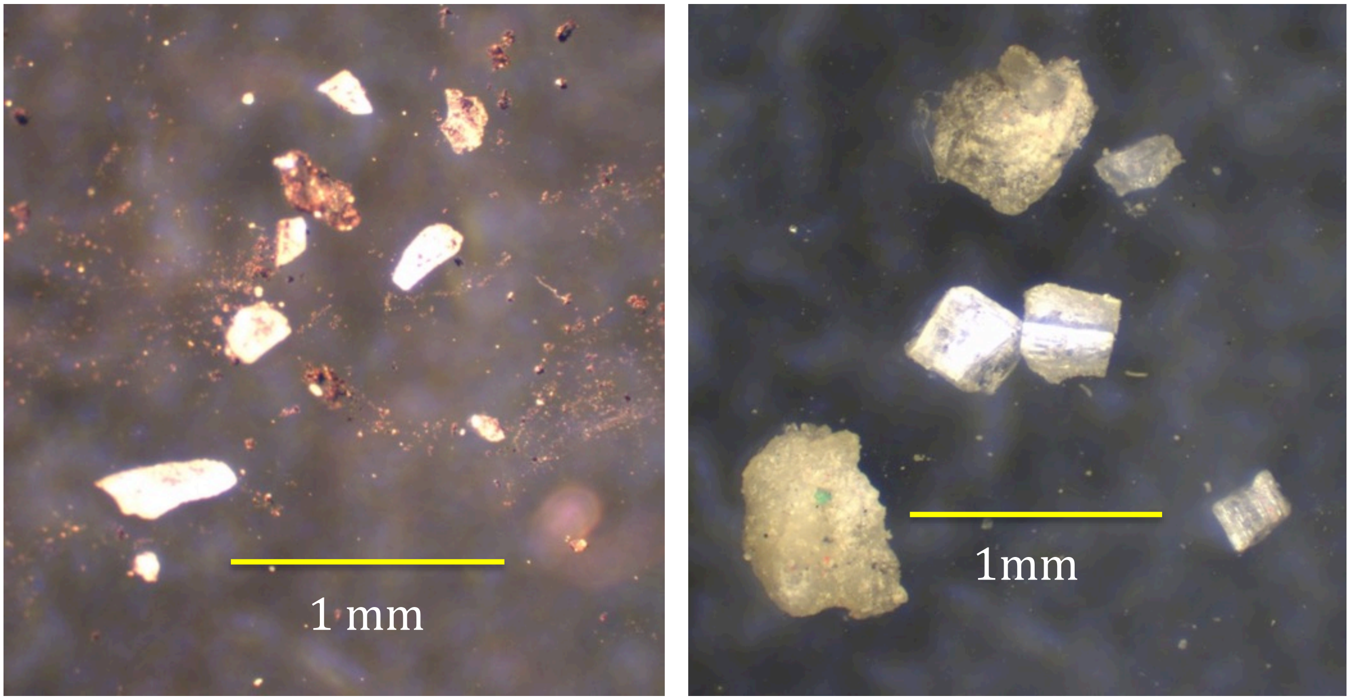


Figure 32. Photomicroscopy images of energetic residue particles from a high-order detonation

2015 – Life Cycle Environmental Assessment Tests

Two tests were conducted. The first involved five co-located shots of two demolitions blocks containing Composition C4. For 10 blocks of C4, each containing 520 g of RDX/HMX, 5.2 Kg of energetics were detonated in total. The second involved the co-located detonation of two IMX-104 81-mm mortar rounds. Shifting winds resulted in the aerial IDA missing the EPA instrumentation, so our results will concentrate on findings from the C4 tests. Deposition data for the co-located 81-mm IMX-104 high-order detonations appear in **Table 18**.

Five multi-increment samples (i>90 increments) were taken from the demarcated surface residues area (IDA) and triplicate MI samples were taken from the 0-3 m and 0-6 m ODAs following completion of the five shots involved with the C4 detonation residues test **(Table 25)**. No residues were detected in the ODAs. Based on the data for the IDA samples, the detonation efficiencies are quite high, >99.999%, indicating high-order detonations of the blocks. The mean and median values of the estimated combined residue masses for RDX and HMX are both 35 mg, indicating a normal distribution of the replicate samples. The mean estimated residues mass is compared to residues estimates derived from the aerial IDA samplers for RDX/HMX. Data for the EPA "flyer" suspended aerial sampling instrumentation packages will be presented first.

Table 25. Residues mass estimates and calculated efficiency of C4 detonations for LCEA test

Sample Rep	IDA Area (m^2)	ODA 0-3 Area (m^2)	ODA 0-6 Area (m^2)	HMX Mass Est. (mg)	RDX Mass Est. (mg)	Detonation Efficiency
1	1600	700	730	0.95	35	99.9993%
2				0.89	27	99.9994%
3				0.99	34	99.9993%
4				1.5	43	99.9991%
5				1.5	36	99.9993%
Means				1.2	35	99.9993%

Each flyer contained an 81-mm square quartz filter through which 1200 L/min (≈2 m^3 total) of air was pulled. These filters were extracted and analyzed for RDX/HMX. No chromatographic peaks corresponding to the energetic compounds were observed in the filter extracts from the background (3-hour run) or 81-mm (IMX-104) samples **(Table 26)**. The following narrative therefore applies only to the C4 detonation tests.

Small peaks corresponding to the retention time for RDX were observed on the GC-μECD primary and confirmation columns for the flyer filter extracts following the C4 detonations. The RDX concentrations in the extracts were 5.1 and 2.7 μg/L for Flyer #2 (Wilber) and Flyer #1 (Orville), respectively. For a frame of reference, the method detection limit for RDX in soil extracts analyzed using the same GC-μECD method is 3.0 μg/L. Thus the RDX concentrations in the filter extracts from the C4 detonations closely bracketed the detection limit using the GC-μECD method. The concentrations were well below the detection limit of 20 μg/L for RDX for the HPLC-UV method.

Given that 50 mL of solvent were used for extraction of the filters, the estimated masses of RDX determined on the primary GC-μECD column were 0.25 and 0.14 μg for Flyer #2 and Flyer #1 respectively. On the confirmation column, the RDX masses were similar (0.20 and 0.13 μg). The masses of RDX calculated from the analytical results are consistent with the physical appearance of the two filters. Soot was visible on both filters. The Flyer #2 filter was black and the Flyer #1 filter was gray. The estimated RDX mass on the #2 filter was approximately twice that of the #1 filter, reflecting the directionality of the aerial plume.

Table 26. LCEA Test Residues Masses: Flyers

Sample ID	Sample Date	Matrix	Remarks	RDX Mass (μg)*
BS-Qfilter-020715	02/07/15	Background	Flyer #1, Outside lab building, ~3 hr sampling	<d, <d
PS-C4-Qfilter-OR-021115-01	02/11/15	C4	Flyer #1, ~0.06 g Carbon	0.14, 0.13
PS-C4-Qfilter-WI-021115-02	02/11/15	C4	Flyer #2, ~0.06 g Carbon	0.25, 0.20
PS-81-Qfilter-OR-021315-01	02/13/15	81mm	Flyer #1	<d, <d
PS-81-Qfilter-WI-021315-02	02/13/15	81mm	Flyer #2	<d, <d

*Masses determined by GC-μECD on the primary and confirmation columns. Estimated detection limit of RDX mass in soil extracts determined under the same analytical conditions is 0.15 μg.

The mass of RDX in the aerial plume was calculated using emission factors based on the flyer filter masses. Sensors on the flyers monitored CO and CO_2 concentrations from air passing through a 37mm PTFE particulate filter. The calculated emissions factors based on the energetics mass on the filters and the CO/CO_2 sensor outputs is 530 and 270 μg RDX per kg of C4, or 580 and 290 μg RDX per kg RDX of the total mass test material. As 5.2 kg of RDX/HMX was detonated over the course of the testing, the estimated energetics in the aerial plume was 2.3 mg of RDX/HMX based on the average of the two flyers. The flyers were positioned within the demarcated snow surface deposition area, so some of this residue may have been recovered in the surface samples, although probably not much. There were no detectable residues in the ODAs.

The two Flyers returned Particulate Matter <2.5 μm ($PM_{2.5}$) emission factors from the C4 detonations of 27 and 32 g/kg RDX/HMX (average = 29 g/kg, RPD = 8%). The hexacopter instrument package returned a $PM_{2.5}$ emission factor of 42 g/kg RDX/HMX **(Fig. 33)**. Readings were obtained for CO and CO_2 during the flight (**Fig. 34**). These factors are quite close for independent systems sampling different parts of the plume and demonstrated the ability of the hexacopter to characterize a detonation plume as well as the flyer system.

a. UAS on ground. EPA Sensors in black box

b. UAS Airborne after a mission

Figure 33. UAF hexacopter UAS with the EPA CO/CO_2 sensor suite payload

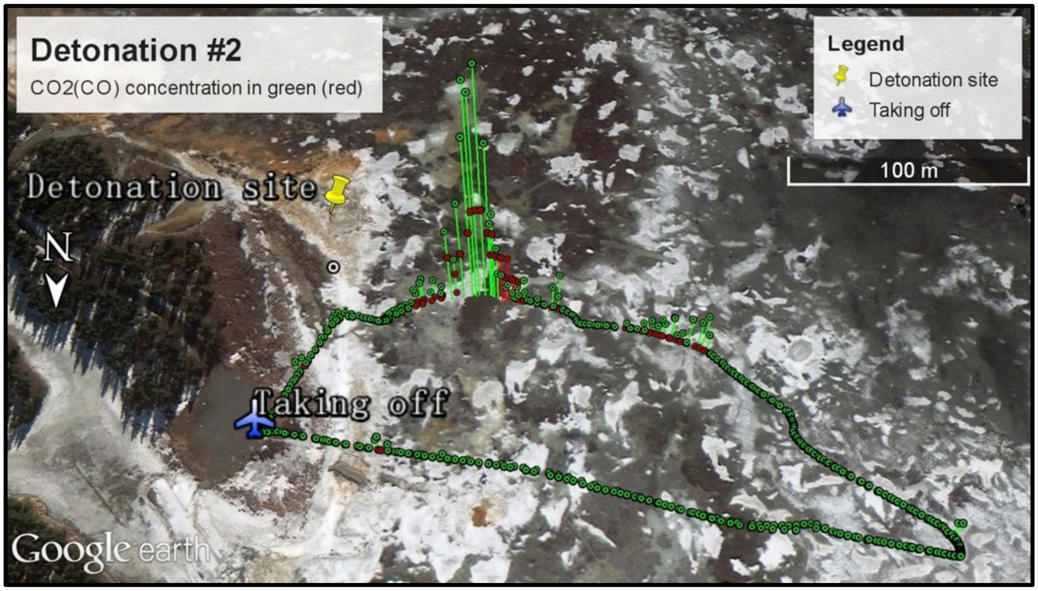


Figure 34. Flight path of UAS and relative concentrations of CO and CO_2 from EPA sensors

Based on the 5.2 kg of energetics consumed during the tests, the total estimated mass of $PM_{2.5}$ is 150 g. These calculations were made using the carbon balance method. The carbon balance method uses a subset of the total emissions to calculate the total amount of emissions. In this method, the target compound is co-sampled with CO and CO_2, the oxidation products that make up the vast majority of the carbon compounds. When the ratio of the sampled target compound mass to the sampled C mass is multiplied by the C in the fuel composition (20.34% for C4), the total amount of the compound released during burning or detonation is determined. This calculated value is the "emission factor," or the mass of target compound emitted per mass of fuel/ordnance. We compared the emission factors for our test against Comp B surface detonations conducted at Tooele, UT. At Tooele, we got 1.1 mg RDX/kg [24].

High-order Detonations – 2017

Samples were analyzed for RDX, HMX, DNAN, TNT, NQ, and NTO. Results will be presented according to the type of round. Quality assurance results will also be presented. Areas of deposition are specified as Inside the Demarcated Area (IDA) and Outside the Demarcated Area (ODA). There are two ODAs: an approximately 3-m wide annulus outside and adjacent the IDA (0-3 m) and a further annulus extending approximately 3 m beyond the ODA 0-3 (ODA 3-6). Total energetics mass is the mean of the explosives residues estimates for all the shots in a test series. The % Analyte and % of

Original Analyte Mass values include the RDX and HMX masses of the fuze booster pellet and the supplemental charge for each round. A discussion of the methods and results follows this section. As noted in the Methods section, we determine the efficiency of the detonation based on detonation efficiency of components of each energetic compound as well as the consumption of the total energetics load. We use ≥99.99% efficiency to describe a high-order detonation and 75% to 99.99% consumption to describe a low-order detonation. We use at most two significant digits in all our data as the precision of most data sets for environmental research and testing do not warrant additional significant digits.

M720 60-mm IMX-104 Mortar Rounds (BA44)

Results of the M720 detonation residues analyses are presented in **Table 27**. Where appropriate, the IDA, ODA, and subsurface results are combined to derive the mass estimate for the shots. The pretest data is included in the table but is not used in the derivation of the estimates for means, medians, % analyte, and standard deviations as the pretest data is based on only one sample. For shots 1-7, the data shown are sums of the mean masses of the replicates for the areas sampled. The overall mean detonation consumption of the RDX/HMX and the DNAN was ≈99.99%, indicative of near-high-order detonations of the IMX-104 filler, the booster, and the supplemental charges. For the NTO, however, the mean detonation efficiency was 97.9%, indicating a slightly inefficient detonation of this compound.

Table 27. M720 60-mm IMX-104 Detonation Residues

9g PBXN-5 booster, 23g PBXW-14 supplemental charge[d]

Shot	IDA (m^2)	ODA 0-3 m (m^2)	ODA 0-6 m (m^2)	Analytes RDX[a] (g)	Analytes DNAN (g)	Analytes NTO (g)	Total Energetics mass (g)	% of Original Analyte Mass[c]
Pretest[e]	197	—	—	0.001	0.006	3.3	3.3	0.9%
1	450	470	360	0.002	0.014	3.6	3.6	1.0%
2	230	290	280	0.001	0.003	2.6	2.6	0.7%
3	240	250	270	0.003	0.006	3.3	3.3	0.9%
4	190	240	250	0.048	0.011	4.7	4.7	1.3%
5	200	230	250	0.004	0.009	4.0	4.1	1.1%
6	200	200	240	0.002	0.006	5.2	5.2	1.5%
7	230	340	280	0.001	0.003	3.2	3.2	0.9%
Mean	**250**	**290**	**280**	**0.009**	**0.007**	**3.8**	**3.8**	**1.1%**
Median	230	250	260	0.002	0.006	3.6	3.6	1.0%
%Analyte[c]	—	—	—	0.012%	0.007%	2.1%	2.1%	—
Standard Deviation	—	—	—	0.017	0.004	0.91	0.92	—

[a] RDX includes some HMX as well (<9% of original mass)
[b] Mean of the combined IDA, ODA, and subsurface estimated masses
[c] Based on mid-range value of formulation specifications
[d] Supplemental charge in filler cavity below fuze well
[e] Not included in analyses at bottom of table

M821 81-mm IMX-104 Mortar Rounds (CA61)

Results of the M821 detonation residues analyses are presented in **Table 28**. Where appropriate, the IDA, ODA, and subsurface results are combined to derive the mass estimate for the shots. The pretest data is included in the table but is not used in the derivation of the estimates for means, medians, % analyte, and standard deviations as the pretest data is based on only one sample. For shots 1-7, the data shown are sums of the mean masses of the replicates for the areas sampled. The overall mean detonation efficiency (consumption) of the RDX/HMX and the DNAN was >99.98%, indicative of near-high-order detonations of the IMX-104 filler, the booster, and the supplemental charges. For the NTO, the mean detonation efficiency was 99.6%, indicating a slightly inefficient detonation of this compound.

Table 28. M821 81-mm IMX-104 Detonation Residues

9g PBXN-5 booster, 45g PBXW-14 supplemental charge[(d)]

Shot	IDA (m^2)	ODA 0-3 m (m^2)	ODA 0-6 m (m^2)	Analytes RDX[(a)] (g)	 DNAN (g)	 NTO (g)	Total Energetics mass (g)	% of Original Analyte Mass[(c)]
wPretest[(e)]	287	—	—	0.003	0.017	0.81	1.6	0.19%
1	740	520	410	0.002	0.012	1.9	1.9	0.23%
2	680	570	410	0.002	0.008	1.3	1.3	0.15%
3	740	420	390	0.001	0.005	1.1	1.1	0.14%
4	740	410	390	0.004	0.016	1.9	1.9	0.23%
5	760	440	400	0.014	0.059	2.0	2.1	0.25%
6	870	440	420	0.050	0.23	3.0	3.3	0.39%
7	830	520	420	0.001	0.006	0.79	0.80	0.10%
Mean	**770**	**470**	**410**	**0.011**	**0.047**	**1.7**	**1.8**	**0.21%**
Median	740	440	400	0.002	0.012	1.9	1.9	0.22%
%Analyte[(c)]	—	—	—	0.007%	0.018%	0.40%	0.21%	—
Standard Deviation	—	—	—	0.018	0.081	0.73	0.81	—

[(a)] RDX includes some HMX as well (<9% of original mass)

[(b)] Mean of the combined IDA, ODA, and subsurface estimated masses

[(c)] Total analyte for each munition based on mid-range value of formulation specifications

[(d)] Supplemental charge in filler cavity below fuze well

[(e)] Not included in analyses at bottom of table

M1122 155-mm IMX-101 Howitzer Rounds (DA51)

Results of the M1122 detonation residues analyses are presented in **Table 29**. Data is for the three shots, composed of one shot of one round and two shots of three rounds. The pretest detonation residues were not sampled and thus there are no data for this test in the table. The area swept to collect the detonation residues for the three shots was 580 m (Shot 1) and 1200 m^2 (Shots 2 & 3). There was a total of approximately 150 g of RDX and HMX in the fuze booster pellet and supplementary charge of the round. Neither of these energetic compounds were detected in the residues, indicating proper functioning of the fuzing system and supplemental charge. For the NTO, the mean detonation efficiency was 86%, indicating that this compound did not detonate properly. The total masses reported for NQ and DNAN are underestimated because of transformation of the compound due base hydrolysis. Cement from the concrete filler of the round was swept up and collected in all the samples, causing the melted samples to become alkaline. The pH of the aqueous samples and the debris extracts was between 11 and 12, very basic **(Appendix C).** The breakdown products were identified later in the analysis process but not quantified.

Table 29. M1122 155-mm IMX-101 Detonation Residues

9g PBXN-5 booster, 150g PBXN-9 supplemental charge[(c)]

Shot	DNAN[(a)] (g)	Analytes NTO (g)	NQ (g)	Total Energetics mass[(a)] (g)	% of Original Analyte Mass[(b)]
1	1.6	31	50	83	7.3%
2	3.6	37	73	110	10%
3	1.5	29	40	71	6.2%
Mean	2.4	33	56	91	8%
Median	1.6	31	50	83	7%

%Analyte[(b)]	0.5%	14%	13%	8%	—

(a) Mean values for multi-round shots

(b) Based on mid-range value of formulation specifications

(c) Supplemental charge in filler cavity below fuze well

M889A2 81-mm Comp-B Mortar Rounds (CA43)

Results of the high-order detonation residues analyses for the M889A2 mortar rounds are presented in **Table 30**. Note that these tests were conducted with the CRREL Fuze Simulator (CFS) system with 12 g of C4 for the booster pellet. Where appropriate, the IDA and ODA results are combined to derive the mass estimate for the detonations. No HMX or TNT was detected in the samples. The overall mean detonation efficiency (consumption) of the RDX/HMX was >99.999%, indicative of high-order detonations.

Table 30. M889A2 81-mmComp-B Detonation Residues

12g Comp-B fuze CFS booster, no supplemental charge

Shot	Analytes HMX (g)	RDX (g)	TNT (g)	Total Energetics mass[(a)] (g)	% of Original Analyte Mass[(b)]
1	BDL[(c)]	BDL	BDL	BDL	—
2	BDL	BDL	BDL	BDL	—
3	BDL	BDL	BDL	BDL	—
4	BDL	BDL	BDL	BDL	—
5	BDL	0.0006	BDL	0.0006	0.00006%
6	BDL	BDL	BDL	BDL	—
Mean	—	*<0.0001*	—	*<0.0001*	*0.00001%*
Median	—	—	—	—	—
%Analyte[(b)]	≈0.0%	0.00002%	≈0.0%	0.00001%	—

(a) Mean values for combined analytes (HMX and RDX)

(b) Based on mid-range value of formulation specifications

(c) Below Detection Limits of analytical instrumentation

Deposition Areas

Demarcated sampled areas for the background samples, pretest initiation systems test detonations, and munitions residues tests are tabulated in **Table 31**. A map of the sampled areas is shown in **Figure 35**. The 40-m x 60-m ice pad was located near the Background 1 sampled area and is not shown on this map. The darker inner areas denote the areas demarcated as inside the demarcated deposition area (IDA). The two surrounding annuli are the outside the demarcated areas 0- to 3-m and 3- to 6-m. The background samples were collected prior to the detonation of any rounds for this test. The access road to the test area ran from the east side of the map, past the west side of the Background 1 collection area, and between the three rows of shots, connecting on both the east and west ends of the test area.

Table 31. Tabulated data for areas sampled for energetics

Sampled Areas	IDA (m²)	ODA 0-3 m (m²)	ODA 3-6 m (m²)
Clunie Background	760	-	-
Tower Background	110	-	-
81-mm IMX-104 Pretest	287	-	-
60-mmIMX-104 Pretest	197	-	-
60-mm IMX-104			
Shot 1	450	470	360
Shot 2	230	290	280
Shot 3	240	250	270
Shot 4	190	240	250
Shot 5	200	230	250
Shot 6	200	200	240
Shot 7	230	310	280
Means	250	280	280
81-mm IMX-104			
Shot 1	740	520	410
Shot 2	680	570	410
Shot 3	740	420	390
Shot 4	740	410	390
Shot 5	760	440	400
Shot 6	870	440	420
Shot 7	830	520	420
Means	770	470	410
81-mm Comp-B			
Shot 1	300	290	290
Shot 2	240	350	350
Shot 3	370	300	310
Shot 4	410	350	330
Shot 5	590	420	370
Shot 6	570	380	360
Means	410	350	340
155-mm IMX-101			
Shot 1 (1 Round)	580	-	-
Shot 2 (3 Rounds)	1200	-	-
Shot 3 (3 Rounds)	1200	-	-

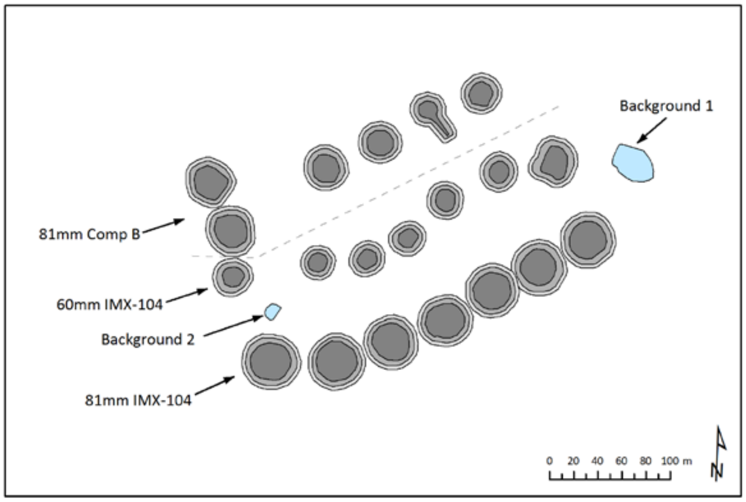


Figure 35: Map of deposition areas for 60- and 81-mm rounds.

Quality Assurance Results

Quality assurance (QA) is a critical component in the determination of data validity and robustness. In both Canada and the US, extensive QA is conducted in the field (sampling), the processing laboratory (sample processing), and the analytical laboratory (analysis). QA has also been used to develop and refine the processes used to develop methods that have enabled us to greatly reduce variability between sample reps for each detonation as well as between detonations.

Table 32. Typical US Quality assurance procedures

Location	Purpose	Typical Number
Field		
Baseline samples	Check for site contamination	2
Multiple detonations	Detonation process variability	7
Replicate sampling	Sampling reproducibility	3 / IDA Up to 3 for ODAs
ODA sampling (0-3 m)	Proper IDA demarcation	All dets
ODA Sampling (3-6 m)	Proper IDA demarcation	All dets
Subsurface sampling (IDAs)	Proper sampling depth	1/Test
Processing Lab		
SPE Triplicates	SPE reproducibility	2–3
SPE Blanks	Verify absence of analytes in reagent water	1 per day
Filtration blanks-Aqueous	Check for processing cross contamination	1 per day
Filtration blanks-Filters	Check for processing cross contamination	1 per day
SPE Lab control samples	Cartridge retention of analyte	1/day
Matrix spikes	Check for interferences and degradation	2–3
Analytical Lab		
Detonation particle analyses	Verify calibration standards	As needed
Dual column analyses	Confirm analyte presence	As needed

2012 QA

Analyses of the two background samples taken prior to testing indicated no detectable levels of the contaminants of concern (COCs: <0.001 mg): HMX, RDX, and DNAN. ODAs contained on average <1.2% of the total estimated residues mass. Subsurface sampling of one detonation indicated ≈2.3% of the residues was below the top 2.5 cm of the snow surface. All SPE and solvent blanks were below detection limits. Recoveries from matrix spikes ranged from 104% to 105%, and lab control sample recoveries ranged from 96% to 111%, all within typical limits. SPE replicates varied between 2 – 4% for RDX, HMX, and DNAN. Data for the IDA residues was normally distributed. Results for the perchlorate analyses conducted at three independent labs agreed within 7%.

2013 QA

Analyses of the two background samples taken prior to testing indicated no detectable levels of the COCs. ODAs averaged 4.3% of overall residues (0.6% without the 81 mm high-order plumes for which we had demarcation difficulties) and subsurface samples averaged 0.2% of the overall residues, indicating that most of the plumes were correctly demarcated and those that were not were compensated for by the ODA samples. In the lab, the SPE triplicates had an average relative standard deviation of <0.3%, indicating reproducibility for the SPE concentration process and lab analyses. The SPE blank had no detectable COCs. The mean recovery values for the SPE control samples were 100% for HMX and 101% for RDX and DNAN, again indicating successful processing and analysis techniques for these tests. Matrix spikes on a sample aqueous aliquot showed no influence on the original concentrations of the COCs due to the spiked solution. The SPE filtration blanks indicated very low (at detection limit) concentrations of DNAN for three of the four aqueous fractions and no detectable COCs for the filter extracts, indicating no carryover from the glassware cleaning process. All QA indicates the data are robust.

2014 QA

Quality assurance procedures were conducted in the field, in the processing lab in Alaska, and in the analytical lab in New Hampshire. The QA procedures are listed in **Table 33**. The results for the QA conducted in 2014 by CRREL will be presented in the order shown below.

Table 33. US Quality assurance procedures – 2014

Location	Purpose	Number
Field		
Baseline samples	Check for site contamination	2
Multiple detonations	Detonation process variability	5 -7
Replicate sampling	Sampling reproducibility	3 / IDA
ODA sampling (0-3 m)	Proper IDA demarcation	All dets
ODA Sampling (3-6 m)	Proper IDA demarcation	18 Dets
Subsurface sampling	Proper sampling depth	8 IDAs
Processing Lab		
SPE Triplicates	SPE reproducibility	2
SPE Blanks	Verify absence of analytes in reagent water	5 (1/day)
Filtration blanks-Aqueous(a)	Check for processing cross contamination	3
Filtration blanks-Filters(a)	Check for processing cross contamination	3
Filtration blanks-Aqueous(b)	Check for processing cross contamination	3
Filtration blanks-Filters(b)	Check for processing cross contamination	3
SPE Lab control samples	Cartridge retention of analyte	5 (1/day)
Matrix spikes	Check for interferences and degradation	2
Analytical Lab		
Detonation particle analyses	Verify calibration standards	6
Direct analyses-DNAN	Compare to SPE analyses	9
Dual column analyses	Confirm analyte presence	As needed

(a) Filtration blanks for RDX, HMX, and DNAN (SPE used for aqueous portion)
(b) Filtration blanks for NTO and NQ (SPE not used for aqueous portion)

Baseline samples: Two baseline (background) samples were taken from 20- x 20-m areas prior to testing. The sample locations are shown in **Figure 8**. No analytes of interest were detected in either sample.

Detonation sampling: Four tests were conducted for which samples were taken and chemical analyses of the residues were performed. These are listed in **Table 34**. Included in the table is the sampling QA performed for the tests. The ranges of the mean mass estimation values for the combined IDA and ODA samples for each analyte are given in **Tables 4 and 9. Table 35** presents the mean masses and the range of total estimated mean mass values for each test. Also shown are ODA and Subsurface masses as a percentage of the mean IDA masses. These last two values are an indicator of the accuracy of the delineation of the IDAs and the sampling depths.

The range of values for the detonation masses averages 1.5 times the lowest value for all five series of tests. A factor of 2 or less is quite good for these types of tests. ODAs average less than 1.2% of the

IDA mass, and subsurface samples averaged less than 1.1% of the total surface residues. All mean ODA and subsurface samples were less than 3% of the IDAs, and most were less than 1.5% of the IDAs.

Table 34. Sampling QA

	High-order Dets		BIPs –1 Block		BIPs – 2 Blocks	
Test / Procedure	QA Operations	Reps[(a)]	QA Operations	Reps[(a)]	QA Operations	Reps[(a)]
155-mm Rounds						
Detonations	7	–	3	–	3	–
Triplicate IDA samples	7	3	3	3	3	3
ODA 0-3 m Samples	3	3	2	1	2	1
	4	1	1	3	1	3
ODA 3-6 m Samples	4	1	1	1	1	1
Subsurface samples	2	1	1	1	1	1
	1	2	–	–	–	–
81-mm Rounds						
Detonations	5	–	7	–		
Triplicate IDA samples	5	3	7	3		
ODA 0-3 m Samples	5	3	4	1		
	–	–	3	3		
ODA 3-6 m Samples	5	1	3	1		
Subsurface samples	1	1	1	1		

[(a)] Replicates per QA operation: For each of seven detonations, three replicate samples were taken from the IDA.

Table 35. QA statistics for detonation residues samples

Test	IDA Mean Mass (g)	IDA Mass Range (g)	ODA: % IDA Mean	Subsurface: % IDA Mean
155-mm High-order	150.	94. – 210.	1.2%	1.2%
155-mm BIP (1 Block)	120.	110. – 140.	1.4%	2.8%
155-mm BIP (2 Blocks)	150.	120. – 160.	2.8%	0.51%
81-mm High-order	0.55	0.36 – 0.72	0.30%	0.28%
81-mm BIP	52.	35. – 76.	0.12%	0.60%
Mean		1.5x[(a)]	1.2%	1.1%

[(a)] Highest mean IDA mass value averages 1.5 timers the lowest mean IDA mass value

Filtration Blanks: Three filtration blanks using Type-1 reagent-grade water drawn from the filtration system at the processing lab were run through the glassware used to process the samples. The glassware used was the last set run through the wash cycle at the lab prior to change out. Both the aqueous fraction and the filters were processed and analyzed. For HMX, RDX, and DNAN, the aqueous samples were processed using SPE prior to analysis. NTO and NQ aqueous analytical samples were prepared directly from the aqueous aliquots. No analytes were detected for any of the samples.

SPE Triplicates: SPE triplicates were performed on two samples. Sample 14FRA113 was taken from an 81-mm BIP detonation ODA. Sample 14FRA059 was taken from a 155-mm BIP detonation ODA area. Data is shown in **Table 36**. The results are for RDX, HMX, and DNAN only because NTO and NQ were not processed through SPE cartridges. Although many values are close to the instrument's detection limits, the agreement is very good in both cases for the three analytes.

Table 36. SPE triplicates QA results

Sample	HMX: mg/L	RDX: mg/L	DNAN: mg/L
IMX-104 (81-mm)			
14FRA113 SPE Rep 1	<0.0002	0.0018	0.0085
14FRA113 SPE Rep 2	<0.0002	0.0020	0.0092
14FRA113 SPE Rep 3	<0.0002	0.0017	0.0081
Mean	<0.0002	0.0019	0.0086
IMX-101 (155-mm)			
14FRA059 SPE Rep 1	<0.0002	<0.0002	0.033
14FRA059 SPE Rep 2	<0.0002	<0.0002	0.032
14FRA059 SPE Rep 3	<0.0002	<0.0002	0.032
Mean	<0.0002	<0.0002	0.032

SPE Laboratory Control Samples: Five 500-mL aqueous laboratory control samples consisting of Type-1 reagent-grade water spiked at 0.004 mg/L with RDX, HMX, and DNAN were run through the SPE process, eluted, and analyzed for retention of the analytes. One sample was run on each day of sample processing in the field lab in Alaska using water drawn from the filtration system that day. Results are shown in **Table 37**. Recoveries of the analytes were within normal ranges (±10%), with no apparent loss of analyte.

Table 37. SPE Laboratory control (spikes) sample results

Sample	HMX: mg/L	Recovery	RDX: mg/L	Recovery	DNAN: mg/L	Recovery
14 March	0.0041	103%	0.0042	106%	0.0046	115%
15 March	0.0041	103%	0.0041	104%	0.0043	108%
19 March	0.0040	100%	0.0040	100%	0.0042	104%
20 March	0.0042	104%	0.0041	102%	0.0042	104%
21 March	0.0042	105%	0.0042	106%	0.0043	108%
Target:	0.0040	100%	0.0040	100%	0.0040	100%
Means	0.0041	103%	0.0041	103%	0.0043	108%

Matrix Spikes: Matrix spikes were conducted on aqueous aliquots of the two samples used for SPE triplicates QA test (**Table 36**). The ODA samples, 14FRA059 and 14FRA113, were spiked at 0.004 mg/L and processed by SPE, extracted with AcN, and analyzed. HMX, RDX, and DNAN were the analytes of concern. A duplicate of sample 14FRA059 was also run. **Table 38** describes the results. All recoveries are at least 100%. There were no apparent matrix effects such as interfering peaks or degradation of the spiked analytes.

Table 38. Matrix spike of samples results

Sample	HMX: mg/L	RDX: mg/L	DNAN: mg/L
Spike concentration	0.004	0.004	0.004
IMX-104 (81-mm)			
14FRA059	<0.0002	<0.0002	0.032
14FRA059-MS 1	0.0040	0.0042	0.037
14FRA059-MS 2	0.0041	0.0044	0.036
Recovery[a]	100%	105%	100%
IMX-101 (155-mm)			
14FRA113	<0.0002	0.0019	0.0086
14FRA113-MS	0.0042	0.0060	0.013
Recovery[a]	102%	102%	100%

[a] For values below detection limits, half the detection limit (0.0001) is used as the sample concentration.

Detonation particle analyses: Five particles that had been collected in the field following a low-order detonation were returned to the processing lab and weighed to obtain their mass. The particles were processed and analyzed to determine how well the results correlate with the manufacturer's specifications. **Table 39** summarizes the results. Recovery rates closely matched the milspecs (military specifications) for the composition.

Table 39. IMX-101 detonation particles analysis results

Particle	Mass (mg)	DNAN (mg)(a)	% of Mass	NQ (mg)	% of Mass	NTO (mg)	% of Mass	Sum(b) (mg)	Recovery(c)
A	101.	41.	40%	40.	39%	21.	20%	102.	101%
B	117.	50.	42%	47.	39%	23.	19%	119.	102%
C	208.	92.	44%	75.	36%	41.	20%	208.	100%
D	82.	36.	44%	29.	36%	15.	19%	81.	98%
E	65.	28.	43%	25.	38%	12.	19%	65.	100%
Means	115.	49.	43%	43.	38%	23.	19%	115.	100%
Specification	—	49.	42.5%	43.	37.5%	23.	20%	115.	100%

(a) Derived from analytical data
(b) Sum of analytically derived masses for listed compounds
(c) Comparison of the sum of the analytically-derived mass to original particle mass

The close match between the analytical values and the manufacturer's specifications indicates that the calibration of the instrument for the columns used (NovaPackC8 for the DNAN, Hypercarb for the NQ and NTO) is accurate. It also demonstrates that the ratio between the ingredients in post-detonation samples is not changed. Specification tolerances for the compounds within the formulation are all ±2.5%.

Direct Analysis of DNAN: A test was run comparing analytical results derived from nine samples processed using solid phase extraction versus direct analysis from aqueous aliquots of the same samples. Results are illustrated in **Figure 36**. There is very close agreement between the two sets of data, indicating that both methods will give equivalent results

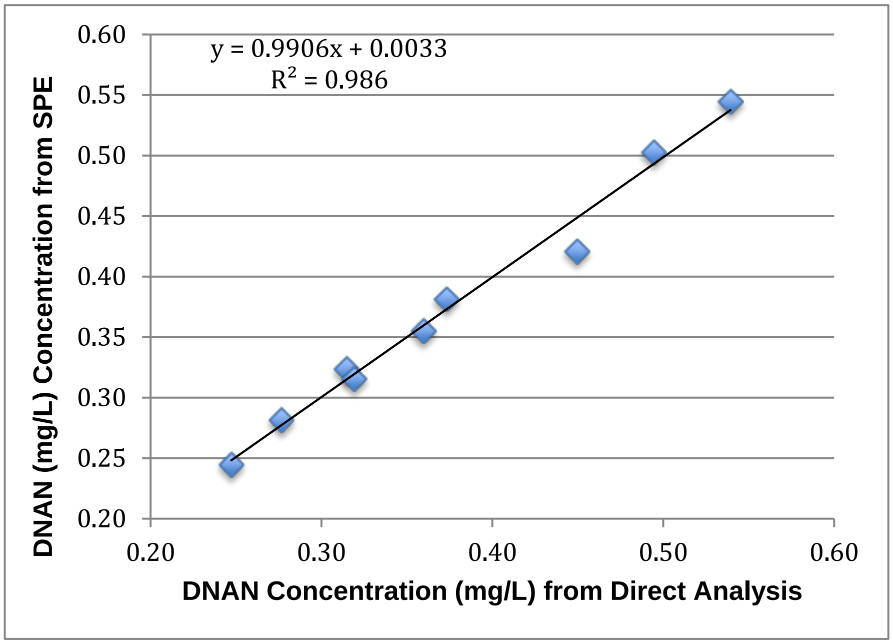


Figure 36. Analytical results for DNAN in aqueous fractions of samples processed using two different methods

SPE Blanks: One blank was run each day we processed samples in the lab in Alaska. Reagent grade water processed through the SPE setup and analyzed for HMX, RDX, and DNAN. No analytes were detected (<0.0002 mg/L) in any of the SPE blank samples.

2015 QA

Quality assurance procedures were conducted in the field, in the processing lab in Alaska, and in the analytical lab in New Hampshire. The QA procedures for 2015 are listed in **Table 40**. The results for the QA will be presented in the order shown below.

Table 40. US Quality assurance procedures - 2015

Location	Purpose	Number
Field		
Multiple detonations	Detonation process variability	2
Processing Lab		
SPE Triplicates	SPE reproducibility	1
SPE Blanks	Verify absence of analytes in reagent water	5 (1/day)
Filtration blanks-Aqueous(a)	Check for processing cross contamination	3
Filtration blanks-Filters(a)	Check for processing cross contamination	3
Filtration blanks-Aqueous(b)	Check for processing cross contamination	3
Filtration blanks-Filters(b)	Check for processing cross contamination	3
SPE Lab control samples	Cartridge retention of analyte	5 (1/day)
Matrix spikes	Check for interferences and degradation	2
Analytical Lab		
Detonation particle analyses	Verify calibration standards	6
Dual column analyses	Confirm analyte presence	As needed

(a) Filtration blanks for RDX, HMX, and DNAN (SPE used for aqueous portion)
(b) Filtration blanks for NTO (SPE not used for aqueous portion)

Before analyses of the results could be finalized, detection limits for the analytes needed to be calculated for the residues samples that encompassed the entire detonation IDA areas. Detection limits will differ from those derived for the MI samples because the samples are much larger (greater aqueous volume) and the mass of residues in the samples is much greater. The mass detection limits are shown in **Table 41**. The detection limit in the sample extracts was 0.02 mg/L for the three compounds, which is equivalent to 0.0002 mg/L in the aqueous samples that were pre-concentrated by a factor of 100 using SPE. NTO differs from the other analytes because it is analyzed using a different method. See Methods above.

Table 41. Mass Detection Limits for Whole-IDA Samples

	Aqueous Fraction				Soot Fraction			Total Sample
Analyte	In SPE Extract Concentration	In Aqueous Concentration	Typ. Filtrate Volume	Detectable Mass (Min.)	Filter Extract Concentration	Solvent Volume	Detectable Mass (Min.)	Detectable Mass (Min.)
HMX	0.02 mg/L	0.0002 mg/L	10 L	0.002 mg	0.02 mg/L	0.25 L	0.005 mg	0.007 mg
RDX	0.02 mg/L	0.0002 mg/L	10 L	0.002 mg	0.02 mg/L	0.25 L	0.005 mg	0.007 mg
DNAN	0.02 mg/L	0.0002 mg/L	10 L	0.002 mg	0.02 mg/L	0.25 L	0.005 mg	0.007 mg
NTO	—	0.005 mg/L	10 L	0.05 mg	0.005 mg/L	0.25 L	0.0013 mg	0.051 mg

SPE Blanks: One blank was run each day we processed samples in the lab in Alaska. Reagent grade water was processed through the SPE setup and analyzed for HMX, RDX, and DNAN. No analytes were detected (<0.0002 mg/L) in any of the SPE blank samples.

SPE Triplicates: SPE triplicates were performed on one sample. Sample 15FRA09 was taken from an 81-mm high-order detonation swept (whole population) deposition area sample. Data is shown in **Table 42**. The results are for RDX, HMX, and DNAN only because NTO was not processed through SPE cartridges. Although many values are close to the instrument's detection limits, the agreement is excellent for the three analytes.

Table 42. SPE triplicates QA results

Sample	HMX: mg/L	RDX: mg/L	DNAN: mg/L
SPE Triplicates			
15 FRA09a SPE	<0.002	0.0057	0.0004
15 FRA09b SPE	<0.002	0.0058	0.0004
15 FRA09c SPE	<0.002	0.0057	0.0003
Mean	<0.0002	0.0057	0.00035

SPE Laboratory Control Samples: Four 500-mL aqueous laboratory control samples consisting of Type-1 reagent-grade water spiked at 0.004 mg/L with RDX, HMX, and DNAN were run through the SPE process, eluted, and analyzed for retention of the analytes. The samples were processed in the field lab in Alaska using water drawn from the filtration system that day. Results are shown in **Table 43**. Recoveries of the analytes were within normal ranges (±10%), with no apparent loss of analyte.

Table 43. SPE Laboratory control (spikes) sample results

	HMX		RDX		DNAN	
Sample	mg/L	Recovery	mg/L	Recovery	mg/L	Recovery
1	0.0039	101%	0.0040	101%	0.0039	101%
2	0.0037	95%	0.0038	96%	0.0036	94%
3	0.0040	102%	0.0040	101%	0.0040	104%
4	0.0040	102%	0.0040	101%	0.0039	101%
Target:	0.004	100%	0.004	100%	0.004	100%
Means	0.004	100%	0.004	100%	0.004	100%

Filtration Blanks: Three filtration blanks using Type-1 reagent-grade water drawn from the filtration system at the processing lab were run through the glassware used to process the samples. The glassware used was the last set run through the wash cycle at the lab prior to change out of the wash and rinse water. Both the aqueous fraction and the filters were processed and analyzed. For HMX, RDX, and DNAN, the aqueous samples were processed using SPE prior to analysis. NTO aqueous analytical samples were prepared directly from the aqueous aliquots. No analytes were detected for any of the samples.

Detonation Particle Compositional Analyses

The results of the analyses of the particles collected from the detonations to determine the explosive filler composition of the munitions tested are presented in **Table 44**. There are quantitative ranges normally associated with the energetic compounds within explosive formulations. The theoretical range of the masses in the collected particles for the three energetic compounds based on the specifications for the compounds in the formulation are given in the "Expected Range" column. The actual mass recovered from each particle is given in the "Mass Found" column. Variance from the expected mass range and differences in summed masses from weighed mass can be attributed to compositional variability in the components found within the particles, rounding errors, small particle sizes, and minor measurement errors.

Table 44. Masses of IMX-104 particles determined by a scale and by HPLC analysis

Particle	Mass (mg) Weighed	Analyte	Expected Mass Range (mg)	Mass (mg) Found
1	21	DNAN	6.2 - 7.1	6.5
		RDX	2.8 - 3.6	3.6
		NTO	11 - 12	11
			sum	21
2	35	DNAN	10 - 12	10
		RDX	4.7 - 6.1	5.8
		NTO	18 - 19	20
			sum	36
3	47	DNAN	14 - 16	14
		RDX	6.3 - 8.1	7.6
		NTO	24 - 26	28
			sum	49
4	54	DNAN	16 - 18	17
		RDX	7.2 - 9.3	10
		NTO	28 - 30	31
			sum	57
5	84	DNAN	25 - 28	25
		RDX	11 - 15	14
		NTO	43 - 46	46
			sum	85

Matrix Spikes: Matrix spikes were conducted on aqueous aliquots of the two samples used for SPE triplicates QA test **(Table 42)**. The samples, 15 FRA09 MS-1and a duplicate, 15 FRA09 MS-2, were spiked with 0.004 mg/L of HMX, RDX, and DNAN and processed by SPE, extracted with AcN, and analyzed. **Table 45** depicts the results. Recoveries for RDX and DNAN are in the 90% range, very good for the low concentrations of the original samples. The HMX recovery appears high, but that is an artifact of interferences attributable to the short elution time for HMX. There were no apparent matrix effects such as degradation of the spiked analytes.

Table 45. Matrix spike of samples results

Sample	HMX mg/L	RDX mg/L	DNAN mg/L
Spike concentration	0.0040	0.0040	0.0040
15 FRA09	<0.0002	0.0057	0.0003
15 FRA09 MS-2	0.0037	0.0089	0.0039
15 FRA09 MS-2	0.0039	0.0095	0.0041
Recovery[a]	93%	88%	91%

[a] For values below detection limits, half the detection limit (0.0001) is used as the sample concentration.

2017 QA

Quality assurance procedures were conducted in the field, in the processing lab in Alaska, and in the processing and analytical labs in New Hampshire. The QA procedures are listed in **Table 46**. The results for the QA will be presented in the order shown below.

Table 46. Quality assurance procedures (IMX Rounds)

Location	Purpose	Number
Field		
Baseline samples	Check for site contamination	2
Multiple detonations	Detonation process variability	6 -8
Replicate sampling[c]	Sampling reproducibility	3 per IDA & 0-3 m ODA
ODA sampling (0-3 m)[c]	Proper deposition area demarcation	All dets w/ replicates
ODA Sampling (3-6 m)[c]	Proper deposition area demarcation	11 of 14 dets/ few replicates
Subsurface sampling[c]	Proper sampling depth	1 ea. 60- & 81-mm IDAs
Processing Lab		
SPE Triplicates	SPE reproducibility	4
SPE Blanks	Verify absence of analytes in reagent water	7
Filtration blanks-Aqueous[a]	Check for processing cross contamination	6
Filtration blanks-Aqueous[b]	Check for processing cross contamination	5
SPE Lab control samples	Cartridge retention of analyte	8
Matrix spikes	Check for interferences and degradation	4
Analytical Lab		
Dual column analyses	Confirm analyte presence	As needed
Acquisition of UV spectra	Confirm analyte presence	As needed
Subsampling replicates	Measure uncertainty of subsampling	IMX-101 solids

[a] Filtration blanks for NTO and NQ and RDX, HMX, and DNAN (SPE used for aqueous portion). In-process blanks.

[b] Filtration blanks for NTO and NQ and RDX, HMX, and DNAN (SPE used for aqueous portion). Post-processing blanks.

[c] Conducted on mortar rounds only. Howitzer rounds were whole population samples collected from ice surface

Baseline samples

Two baseline (background) multi-increment samples were taken prior to testing. The sample locations are shown in **Figure 9**. No analytes of interest were detected in either sample.

Detonation sampling

Four tests were conducted for which samples were taken and chemical analyses of the residues were performed. Three tests were conducted on IM rounds and one on a conventional (Comp-B) round. The tests are listed in **Table 47**. A total of 233 samples were taken to characterize the 27 rounds tested. If the baseline and initiator test samples are included, the total becomes 237. The ranges of the mean mass estimation values for the combined IDA and ODA samples for each analyte are given in **Tables 27, 28, and 30**. **Table 48** presents the mean masses and the range of total estimated mean mass values for each test. Also shown are ODA and SS masses as a percentage of the mean IDA masses. These last two values are an indicator of the accuracy of the delineation of the IDAs and the sampling depths.

The range of values for the detonation masses averages about three times the lowest value for the three series of tests for which a determination can be made. A factor of 3 or less is good for these types of tests and indicates reproducible data. Energetics in the ODAs average less than 0.5% of the IDA mass, and subsurface samples averaged less than 0.2% of the total surface residues. Both means are quite low, indicating that the demarcation and sampling of the IDAs was done correctly.

Table 47. Field Sampling QA

Test / Procedure	Operation	Reps(a)
60-mm Rounds		
Detonations	7	–
IDA Samples	7	3
ODA 0-3 m Samples	7	3
ODA 3-6 m Samples	7	1
IDA subsurface samples (SS)	1	1
81-mm Rounds (IMX-104)		
Detonations	7	–
IDA Samples	7	3
ODA 0-3 m Samples	4	3
	3	1
ODA 3-6 m Samples	1	3
	3	1
IDA Subsurface Samples (SS)	1	1
81-mm Rounds (Comp-B)		
Detonations	6	–
IDA Samples	6	3
ODA 0-3 m Samples	4	3
	2	1
ODA 3-6 m Samples	3	1
IDA Subsurface Samples (SS)	0	0
155-mm Rounds (IMX-101)		
Detonations	7	–
IDA Samples	3	1

(a) Replicates per QA operation: For each of seven detonations, three replicate samples were taken from the IDA. For the 155-mm rounds, the whole population was sampled and no ODA samples were collected.

Table 48. QA statistics for detonation residues samples

Test	IDA Mean Mass (g)	IDA Mass Range (g)	ODA: % of Total Mean	SS: % of IDA Mean
60-mm IMX-104	3.8	2.6 – 5.2	0.3%	0.4%
81-mm IMX-104	1.8	0.80 – 3.3	0.5%	<0.0001%
81-mmComp-B	0.0001	0.0 – 0.0006	<0.0001%	—
Mean		≈3x(a)	<0.3%	<0.2%

(a) Highest mean IDA mass value averages 3 times the lowest mean IDA mass value

SPE Triplicates

SPE triplicates were performed on four samples. Samples 17FRAP36 and 17FRAP37 were taken from 81-mm IMX-104 detonation ODA annuli. Sample 17FRAP076 was taken from a 60-mm IMX-104 ODA annulus. 17FRAP111 was from an 81-mm IMX104 detonation inside the deposition area. Three sets of triplicates were blank. Data are shown in **Table 49** for the two samples with detectable analytes. The results are for RDX, HMX, and DNAN only because NTO and NQ were not processed through SPE cartridges. Although many values are close to the instrument's detection limits, the agreement is very good in both cases for the analytes.

Table 49. SPE triplicates QA results

Sample	HMX: mg/L	RDX: mg/L	DNAN: mg/L
IMX-104 (81-mm)			
17FRAP37 SPE Rep 1	<0.0002	0.00029	<0.0002
17FRAP37 SPE Rep 2	<0.0002	0.00029	<0.0002
17FRAP37 SPE Rep 3	<0.0002	0.00029	<0.0002
Mean	<0.0002	0.00029	<0.0002
IMX-104 (81-mm)			
17FRAP111 SPE Rep 1	<0.0002	0.0015	0.0014
17FRAP111 SPE Rep 2	<0.0002	0.0016	0.0014
17FRAP111 SPE Rep 3	<0.0002	0.0016	0.0014
Mean	<0.0002	0.0016	0.0014

SPE Blanks

Six blanks were processed with the samples in the lab in Alaska and one blank was processed in Hanover along with the final filtration blanks. Reagent grade water was passed through the SPE setup and analyzed for HMX, RDX, and DNAN. No analytes were detected (<0.0002 mg/L) in the SPE blank samples.

Filtration Blanks

Six filtration blanks using 2 L of Type-1 reagent-grade water drawn from the filtration system at the field lab were run through the glassware used to process the samples. The glassware used was the last set run through the wash cycle at the lab prior to change out. Five filtration blanks were processed after the final glassware washing. Both the aqueous fraction and the filters were analyzed. For HMX, RDX, and DNAN, the aqueous samples were concentrated using SPE prior to analysis. NTO and NQ analytical samples were prepared directly from the aqueous aliquots. No analytes were detected for any of the samples.

SPE Laboratory Control Samples

Eight 500-mL aqueous laboratory control samples (LCSs) consisting of Type-1 reagent-grade water spiked with RDX, HMX, and DNAN were run through the SPE process, eluted, and analyzed for retention of the analytes. Six LCSs were produced in the field lab during the sample processing. The last two LCSs were produced in Hanover for analysis with the final filtration blanks. Results are shown in **Table 50**. Recoveries of the analytes were within normal ranges (±10%), with no apparent loss of analyte for all but LCS2.

Matrix Spikes

Matrix spikes/matrix spike duplicates (MS/MSD) were conducted on aqueous aliquots of four samples. The ODA samples, 17FRAP036, 17FRAP037, and 17FRAP076, and IDA sample 17FRAP112 were spiked and processed by SPE, extracted with AcN, and analyzed. HMX, RDX, and DNAN were the analytes of concern. **Table 51** describes the results. All recoveries except one for HMX were near 100%. There were no apparent matrix effects such as interfering peaks or degradation of the spiked analytes.

Table 50. SPE Laboratory control (spikes) sample results

Sample	HMX: mg/L	Recovery	RDX: mg/L	Recovery	DNAN: mg/L	Recovery
LCS1 22 Feb	0.00077	96%	0.0039	98%	0.010	100%
LCS2 24 Feb	0.00053	66%	0.0028	70%	0.0071	71%
LCS3 24 Feb	0.00079	99%	0.0040	100%	0.010	100%
LCS4 25 Feb	0.00078	98%	0.0040	100%	0.011	110%
LCS5 25 Feb	0.00079	99%	0.0040	100%	0.011	110%
LCS6 25 Feb	0.00067	84%	0.0036	90%	0.0093	93%
Target:	0.0008	100%	0.0040	100%	0.010	100%
Means	0.00072	90%	0.0037	93%	0.0097	97%
LCS7 14Jun	0.0041	103%	0.0042	105%	0.0043	108%
LCS8 14Jun	0.0037	93%	0.0038	95%	0.0039	98%
Target:	0.004	100%	0.004	100%	0.004	100%
Means	0.0039	98%	0.0040	100%	0.0041	103%

Table 51. Matrix spike of samples results

Sample	HMX: mg/L	RDX: mg/L	DNAN: mg/L
Spike concentration	0.0008	0.004	0.010
IMX-104 (81-mm) ODA			
17FRAP036	<0.0002	<0.0002	<0.0002
17FRAP036-MS	0.00080	0.0040	0.011
17FRAP036-MSD	0.00082	0.0042	0.011
Recovery	101%	103%	110%
IMX-104 (81-mm) ODA			
17FRAP037	<0.0002	0.00029	<0.0002
17FRAP037-MS	0.00087	0.0045	0.011
17FRAP037-MSD	0.00081	0.0043	0.010
Recovery	105%	103%	105%
IMX-104 (60-mm) ODA			
17FRAP076	<0.0002	<0.0002	<0.0002
17FRAP076-MS	0.00076	0.0041	0.011
17FRAP076-MSD	0.00061	0.0036	0.0086
Recovery	86%	96%	98%
IMX-104 (81-mm) IDA			
17FRAP112	<0.0002	0.0008	0.0016
17FRAP112-MS	0.00081	0.0047	0.012
17FRAP112-MSD	0.00081	0.0047	0.012
Recovery	101%	98%	104%

Canadian Tests

GIM and PBX CX-85 tests – 2013

All twelve rounds detonated high order. This determination was made by the EOD personal monitoring the tests and was based on the size of the fragments and the noise generated by the detonations. RDX, HMX, and TNT were measured in the residues deposition areas from the GIM explosive, which contains ETPE (9.5%), TNT (40%), and HMX (50.5%) and the CX-85 contain which contains HMX. All twelve deposition areas were measured with GPS. Most of the ODA samples showed no energetic residues, indicating that the areas were well delineated. The exception was for the BIP of the GIM rounds, where traces of TNT were found.

The residues deposition areas for the GIM detonations are larger than the PBX areas for both scenarios **(Table 52)**. This was anticipated since the GIM formulations are more powerful than the CX-85 formulations. For GIM, the first and second nose initiations gave the largest IDAs with the third triplicate being a little smaller than the others. The mean value for this triplicate is 1600 m^2, which is still larger than the BIP IDAs. The GIM BIP IDA areas are of similar sizes indicating reproducibility, and the mean value is 1200 m^2. The energy released by a BIP detonation is lower than the energy released by the normal functioning methods, indicating that the BIP method is not as efficient in igniting the formulations. More C4 may have been needed to ignite the formulations as effectively as the nose initiation. On the other hand, these results show that it is possible to blow in place these munitions using conventional C4 block methodology. For the PBX formulations, the IDA areas from both initiation methods are of the same size, indicating that the quantity of C4 was adequate at igniting the formulation in the BIP scenario. Again, these formulations can be disposed of by blow in place procedure with C4.

Table 52: GIM and CX-85 105-mm munitions detonation IDAs areas

Detonation operation	IM Energetic formulation	Deposition Area (m^2)	Mean values for the triplicate areas (m^2)
Nose initiation	GIM	1900	1600
(High order)	GIM	1700	
	GIM	1200	
	PBX	860	850
	PBX	760	
	PBX	940	
BIP	GIM	1300	1200
	GIM	1200	
	GIM	1100	
	PBX	910	940
	PBX	860	
	PBX	1000	

Deposition rates were determined for both GIM and CX-85 formulations. Deposition rates for other munitions formulations such as Comp B and PAX-21 are included in **Table 53** for comparison **[2, 9]**. The nose-initiated command detonations were referred to as high order in **Table 53** since they were all high-order reactions. For GIM and PBX CX-85 105-mm munitions, the mean values of the triplicates were used for the deposition rates. For the other munitions, the mean values were extracted from previous studies.

Table 53: Depositions rates for insensitive munitions in high order and BIP scenarios

Detonation operation	Munitions	Deposition rates
High Order	105-mm Comp B	0.000007% (RDX) [2]
	60-mm Comp B	0.00003% (RDX) [2]
	105-mm GIM	0.0003% (HMX)
	105-mm PBX	0.0006% (HMX)
	60-mm PAX-21	0.006% (DNAN and RDX) 15% (AP) [9]
Blow in place	105-mm Comp B	0.0003% (RDX) [2]
	60-mm Comp B	0.03% (RDX) [2]
	105-mm GIM	0.07% (HMX) 0.0002% (TNT)
	105-mm PBX	0.02% (HMX)
	60-mm PAX-21	0.6% (DNAN) 0.7% (RDX) [9] 35% (AP)

Results for the deposition rates of the GIM high-order triplicates varied from 0.0002-0.0004%, leading to a mean value of 0.0003%. These deposition rates were quite reproducible showing that the snow cover collection method was adequate. The BIP values varied much more, from 0.0002% to 0.14%, indicating that the BIP procedure was not as reproducible, probably due to a lack of energy released by the C-4 block. This was also confirmed by the size of the IDA in **Table 52**. The mean value for the BIP of GIM triplicates is 0.07%. In the GIM BIP, TNT was also observed inside the IDA and outside the IDA at 0.0005 - 0.011%, another indication the BIP was missing energy to effectively ignite the formulation. For the nose initiation of the PBX CX-85 formulations, values for the deposition rates varied from 0.0003 - 0.0008% leading to a mean value of 0.0006%. The BIP of the PBX triplicates gave reproducible values at 0.02%.

As one can see in **Table 53**, the munitions containing Comp B gave lowest deposition rates for both high order and BIP detonations and for all calibers tested. The GIM formulations gave high-order deposition rates of 0.0003%, similar to the BIP rates of Comp B, which is considered acceptable. In the high order scenario, the PBX formulation had twice the deposition of the GIM at 0.0006%. For BIP testing, the worst formulation was PAX-21 at ten times the PBX value at 0.006% with a much higher deposition rate for ammonium perchlorate (15%). All the BIPs were less efficient at burning all the constituents and deposited more residues. The BIP of the GIM triplicate varied much and gave a mean value of 0.07%, much higher than the Comp B deposition rate. This was explained earlier by the fact that more C4 would have been needed to blow these formulations. The BIP of PBX resulted in 1/3 as much residue as for the GIM, with a mean residue rate of 0.2%. It was observed for the PBX that the IDAs of the BIP were similar to the IDAs of the nose initiated triplicates, indicating that the conditions for the BIP in this case were adequate to ignite these formulations. BIP of PAX-21 formulations showed moderate values for DNAN and RDX at 0.6 - 0.7% and a very high value for ammonium perchlorate at 35%. This indicates that this formulation is really insensitive and that the BIP procedure with the C-4 block was inadequate to perfectly ignite this formulation.

Shaped-charge Tests (summer test)

The desired outputs (high- or low-order detonations) were successfully obtained on the whole set of conventional non-insensitive ammunition. **Fig. 37** illustrates the set up for a hand grenade test using a stand-off distance of 76 mm at an angle of 90°. **Fig. 38** shows the remains after the shaped-charge initiated a high order detonation. Various scenarios were assessed using either SM- EOD 20 or SM-EOD 33, including directing the jet at the base plate, at the side, at a buried munition, and with a misfire or dudded configuration. The assessment from the tests with conventional munitions was that the SM-EOD shaped-charges were an effective, cleaner, safer, and reliable tool to trigger the desired reaction in various UXO disposal scenarios.

Tests conducted on the five 105-mm rounds filled with IMX-104 provided by GD-OTS Canada gave different results. Three projectiles were used in the initial tests with the SAAB shaped-charges and two were kept for further testing against higher calibers SM-EOD shaped-charges. A first test was conducted using two SM-EOD 33 charges that were connected in series, using a 100-mm stand-off, and detonated simultaneously **(Fig. 39)**. A low order reaction resulted, with IMX-104 in the bottom of the casing **(Fig. 40)**. This contrasts with the high-order detonation of a 105-mm conventional round under the same test conditions.

Figure 37. Hand grenade and SM-EOD 20 prior detonation.

Figure 38. High order crater after BIP of the hand grenade with SM-EOD 20.

Figure 39. 105-mm IMX-104 round with two SM-EOD 33 at 100-mm stand off distances.

Figure 40. 105-mm filled with IMX-104 after a low-order reaction

The test was repeated using the same set-up with the exception of the shaped-charges being ignited in parallel instead of in series. The hypothesis was that the ignition in series could have weakened the detonation efficiency by creating a de-confinement for a fraction of second when the jet penetrated at the first impact location. The use of parallel hits resulted in another low-order reaction, indicating that the SM-EOD 33 does not trigger high order reactions even with a double attack on the 105-mm filled with IMX-104. In order to validate if a larger shaped-charge would trigger the desired reaction, the warhead from an 84-mm Carl Gustav anti-tank rocket was removed to extract its shaped-charge. The single 84-mm shaped-charge was used against the remaining 105-mm filled with IMX-104 using a 178-mm stand-off. A high order detonation resulted (**Figs. 41, 42**).

Figure 41. IMX-104 filled 105-mm with one 84-mm shaped-charge at 178 mm stand-off.

Figure 42. IMX-104 filled 105-mm after a high-order reaction.

<u>HO and BIP winter Tests of PAX-48 filled tank rounds: Five-year study (2013-2017)</u>

Mass deposition for the detonations was estimated from the analytical results for the soot and aqueous portions of the melted snow samples. The water extract and filter solid residues data were integrated over the whole IDA and led to a quantity of analyte in mg per IDA. The quantity within the IDAs and the ODAs were added and the deposition rate was calculated by dividing the amount deposited on the snow profile by the quantity of analyte in the round. The overall detonation efficiency can then be calculated by adding the total masses of analytes deposited divided by the original mass of energetic materials in the round. In this unclassified text, the results on the mass of each component will not be included, only the deposition rate and detonation efficiencies. These estimates also provide data on the efficiency of the separate compounds within the formulation. More details (mass estimates) have been provided to Mr. Walsh in a “Protected-A” document.

The mean IDA areas and the ratio of analyte detected in ODA versus IDA are presented in **Table 54**. It is obvious from the size of the IDAs that HI detonations led to stronger detonation events than BIP configurations, at the exception of the attack by C4 in configuration C and by a 84-mm shaped charge from the base plate of the round.

Table 54. Mean IDA area per type of event and percentage of analyte detected in ODA

Detonation operation	Mean IDA Area (m^2)	Mean ODA Area (m^2)	Analyte Ratio-ODA:IDA*
High order (HI) detonations	1400	290	10%
BIP/ C4 configuration A	940	240	2.0%
BIP/C4 configuration B	700	260	4.0%
BIP/C4 configuration C	1500	280	1.0%
BIP/ C4 configuration D	880	220	0.5%
BIP/33 mm shaped charge-nose	1200	300	2.0%
BIP/67 mm shaped charge-nose	1304	320	0.8%
BIP/67 mm shaped charge/side	1200	260	1.0%
BIP/84 mm shaped charge/base plate	1500	300	0.3%

*Amount of analyte in the ODA as a percent of the analyte in the IDA

The ratio of analyte detected in the ODAs versus the IDAs was less than 5% in all BIP scenarios, meaning that the delineation of the IDAs that were made led to the capture of more than 95% of the mass deposited. One exception was the HI detonations. The ratio of analytes detected in the ODA versus the IDA was 10% and showed higher variation between IDAs. The overall results obtained for HI and BIP scenarios for the three analytes are presented in **Table 55**.

Table 55. Deposition rate (DR) of analytes* and overall BIP detonation efficiencies

Detonation operation	DNAN DR	HMX DR	NTO DR	Detonation efficiency
BIP/C4 configuration A	6.0%	1.0%	26%	84%
BIP/ C4 configuration B	13%	1.0%	43%	72%
BIP/C4 configuration C	6.0%	3.0%	0.3%	97%
BIP /C4 in configuration D	18%	19 %	37%	72%
BIP/33 mm shaped charge-nose	0.6%	0.4%	1%	99.14%
BIP/67 mm shaped charge-nose	53%	23%	74%	40%
BIP/67 mm shaped charge-side	1.0%	1.0%	10%	94%
BIP/84 mm shaped charge-base plate	0.001%	0.02%	0.0001%	99.999%

*As a percentage of the original mass of analytes in the munitions load

The BIP results showed that C4 always lead to weak detonation efficiencies, ranging from 72 to 97 %. At 97 % detonation efficiency, there is still 84 g of insensitive ingredients dispersed at the detonation point, which is judged non-acceptable. This is the rationale why shaped charges donor charges were investigated. One configuration came out with an acceptable DR, which is when the round is attacked by the base plate, by a larger 84 mm shaped charge.

Between 0% and 60 % of the analyte were dispersed in the solid form, with the exception of NTO for which 100% of the analyte was found in the aqueous phase. No conclusions could be drawn for the ratios in solution versus solid for DNAN and HMX, as it might be dependent on the residence time of the analyte in the melted aqueous fraction, on the water temperature, and on the initial concentration of the analyte in presence of the aqueous phases. In other words, the melted sample had not stabilized prior to filtration. Our results clearly demonstrate that both fractions must be analyzed to get a representative result.

High-order (HI) Detonation Tests

Post-detonation residues data for high-order tests were extrapolated over their respective sampling units and totals for each test were calculated respectively for DNAN, HMX and NTO **(Table 56)**. When appropriate, the IDA and ODA results were combined to derive a total mass estimate for the IDAs **(Table 54)**. The DR for the three analytes varies from 0.0004% to 0.002%, which indicates a HI event (>99.99% efficient). These DR are considered low and should not lead to the build-up of concentrations of concern of the analytes. All the recovered NTO and HMX are found in the aqueous portion of the samples, while 17% of DNAN was recovered in the solid form. While HMX is the least soluble of the three analytes, we think that 100% of what is deposited was solubilized in the sample processing because of the small amount in the formulation. NTO is highly water-soluble and 100% was solubilized. The detonation efficiency for the HI event is 99.9987% or equal to the deposition of 40 mg of the energetic analytes in the environment upon detonation. This is considered acceptable and should not lead to the build-up of concentrations of concerns in impact areas.

Table 56. Deposition rate (DR) of analytes and overall high-order detonation efficiencies

Detonation operation	DNAN DR	HMX DR	NTO DR	Detonation efficiency
High order (HI) detonations	0.001%	0.0004%	0.002%	99.999%

Quality Assurance Results - Canada

Data validity

All quality assurance procedures indicate that the data are robust. The field blank results came back with no detection of any explosive residues indicating a pristine snow cover, relevant for all the trials. The laboratory blanks came back with non-detected results, indicating an efficient cleaning process in 2013, 2015, 2016, and 2017 but not in 2014. In 2014, two laboratory blanks came back with detection of very low levels of the analytes (at the detection limit of the GC method) at least five order of magnitude lower than the measured concentrations in the IDAs. In 2015, five rinsing cycles were used to avoid that and proven successful. Recoveries of the analytes from the spiked samples were within normal range (± 12%) with no loss or degradation of analytes in the extraction process. When the HPLC-UV results showed non-detectable concentrations of the analytes, the GC method was proven useful since it decreases significantly the detection limit and in the majority of the case, detection was accomplished.

Replicate reproducibility

Inter-laboratory analytical reproducibility: In 2014, fifteen sample extracts were sent to BRI for confirmation. Analytical results obtained for DNAN and NTO obtained at DRDC and BRI for the sample extracts were compared. The standard deviation between inter-laboratory results varied between 1 % and 13 %, which was considered acceptable.

Sample replicate reproducibility (Sampler bias)

In order to verify the bias introduced by the person sampling the IDAs, the name of the sampler was written on each sampling bags. The results between sample replicates in the same IDA by different samplers were analyzed. The standard deviations between results ranged from 1% to 23 %, with most of them below 10%, which was considered acceptable. This proves that the systematic sampling method minimized the sampling bias. The highest discrepancies were observed in HI IDAs. The lower deposition levels might partially explain this. In general, the triplicate results were such in good agreement in 2014 that it was decided to collect duplicate samples in 2015 in the IDA to minimize the workload and associated costs. The variation between these duplicate was acceptable in 2015, with a maximum standard deviation of 14%.

Field replicate reproducibility (reproducibility from detonation to detonation)

The mean values of the sample replicates within each IDA area were compared to evaluate the sample-to-sample variability for all sets of HI The standard deviation between samples for the five HI detonations ranged from 5 to 12 %, which is excellent. All HI were conducted in the first two days of the trial, with identical meteorological conditions and no deposition area overlap.

The standard deviation between the BIP replicates went up to 18 %, which is a little higher. The highest variability was for the two detonation IDA areas that overlapped in 2015. The weather conditions also varied between field replicates, with a colder temperature and stronger winds during the last two detonations, which could have led to particle losses. Also, the BIP events are known to be less reproducible, as a slight variation in the detonation set-up could lead to a measurable variation in the DR. In 2015, three field replicates were done instead of five, as the total number of 120 mm rounds was limited and also to minimize the associated workload and costs.

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DISCUSSION

Analytical Methods

Marianne Walsh completed development of analytical methods for PAX-21, IMX-104, and IMX-101 insensitive munitions formulations. She validated a new column that reduces the run time for analytes by a factor of 5, speeding analyses greatly. She ran side-by-side comparative analyses of the IMX-101 samples to determine if solid phase extraction is necessary for the analysis of NTO and NQ or if aqueous aliquots of the filtrate from the samples are sufficient for quantification estimates of these compounds. Both NTO and NQ appear to rapidly dissolved from the solids residue into the aqueous portion during the melting and filtering of the snow samples (<4°C). The aqueous fraction of processed (melted) IMX-104 and IMX-101 detonations conducted on snow were quite acidic (pH ≈4). Although NTO is quite acidic, buffering from the cement in the M-1122 155-mm practice rounds resulted in a very high pH in the aqueous portion of the processed high-order detonation samples in 2017, ≈pH 14, resulting in the conversion of DNAN into 2,4-dinitrophenol. Because the reaction was so rapid, unstable, and unexpected, we were not able to derive a mass balance on the DNAN and NQ compounds for these samples, very likely underreporting the mass of these compounds in the residues following detonation. NTO seemed stable, and mass estimates for the detonations were based on this compound. The 2014 IMX-101 tests likely have much more stable results, but the use of two different fuze simulators for these tests makes extrapolations between the tests difficult.

Following the 2014 project In-Process Review (IPR), SERDP requested CRREL look into the differences between UV and Diode Array Detectors (DAD) for the CRREL-developed HPLC processes. A request was also made to discuss the detection of 5-Amino-1,2,4-triazol-5-one (ATO), a reduction product of NTO. The reported responses, found in the CY15 Q3 quarterly progress report, follow.

HPLC-UV vs HPLC-DAD

With HPLC-UV, a single wavelength is monitored to detect the analytes of interest. The wavelength is chosen to maximize response from the analyte while minimizing background noise. For the analytes in the insensitive munitions formulations, the following wavelengths were used: NTO (315 nm); DNAN (295 nm); NQ (263 nm); RDX (230 nm). We used single wavelength monitoring to maximize sensitivity of the analytical method.

An HPLC-DAD (Diode Array Detector) provides spectral data over wide range of wavelengths. Thus, a spectrum can be used to evaluate the purity of a chromatographic peak. This evaluation is particularly useful in matrices (e.g., biological media or organic soil extracts) that have interfering peaks. In the past, DAD detectors were less sensitive than single wavelength or dual wavelength UV detectors. Therefore, when a DAD detector is used, quantitative data are generally obtained at a single, optimal wavelength. However, analytical instrumentation continues to improve and CRREL has recently purchased an Agilent HPLC-DAD for future analyses. We can evaluate the sensitivity of both techniques with this instrument.

Analytical Method for ATO (5-amino-1,2,4-triazol-3-one)

ATO is produced by reduction of the nitro-group of NTO (3-nitro-1,2,4-triazol-5-one). Field et al. (2014) determined ATO using the same chromatographic separation as for NTO, and the wavelength for detection was 216.5 nm. Development of an analytical method for this compound will require the following initial steps:

i. **Production of a standard analytical reference material.** Field et al. (2014) synthesized ATO from NTO using palladium-coated carbon in methanol with hydrogen gas. The material would need to be purified and the purity verified so that a calibration standard can be produced.

ii. **Optimized HPLC separation and detection**. The optimal wavelength for detection without interference needs to be determined. Lower wavelengths (<220 nm) are susceptible to interferences. The solubility of ATO in solvents used for chromatography would need to be verified as well the affect of pH on retention.

iii. **Stability of ATO in the matrices of interest**. Current research indicates that ATO is sensitive to matrix conditions. Field et al. (2014) reported that ATO was formed stoichiometrically from NTO under anaerobic conditions in soil. ATO persisted if conditions remained anaerobic. However, once conditions were changed to aerobic, ATO biodegraded completely. In contrast, ATO was persisted for 25 days (the length of the study) in "media-only" samples under aerobic conditions. Holding time studies for soil and water samples under various storage conditions will need to be conducted.

Detonation Residues and Munition Efficiencies

US Tests

The investigation of insensitive munitions has shown that they have very different detonation residues characteristics from their predecessor rounds. A comparison of mean estimated detonation residues for the 81-mm rounds is given in Tables 57 and 58.

The differences between the detonation of munitions containing conventional HE (Comp B) and insensitive HE (IMX-104) are clearly illustrated in **Table 57**. For the conventional and insensitive high-order detonations, RDX and HMX both detonated quite efficiently, with over 99.99% of the mass of these compounds estimated to be consumed during the detonation process. No TNT was detected in the Comp B residues. The resulting overall efficiency for the Comp B round was thus very high, >99.999%. For the IMX-104 round, the NTO efficiency was not sufficient to be characterized as high order. Comparative data ranges for the results are shown in **Table 58**. The table shows overlap in values for RDX/HMX and DNAN, indicating similar performance for those compounds for all the booster loads. There is no overlap in values for NTO with the two different C4 booster loads, indicating a significant difference between detonation efficiencies of NTO with the increase in fuze booster mass. However, the overall detonation efficiency difference is quite small, <0.2%. The data are normally distributed for both C4 booster data sets **(Figure 17)**.

The differences between the BIP performance of the two munitions is similar to that found for the high-order detonations. There is about an order of magnitude difference between the high-order efficiency and BIP efficiency for the Comp B rounds and two orders of magnitude for the IMX rounds. The use of the BIP procedure developed by the ARDEC EOD shop greatly improved the BIP performance over the results obtained using the standard EOD practice. Although 45g/BIP in residues per operation may seem high, it is much better than we expected and may be the best that can be anticipated for a round that is designed not to detonate from an external stimulus.

Table 57. Comparison of Comp-B and IMX-104 81-mm mortar munitions: High-order dets

Explosive Filler	IDA (m^2)	ODA 0-3 (m^2)	Analyte(a)	Estimated Total Mass(b) (g)	% of Original Analyte Mass(c)
<u>High-Order Detonations</u>					
Comp-B(d,e)	230.	—	RDX + HMX	0.008	0.0014%
(Standard fuze)			Overall Efficiency	>99.999%	
IMX-104: 2013	250.	200.	RDX + HMX	0.005	0.006%
(12 g Booster)			DNAN	0.005	0.005%
On Snow			NTO	2.2	1.2%
7 shots / 7 IDAs			Overall Efficiency	99.77%	
IMX-104: 2014	670.	340.	RDX + HMX	0.008	0.005%
(18 g Booster)			DNAN	0.008	0.003%
On Snow			NTO	0.54	0.13%
5 shots / 5 IDAs			Overall Efficiency	99.93%	
IMX-104: 2015	620.	260.	RDX + HMX	0.004	0.003%
(18 g Booster)			DNAN	0.013	0.005%
On Snow			NTO	1.2	0.27%
2 shots / 1 IDA			Overall Efficiency	99.93%	
IMX-104: 2015	460.	—	RDX + HMX	0.004	0.003%
(18 g Booster)			DNAN	0.017	0.007%
On Ice			NTO	0.72	0.17%
2 shots / 2 IDAs			Overall Efficiency	99.91%	
IMX-104: 2017	770.	470.	RDX + HMX	0.011	0.007%
(9 g Booster)f			DNAN	0.048	0.018%
On Snow			NTO	1.7	0.40%
7 shots / 7 IDAs			Overall Efficiency	99.8%	
<u>BIP Detonations</u>					
Comp-B(e)	820.	410.	RDX + HMX	0.15	0.014%
			Overall Efficiency	>99.999%	
IMX-104	820.	340.	RDX + HMX	2.1	0.31%
(12 g Booster)			DNAN	5.0	2.0%
			NTO	45.	11%
			Overall Efficiency	96%	

(a) RDX includes some HMX as well (<9% of original mass)

(b) Mean of the combined IDA, ODA, and subsurface estimated masses

(c) Based on mid-range value of formulation specifications. Includes 520 g RDX/HMX for BIP donor block.

(d) 14 rounds in various multiple detonation groupings. No ODAs. Live-fire test.

(e) Reference: Walsh et al. 2011

(f) PBXN-5 Fuze booster pellet (Modified standard fuze for cartridge)

Table 58. Comparison of detonation efficiencies for various booster loads in 81-mm IMX-104 projectile fuze simulators

Booster Load	RDX+HMX (mg)	DNAN (mg)	NTO (mg)	Overall Efficiency	Notes
7.1 g	—	—	—		Partial detonation(a)
9.0 g	—	—	—		Low-order detonation
12.7 g	—	—	—		≈ High-order detonation
12. g	0.6 – 47.	2.1 – 71.	900. – 2800.	99.77%	≈ High-order detonation(b)
18. g	<0.4 – 15.	1.7 – 23.	370. – 700.	99.93%	≈ High-order detonation(b)
9. g	1.0 – 50.	5.0 – 230.	790. – 3000.	99.8%	≈ High-order detonation(b)

(a) Nose of round blown off but body and filler mostly intact

(b) RDX, HMX, and DNAN detonated high order. NTO did not.

The data for the 155-mm IMX-101 practice round show a more significant contrast to the results form conventional munitions **(Table 59)**. This is likely due as much to the nature of the rounds as it is to the explosive fillers. The TNT and Comp B rounds were HE projectiles with 6.6- to 7 kg of explosive filler running the length of a high-fragmentation steel body. The IMX-101 rounds were practice rounds containing 1 kg of IMX-101 in a forged aluminum screw-on ogive at the end of the round. IM data is given only for the 2014 tests as base hydrolysis of the DNAN interfered with the results from the 2017 tests. Extrapolation of the data, based on the NTO recovery, which did not seem to be affected by the high pH, indicates that similar results would have been likely from the use of the ARDEC command detonation fuzing system.

Table 59. Comparison of three 155-mm howitzer munitions

Explosive Filler	IDA (m^2)	ODA 0-3 (m^2)	Analyte(a)	Estimated Total Mass(b) (g)	% of Original Analyte Mass(c)
High Order Detonations					
TNT	760.	390.	TNT	BDL(d)	<0.0001%
			Overall Efficiency	>99.999%	
Comp-B(d,e)	940.	450.	RDX + HMX	0.0003	<0.0001%
			Overall Efficiency	>99.999%	
IMX-101	320.	260.	RDX + HMX	0.012	0.0070%
			DNAN	2.4	0.49%
			NTO	15.	6.6%
			NQ	130.	31%
			Overall Efficiency	89%	
BIP Detonations					
TNT(e)	1300	570	TNT	0.006	<0.0001%
			Overall Efficiency	>99.999%	
Comp-B(e)	1600	550	RDX + HMX	0.015	0.0003%
			Overall Efficiency	>99.999%	
IMX-101(d)	650	310	RDX + HMX	0.034	0.003%
			DNAN	13.	2.7%
			NTO	20.	8.5%
			NQ	100.	24%
			Overall Efficiency	94%	

(a) RDX includes some HMX as well (<9% of original mass)
(b) Mean of the combined IDA, ODA, and subsurface estimated masses
(c) Based on mid-range value of formulation specifications. Includes 520 or 1040 g RDX/HMX for BIP donor block(s).
(d) All 50-g tests (n=6)
(e) Reference: **[14]**

Detonation kinetics for the 155-mm practice round will likely not be as effective as with the full-up IHE rounds (M795). The small, narrow area containing the IMX-101 filler may be too restrictive to allow a detonation wave to build and propagate through the explosive load. There may also be issues with critical diameter of the IHE filler. We are seeing something like this with the M1122 where the BIP is more efficient at consuming the total explosive load (including donor charge) than the HI detonation. If the mass (and efficiency) of HE in the donor charge is excluded, there is little difference in the detonation efficiencies. The HI detonation, with 31% of the NQ not consumed, is not functioning efficiently, even when the fuze booster charge is twice the normal mass. A direct comparison between the conventional and IM rounds is not valid as the mass of the donor charge for the BIPs is as much as the IHE filler. We also feel that extrapolating the HI results from the M1122 practice round to the M795 IM round will result in a gross overestimation of the detonation residues mass for the IM round, for which the detonation is more likely to propagate through the length of this large diameter munition. The validity of these assumptions will need to be confirmed through future testing.

The data are still useful, however, in that they will give the military a sense of the deposition rates that can be expected through the use of these rounds on training ranges. Although there is only 1 kg of IMX in the rounds, both high-order and BIP detonations will result in tens of grams of NTO and hundreds of grams for NQ deposition per round. As hundreds of practice rounds are often used during training events, these two compounds have the potential to accumulate rapidly on a range. The rapid dissolution of both these compounds, >99% dissolution in less than 12 hours, will make surface detection and cleanup difficult, and the potential for groundwater contamination should be seriously considered.

Canadian Tests

The results obtained for the Canadian IM melt cast and PBX formulations showed a lower deposition rate in BIP scenarios than the corresponding IMX formulations. Both Canadian experimental formulations are not as insensible as the IMX family. They are less sensitive than their comp B analogues, while more sensitive than the IMX analogues. Both formulations resist to the bullet impact test, while they do react violently to some other IM tests. In other words, their level of insensitivity is lower, which drives better DR, which is in fact observed.

The results obtained for the IMX-104 in the summer tests to evaluate its reaction in BIP scenarios showed that a high order could be obtained with 105 mm when using a larger shaped charge attack, while low order were obtained either when using C4 donor charges or smaller shaped charges.

The winter tests conducted on the 120 mm tank round filled with PAX-48 over a span of five years demonstrated that the HO detonation of the rounds lead to an acceptable DR, while most of the BIP trials lead to non-acceptable DRs, which would lead to a potential accumulation of concentration of concern of the insensitive ingredients. One set-up involving an 84-mm shaped charge by the base plate led to an acceptable DR. This will be further discussed with the ammunition stakeholders to identify an action plan that would allow the sustainable training with these rounds in Canadian RTAS.

Quality Assurance

Field sampling QA indicated very robust data for all tests in the US and Canada. The heterogeneous distribution of particulate residues makes characterization of large areas very difficult. Protocols developed over 15 years of testing enabled us to obtain reproducible, normally distributed data for all tests. The mean deposition rates were similar for each set of tests with the range of estimated mass deposition generally averaging a factor of two over each test. The very low mean residues mass recovery from the ODAs and subsurface samples compared to the IDA mass samples indicates that the IDAs were sampled appropriately.

All QA procedures indicate the data are robust. It was essential that this level of QA be conducted as the PAX-21, PAX-48, IMX-104 and IMX-101 formulations are new to the analytical chemistry world, and methods had to be developed or optimized by CRREL and DRDC to analyze for the multiple compounds within the formulations rather than the IHE compounds separately. The compounds behave differently, with RDX and HMX, both nitramines, having well established methods; DNAN, a nitroaromatic; NTO, a heterocyclic compound; NQ, a nitramine; and AP an inorganic salt. Methods were developed, optimized, and tested several times to ensure data quality was sufficient to reproducibly detect these compounds at very low concentrations.

The fuze simulators

Do these tests accurately represent detonation efficiencies for these munitions? The BIP tests do not differ from tests done over the last dozen years. We use fully enclosed (fuzed in the US) rounds containing booster charges and supplemental charges (when part of the munition) to ensure a realistic test. The EOD specialists, all trained in disposal of ordnance, do all the set up and detonations related to the BIP tests. In 2014, we also consulted with ARDEC EOD and NAVSEAEOD on placement of donor blocks for the two rounds. Significant improvement was seen for the BIP tests on the 81-mm IMX-104 tests by using methods promulgated by NAVSEAEOD. We experimented with the set up for BIP of the 155s and found the NAVSEAEOD-recommended method also worked best.

For high-order detonations, CRREL uses a fuze simulator similar to the M10 Universal Explosive Destructor (DODIC M241). In our case, the CRREL fuze simulator is designed to match the dimensions of the inserted portion of the normally issued fuze. This makes the booster cup the same size as the regular fuze booster cup. The concept was developed and tested in 2010. Test shots (n=3) with the CRREL fuze simulator booster mass the same as the original fuze booster mass resulted in high-order detonations of all rounds with >99.998% Comp-B HE consumption **[14]**. This was comparable to the detonation efficiencies of live fire detonation (n=14), which averaged 99.9991% HE consumption **[2]**. It should be noted that for one of the three fuze-simulator tests the shot penetrated to ground. The test area was a highly contaminated demolitions training range. The comingling of residues from prior operations skewed the results much higher than for the other two shots, although the shot efficiency (99.995%) was still within the range of a high order detonation. The fuze booster cup material in the M524 fuze of the M374 rounds tested is normally Composition A5, which consists of 98.1% RDX. Composition C4, used in the fuze simulators tested, contains 91% RDX and has a similar detonation velocity. These tests indicate that, for simulating a high order detonation of a round, the fuze simulator is a valid substitution for issued fuzes of the tested rounds.

A test of this hypothesis can be derived from the command detonation procedure used by Aberdeen Test Center and Picatinny Arsenal (ARDEC/METC) to test the M720 rounds. For these tests (n=2), the fuze was modified to allow initiation of the original booster material. Results of the detonations conducted during the LCEA tests indicate that the mass of perchlorate recovered from the two rounds tested is in the 4 – 21g range (Mean = 13g, n=2), well within the range we recovered using the CRREL fuze simulator in the field (6.6 – 25g: Mean=14g, Median=13g, n=7). From these data, the two command detonation methods give comparable results.

In 2017, the ARDEC-designed command detonation fuzing system was tested under the same conditions as the CRREL fuzing system to determine if there are any significant difference in the post-detonation energetics residues for the IM rounds tested previously by CRREL. Results indicate very similar results between these two systems, with the ARDEC system resulting in slightly higher but significant detonation residues over those from the CRREL system. The ARDEC system provides closer simulation of the design initiation explosive train and thus likely results in a closer approximation to a live-fire detonation than the much simpler CRREL system, which relies on an estimated mass of C4 for the fuze booster load. Both systems could be used early in the munitions development process to gauge how efficient a munition detonates, providing data on overall munition efficiency as well as the efficiency of the explosive compounds within the munition’s explosive load.

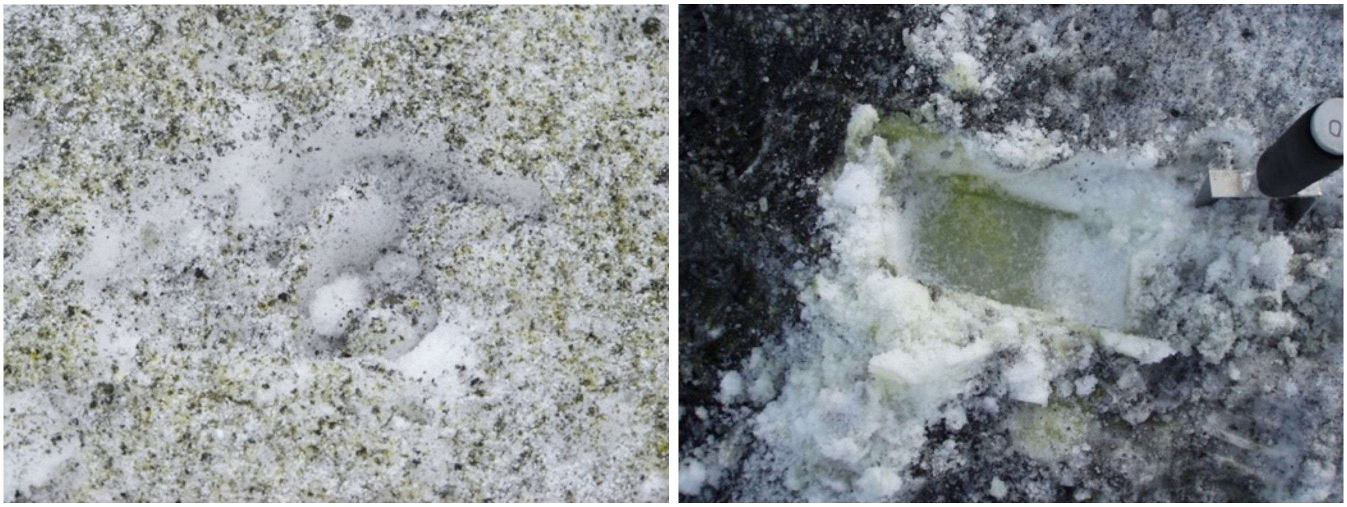
Prior to conducting the high-order and BIP tests, we conduct booster mass tests to ensure that the mass of C4 in the booster cup of the fuze simulator will be sufficient to initiate the supplemental charge of the rounds being tested. For the 155-mm tests, several booster cup loads were tried before settling on 50g of C4. There was a significant difference between the residues resulting from the detonation of rounds containing a 40- and 50-g booster cup load, whereas there was not a significant difference between the 50- and 60-g booster cup loads (Table 6). In addition, there was very little HMX in the post-detonation high-order residues. The supplemental charge consisted of 138 g of HMX and the booster charge consisted of up to 4.5 g of HMX for a total of 142 g. Only 0.005 g of HMX was recovered from one of the 10 high order shots, giving an HMX consumption efficiency for that one shot of 99.996%. Averaged over the 10 shots, it is 99.9994%. Both values indicate high-order detonation of the supplemental charge. If the supplemental charge functions properly, the round as a whole should also.

The preliminary booster mass tests for the 81-mm IMX-104 rounds were conducted in 2013, resulting in a mass of 12 g of C4 to properly initiate the supplemental charge of the round. We increased the booster mass for the 2014 tests 50% to 18 g to determine if the higher mass would cause the round to detonate more efficiently. It did not **(Tables 4 and 5)**. Although the mean detonation efficiency of the 18-g booster test was significantly higher than for the 12-g booster test, there was very little difference between the mean detonation efficiencies for the two tests, < 0.17%. Thus, there was very little overall gain in efficiency by increasing the booster mass of C4 by 50%.

Finally, there is very good agreement between the mean efficiency rates for the shots for all the tests, even the BIP tests. This is a good indication that the rounds are functioning properly.

Toxicity issues

The determination of the toxicity of the different compounds within the formulations is well established with the possible exception of NTO. The low pKa and high acidity in solution of NTO is an issue, mostly because of NTO's high aqueous solubility. We checked aqueous aliquots of the IMX-104 samples taken in 2013 and all that contained NTO had low pH (3 – 4), even when the aqueous fraction of the field sample exceeded 5 L. In 2017, the presence of concrete in the M1122 155-mm practice round drastically changed the pH of the melted snow samples. The pH shifted from 4 to 12, resulting in a highly alkaline aqueous fraction of the sample. Base hydrolysis of the aqueous sample resulted in significant transformation of the DNAN in the sample to dinitrophenol. Rapid dissolution of the NTO out of the residues will occur, which may lead to a high-concentration slug of contaminant moving through the soil column **(Figure 43)**.



a. Fresh residues on snow surface b. Migration of IMX through 12 cm of snow to ice surface after 3 hours

Figure 43. Leaching of IMX through the snow following detonation of a round on the Eagle River impact area

Particle distribution

The particle distribution tests were very enlightening. Particle distribution models assume a uniform angular distribution of particles as well as a radial distribution based on ideal particle size and trajectory. As with previous observations of low-order detonations, this was not the case with our tests. Very little material was deposited in the first meter from the detonation, having been blown away by the force of the detonation, leading us to gather particles from a 2-m annulus from the detonation point rather than 0-1 m and 1-2 m annuli. The IHE formulation also appeared to react differently to a low- or partial-detonation event than conventional HE. Particles were quite fine with few larger chunks evident. More research on this subject needs to be conducted.

Different testing, sampling, and processing procedures were developed and tried during our research. Sweeping the residues from the ice surface worked quite well, and mapping larger particles with a GPS seemed to work well, although it was a bit time consuming. The freeze-dry desiccation process worked really well once we got the procedure down. We will not pick particles from the mixed residues in the future. Unfortunately, we lost a few of our annular ring samples from one of the low-order detonations while refining the freeze-drying process. This should not happen again.

We had quite a bit of difficulty simulating the LO detonations with IMX-104. The low sensitivity may have been the reason for this. The rounds were difficult to initiate, with four of the seven rounds not detonating low order. Fortunately, we are able to use the data from the two partial detonations and the two rounds that had only the fuze simulators detonate. No data had previously been obtained for these types of detonations. The lack of replicates for the LO dets hampers the usefulness of this data, but it is valuable nonetheless as it is the only particle spatial distribution data for a simulated low-order detonation in existence.

LCEA Tests

The field tests conducted in conjunction with the EPA pointed to a possible correlative link between air emissions and ground deposition of energetics. However, difficulties with the weather and equipment limited the usefulness of the data. To establish a true correlation (or not), more tests must be conducted to provide replicate data and build a dataset. The hexacopter showed promise, but a video link is necessary to really utilize the aerial system as standoff distances make it too difficult to position the equipment before the IDA dissipates. Equipment has already been developed by the EPA for a larger UAV system that will allow sampling of particles much like the ground-based systems currently in use.

The review conducted on a limited number of LCEAs strongly indicates that a better method than monitoring combustion products to determine the mass of energetics remaining after detonation is needed.

Wrap-up

High-order detonation residues masses for the IM tested were significantly higher than those estimated for conventional (TNT and Comp-B) rounds. The IMX-104 rounds were much more efficient than the IMX-101 rounds tested, but that may have been related to the types of rounds tested: full-up IMX-104 IHE rounds vs. the IMX-101 practice 155-mm round. The PAX-21 rounds, with their high perchlorate residues mass per detonation, have been reclassified and are no longer used on US or Canadian training ranges. The IMX-104 rounds tested detonated nearly high order and may be determined to perform well enough to be used for training as is. Increasing the booster load may push these rounds up to full high-order performance. That determination will need to be made elsewhere. The IMX-101 rounds have serious performance issues, which ARDEC is now fully aware, and consideration is being made to change out both the spotting charge from IMX-101 to another more efficient explosive and the inert filler to a material with a pH closer to normal (pH 7).

The disposal of individual rounds in the field occurs during range cleanup operation. The BIP of the 155s was much more efficient than anticipated and not significantly different from the high-order detonation of the same round (94% vs. 89%). The disposal of large numbers of these rounds will need to be carefully considered, though, based on the NTO residues. As the location containing the IHE is in a narrow section of the round, the ogive at the nose, and there will be a problem transmitting the shock of detonation from one round to the next. This matter needs consideration by experts in the fields of munitions disposal and detonation efficiency.

Results obtained in Canada from testing of the PAX-48 filled 120 mm rounds indicated that high-order detonations will lead to acceptable DR of the IM energetic compounds, while the BIP with C4 donor charges will lead to DR of concern, indicating a high risk of accumulation of energetic residues in the impact areas. An acceptable BIP method was identified by using a shaped charge directed at the base plate of the rounds. However, this method still has to be accepted by the EOD community. One of the biggest drawbacks introduced by the use of IM is that EOD personnel may have difficulties in the future differentiating between older conventional 120-mm UXO and the newer IM UXO. As a result, it will be difficult to determine whether to use a C4 donor charge or a shaped charge on an unidentifiable UXO. This issue will be discussed in Canada with the ammunitions stakeholders and has been brought up in the US as well. The Canadian results also demonstrate that the level of insensitivity of a round drives its deposition rate. This was also shown for the US tests, with IMX-101 showing much higher DR than IMX-104. The link between insensitivity and increased DRs should initiate a discussion with munition’s stakeholders in our countries on the level of insensitivity desired and needed for our munitions. Highly insensitive rounds will be better from a safety standpoint for storage and transport when considering detonation triggered by external stimuli, while IM detonation efficiencies might represent a longer term environmental and human health threat through their higher deposition rate. Moreover, a high level of insensitivity will trigger a higher risk for EOD operations in combat scenarios.

Additional research on low-order detonation particle distribution needs to be conducted. Our tests were limited to one formulation (IMX-104), one type of round (81-mm mortar round), and only one fully successful test. However, we now know how best to collect and separated the detonation particles from the mixed residues on the ice surface. Also, the data we have should be quite useful the current particle dispersion models are ever refined to better simulate real-world conditions.

Fate and transport was not considered during these tests and is beyond the scope of this report. SERDP is funding several projects on fate and transport of IHE formulations. Post-detonation materials were sent from this and previous tests to the principle investigators for those projects. The only post-detonation environmental characteristics investigated during these tests were the dissolution of the various compounds during sample processing and post-processing pH of the aqueous aliquots. We found very high dissolution rates for AP, NTO, and NQ, with DNAN behaving more like conventional high explosive compounds. Both issues have an impact on fate and transport and will be of concern to the other investigators.

The use of C4 as the fuze simulator booster charge is not the ideal test configuration because of the difference in detonation properties of C4 compared to the original fuze booster material. To address this difference, testing on the IMX-104 and IMX-101 rounds conducted previously with C4 fuze boosters was conducted in 2017 using fuze simulators designed by the ARDEC Detonation Physics group that contained the original fuze booster material and mass. The hypothesis for these tests was that the estimated mass deposition rates will more accurately represent the actual live-fire detonation residues as the detonation train will more closely resemble that of an actual complete round. Results indicate that a small but significant increase in post-detonation residues over those from the CRREL fuze simulator occurred. Both systems demonstrated similar performance results for all the energetic compounds in the IHE formulations tested. If the use of fuze simulators can be validated through live-fire confirmation testing, these devices may prove to be a powerful tool in obtaining critical munitions performance data earlier in the development process.

Looking Forward

As with all research, results often indicate additional areas of research that will greatly enhance the value of the current results. For the high-order detonation work, we see two areas that need further investigation. Both involve the initiation of the rounds. We have conducted extensive research on IM detonation residues using various configurations of command-detonation fuzing systems. The logical follow-up to these high-order detonation tests is to conduct a live-fire exercise with the insensitive munitions. Results from this research will determine if command-detonation of munitions is a valid proxy for live-fire testing by comparing test data to those obtained from the CRREL and ARDEC fuzing tests. High-order detonation research has been conducted on 81-mm Comp-B mortar rounds in the past with no significant difference in RDX residues mass between the live-fire and the CRREL command-detonation fuzing system. This type of research also needs to be applied to munitions containing insensitive high explosives because of their differences in detonation efficiency.

Additional research on particle spatial distribution will also be needed. The results we saw with the various detonation events as well as the much improved particle collection and processing methods developed in March of 2015 both indicate that particle dispersion models do not adequately approximate detonation residues dispersion. Particularly surprising was the tremendous number of fines resulting from both the low-order and partial detonations, something we had not seen before. Additional research on IMX-104 and at least two types of conventional munitions should be conducted and compared to current model results to determine if the models can be modified to reflect the empirical data.

SUMMARY

There is a tremendous amount of information in this final report. To make the significant information more available, we have put together this summary section, which tabulates and lists the findings from SERDP Project ER-2219. As you have read in the body of this report, there are corroborating data for all the findings listed in this section. **Appendix A** contains most of the publications that have resulted from research leading up to and conducted during ER-2219.

Table 60. Significant findings for SERDP Project ER-2219

Topic Area	Formulation	Significant Findings	Outcomes
Analytical Methods	PAX-21, IMX-101, & IMX-104	Hydrophilic-interaction chromatography separation method using trifunctionally-bonded amide phase can be used to retain polar analytes. An acetonitrile/water eluent acidified with acetic acid was used.	The reduction in the run time for the analysis of IMX-101 was cut from 30 minutes to <3 minutes. The method is applicable to LC/UV, LC/DAD, and LC/MS instruments.
IM Residues	PAX-21	Significant (15%) mass of perchlorate deposition from high-order detonations.	Munitions reclassified; No longer used on test and training ranges. Canada also banned use on ranges. Journal articles.
		Detonation efficiencies of PAX-21 components varied significantly.	
	IMX-104	Slight decrease in overall detonation performance compared to Comp B.	Picatinny Arsenal requested a rerun of tests using ARDEC fuze.
		ARDEC fuzing system resulted in slightly lower HI detonation efficiencies.	CRREL fuzing system results validated. Journal article.
		Detonation efficiencies of IMX-104 components varied significantly.	Overall efficiency near 99.99%, customary efficiency for high order.
		Aqueous fraction of samples acidic (pH 4). High (rapid) dissolution rate for NTO.	
	IMX-101	Very poor detonation performance using both CRREL and ARDEC fuzing systems.	Picatinny Arsenal requested a rerun of tests using ARDEC fuze.
		ARDEC fuzing system resulted in similar estimated detonation efficiencies.	CRREL fuzing system results validated. ARDEC will investigate alternative explosive filler.
		Aqueous fraction of sample basic (pH 14). High dissolution rates for NTO and NQ.	ARDEC investigating use of gypsum as filler to replace concrete.
	PAX-48	Very clean detonation: True high-order	Passed evaluation tests by Canada.
	GIM	Very high detonation efficiency	Under consideration in Canada
	CX-85 PBX	Very high detonation efficiency	Under consideration in Canada
IM Residue Particles	PAX-21, IMX-101, & IMX-104	Three-part multicomponent formulations used in IM result in finer post-detonation particle distributions.	Journal articles.
		Finer residues result in accelerated dissolution rates.	
LCEA	All	Post-detonation combustion product analysis and models do not adequately estimate detonation residues.	Journal article.

Table 61. Detonation Residues of IM from SERDP ER-2219 Research

Munition	Explosive Filler	IDA (m^2)	ODA 0-3 (m^2)	Analytes(a)	Estimated Total Mass(b) (g)	% Original Analyte Mass(c)
60-mm Mortar Rounds						
	Comp B(g)	210	190	RDX + HMX	0.0007	<0.001%
	7 Shots / 7 IDAs			Overall Efficiency	>99.999%	
	IMX-104: 2013	250	200	RDX + HMX	0.009	0.007%
	(12 g C4 Booster)			DNAN	0.007	0.006%
	On Snow			AP	14	15%
	7 Shots / 7 IDAs			Overall Efficiency	96%	
	IMX-104: 2017	250	290	RDX + HMX	0.009	0.012%
	(12 g C4 Booster)			DNAN	0.007	0.006%
	On Snow			AP	3.8	2.1%
	7 Shots / 7 IDAs			Overall Efficiency	97.9%	
81-mm Mortar Rounds						
	Comp B(d,e)	230	—	RDX + HMX	0.008	0.0014%
	(Standard fuze)			Overall Efficiency	>99.999%	
	IMX-104: 2013	250	200	RDX + HMX	0.005	0.006%
	(12 g C4 Booster)			DNAN	0.005	0.005%
	On Snow			NTO	2.2	1.2%
	7 Shots / 7 IDAs			Overall Efficiency	99.77%	
	IMX-104: 2014	670	340	RDX + HMX	0.008	0.005%
	(18 g C4 Booster)			DNAN	0.008	0.003%
	On Snow			NTO	0.54	0.13%
	5 Shots / 5 IDAs			Overall Efficiency	99.93%	
	IMX-104: 2015	620	260	RDX + HMX	0.004	0.003%
	(18 g C4 Booster)			DNAN	0.013	0.005%
	On Snow			NTO	1.2	0.27%
	2 Shots / 1 IDA			Overall Efficiency	99.93%	
	IMX-104: 2015	460	—	RDX + HMX	0.004	0.003%
	(18 g C4 Booster)			DNAN	0.017	0.007%
	On Ice			NTO	0.72	0.17%
	2 Shots / 2 IDAs			Overall Efficiency	99.91%	
	IMX-104: 2017	770	470	RDX + HMX	0.011	0.007%
	(9 g Booster)[f]			DNAN	0.048	0.018%
	On Snow			NTO	1.7	0.40%
	2 Shots / 2 IDAs			Overall Efficiency	99.8%	
105-mm Howitzer Rounds						
	GIM: 2013(h)	1600	—	RDX + HMX	—	0.0003%
	3 Shots / 3 IDAs			Overall Efficiency	>99.999%	
	CX-85 PBX: 2013(h)	850	—	RDX + HMX	—	0.0006%
	3 Shots / 3 IDAs			Overall Efficiency	>99.999%	
120-mm Tank Rounds						
	PAX-48: 2017(h)		—	HMX	—	0.0004%
				DNAN	—	0.001%
				NTO	—	0.002%
	3 Shots / 3 IDAs			Overall Efficiency	99.9987%	

Continued on next page.

Munition	Explosive Filler	IDA (m^2)	ODA 0-3 (m^2)	Analytes(a)	Estimated Total Mass(b) (g)	% Original Analyte Mass(c)
155-mm Howitzer Rounds						
	TNT(g)	760	390	TNT	BDL	<0.0001%
	7 Rounds / 7 IDAs			Overall Efficiency	>99.999%	
	Comp B(g)	1600	550	RDX + HMX	0.0003	<0.0001%
	7 Rounds / 7 IDAs			Overall Efficiency	>99.999%	
	IMX-101: 2015	320.	260.	RDX + HMX	0.012	0.0070%
	(50 g C4 Booster)	320	260	DNAN	2.4	0.49%
	On Snow			NTO	15	6.6%
	7 Shots / 7 IDAs			NQ	130	31%
				Overall Efficiency	89%	

(a) RDX includes some HMX as well (<9% of original mass)
(b) Mean of the combined IDA, ODA, and subsurface estimated masses
(c) Based on mid-range value of formulation specifications. Includes 520 g RDX/HMX for BIP donor block.
(d) 14 rounds in various multiple detonation groupings. No ODAs. Live-fire test.
(e) Reference: Walsh et al. 2011
(f) PBXN-5 Fuze booster pellet (Modified standard fuze for cartridge)
(g) Live-fire tests conducted on snow-covered ice
(h) Conducted on ice blocks placed on snow-covered frozen soil

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CONCLUSIONS

SERDP Project ER-2219 has had a significant impact on how we assess insensitive munitions. The test results from both the PAX and IMX trials were unexpected and have led the Army to rethink how to evaluate insensitive munitions prior to certification and issue. The impact has not just been in the US and Canada. Through our participation in a NATO Research and Technology Group, other countries are now aware of the necessity to carry out environmental performance testing similar to what has been developed and conducted through SERDP to ensure proper functioning of all new munitions, not just IM, as well as to ensure the sustainment of their training ranges. In Canada, where, like in the U.S, the PAX-21 rounds had been issued for training, the environmental impact of the perchlorate residues from detonating rounds was assessed. As a result of the joint US / Canada testing conducted under SERDP, the use of munitions containing PAX-21 is now not allowed. SERDP-funded munitions research has benefitted both partners on ER-2219. The IMX-101 filled 155-mm practice round is now under review by Picatinny Arsenal, based in part on the performance issues uncovered by our research.

Particle dispersion tests conducted in 2015 demonstrate the need for further research on this topic. Particle distributions are not matched by what is seen in the modeling software. This is especially true for IM residues, which ted to be finer because of the multi-component composition of the formulations. To better adapt the models to empirical data, more field research must be conducted. We have the procedures set for the efficient testing detonations, mapping, and collection of particles for low-order if this research gets funded in the future.

Review of available LCEAs for munitions indicates that a better method than monitoring combustion products following the detonation of munitions for determining energetics mass is needed. The LCEA field tests, although quite limited, demonstrated that airborne residues represent a very small fraction (≈7%) of the energetics that remain after detonation. The use of fuze simulators, developed and refined for this project, gives ordnance developers a valuable tool to enable testing of munitions earlier in the LCEA process, thus avoiding performance and environmental impact issues later in the certification process or after acquisition.

Insensitive munitions were constructed to resist external stimuli such as bullet impact or fire, and because of that, they resist unintentional detonation. This insensitivity has resulted in a less-efficient detonation, differential performance among the formulation components, and increased residues caused by disposal of UXO by a BIP procedure. We have found through this research that the more insensitive the munitions are, the less efficient they become and the more they deposit residues. In the case where IM constituents are toxic, the live firing of IM rounds into our RTAs will represent an environmental risk and, upon reaching potential receptors, a human health risk.

We strongly believe in the benefit of developing and issuing insensitive munitions. However, it is critical that all stakeholders be closely involved, as IM represent challenges both in terms of higher energetic constituent deposition rates and the difficulty in performing efficient BIP disposal operations. The importance of obtaining reproducible estimates of energetic constituent's deposition rates following all detonation scenarios for future munitions has been clearly demonstrated within this project. In the US, awareness of the potential contamination from munitions on training ranges and the necessity for testing rounds in the field prior to certification is becoming evident to ordnance developers. In Canada, plans are to include deposition rate testing as a critical component of the environmental assessment conducted prior acquisition.

The DRDC, CRREL, and EPA teams wish to thank SERDP for their continued support for this research. We have published over 30 journal publications for ER-1481 and ER-2219, demonstrating the significance and importance of our work.

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APPENDIX A

List of Publications for SERDP Project ER-2219

Journal Articles

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APPENDIX B
Characterization of Air Emissions from Open Detonation of Insensitive Munitions:
EPA Quality Assurance Project Plan – Category III, Measurements

1. Project Description and Objectives

1.1 Background

Prior to fielding of new munitions, a process known as the Life Cycle Environmental Assessment (LCEA) is conducted to evaluate the environmental impact of the munition. Recent tests conducted by the US Army Cold Regions Research Engineering Laboratory (CRREL) under the Department of Defense's Strategic Environmental Research and Development Program (SERDP) Project ER-2219 have assessed the environmental impact of the use of munitions on training ranges. During SERDP Project ER-2219, field and laboratory experiments were conducted to assess the deposition of uncombusted, residual explosives on the surface surrounding the detonation point. These tests were conducted to mimic actual field training activities that involved the detonation of the munitions **[B-1]**.

In brief, detonations are carried out on snow-covered ranges and the surface of the snow is sampled for residual energetics. The fresh snow matrix allows for deposition of potential ordnance residuals without concern regarding cross contamination from previous testing. Samples are gathered in a geometrical pattern and statistically assessed to determine the mass of residual energetics from the detonation **[B-2]**.

Three munitions have recently been completed, one on 60-mm mortar cartridges containing PAX-21, one on 60- and 81-mm mortar projectiles containing IMX-104, and one on 155-mm howitzer projectiles containing IMX-101. High order detonation tests showed that on average (N=7) 15% of the ammonium perchlorate (AP) in the PAX-21 was not consumed during the detonation and dissolved immediately into the aqueous portion of the samples **[B-3]**. That translates to 14g of perchlorate per high-order detonation, enough to contaminate 7 M liters of water above drinking water limits. The loss of use liability for the PAX-21 approaches $200M and the environmental liability is estimated to have exceed $1B had the Army not reclassified the rounds for combat use only. Tests for the IMX-104 rounds resulted in 47 g of residual, soluble explosive Nitrotriazolone (NTO); these munitions have now been put on hold until definitive toxicological tests and are completed and dosage levels established (Walsh et al., 2014). The IMX-101 rounds did not detonate high-order under any scenario, the best results indicating that 31% of the nitroguanidine and 6.6% of the NTO remained after the most efficient detonation scenario **[B-4].**

In assessing the LCEA process, questions arose as to whether energetic material in the detonation aerial plume can be estimated using aerial sampling methods and if that estimate can be correlated with surface sampling residues estimates. This is the question that this research addresses.

1.2 Objective

The objective of this research is to sample and quantify the residual particulate matter (PM) and energetics in the aerial plume from ground-based detonations. Quantification of the whole-plume PM and energetics entails determination of an emission factor, which relates the target analyte mass to the sampled carbon (as CO + CO_2) and then to the residual energetic composition through knowledge of its C composition. These values can be added to the snow-deposited explosive residuals sampled by the Principal Investigator to estimate the order, or effectiveness, of the explosive detonation.

1.3 Method

These tests will involve munition detonations at Eagle River Flats impact range at the DoD's Joint Base Elmendorf Richardson (JBER) near Anchorage, AK. This site has been used by the PI for over 20 years for various detonation tasks. The Flats are ice- and snow-covered in the winter, allowing safe operations in a clean impact area. Lab facilities are nearby for sample processing, equipment staging, and instrumentation troubleshooting. A series of munitions will be detonated high-order using a blasting cap or a fuze simulator device. The air emissions will be sampled during the detonation and dissipation processes. The snow surface will by sampled by CRREL for detonation residues **(Fig. B-1)**. Five shots of C4 will be characterized in this manner to allow for repeat measurements. Two trial detonations of 81 mm mortars will be conducted as a preliminary examination of methods for potential future testing.

Figure B-1. Detonation residues on snow

This work will involve a two-week sampling program, targeted from February 5, 2015 to February 18, 2015. The OD activities will be performed by US Army Explosive Ordnance Disposal (EOD) personnel while an EPA/UDRI team will be sampling the gaseous and particulate emissions. The EPA/UDRI team will use its aerial sampling equipment (termed the Flyer) in a trolley- and cable-mounted scenario to capture gas and particles emitted from these test scenarios. This equipment has been used in four prior test campaigns on open burning (OB) and OD activities with the U.S. DoD and Canadian Department of National Defence.

At press time of this QAPP (12/1/14), discussions were underway between the parties to this QAPP and the University of Alaska-Fairbanks (UAF) (Michael Hatfield) to provide for aerial sampling during the detonation plumes. This sampling will be accomplished by a UAF unmanned aerial vehicle (UAV), specifically a hexacopter. UAF would fly the UAV into the detonation plumes, carrying sensors provided by EPA. The trial testing of these sensors is discussed under a QAPP addendum to "Application and Evaluation of CO and CO_2 Sensors and Lightweight VOC and $PM_{2.5}$ Samplers" entitled "Application and Evaluation of Continuous Samplers" (ca. November 10, 2014). These measurements would include CO, CO_2, and $PM_{2.5}$ and are a category B level. Operation and calibration of the sensors is included in the QAPP and its Addendum. If this system function as desired, emission factors for $PM_{2.5}$ could be compared with those derived from the Flyer on the trolley system.

2. Organization and Responsibilities

This research effort is headed by Mr. Michael Walsh (USA CRREL), the Principal Investigator. Mr. Walsh is responsible for overall project coordination including JBER facilities and personnel as well as snow sampling for energetics (not part of this QAPP). He is also responsible for analyzing the filter samples, provided by the air sampling team, for energetics. The air-sampling component is comprised of participants from U.S. EPA/ORD and the University of Dayton Research Institute (UDRI). Dr. Brian Gullett (EPA) is the Air Technical Lead and Dr. Johanna Aurell (UDRI) is the Field Sampling Lead. Dr. Gullett is responsible for EPA and UDRI team coordination and personnel logistics, the project QAPP, the conduct of the project in the field, and the analysis and dissemination of the results to

CRREL. Mr. Dennis Tabor will coordinate methods of sample transferal to the PI for energetics analysis. Dr. Johanna Aurell (UDRI), as Sampling Lead, will conduct equipment checks prior to shipment including pump flows and gas calibration checks. She will lead the equipment packaging, providing shipment data to ARCADIS US, Inc., (Dr. Touati). She will be the lead operator of the Flyer samplers at JBER and will be responsible for downloading, storing, and reducing the instrument data for analysis. Mr. Bill Mitchell (EPA) is responsible for the electronic components, including the Flyer computer and transmission/receiving systems. Mr. Dale Greenwell is in charge of power systems, battery charging, and assistance in set up. Mr. Bill Squier is in charge of the trolley system for the field sampling apparatus. This includes the rigging systems for the poles and cables that will support the trolley run that holds the Flyer samplers. ARCADIS US, Inc., EPA's on-site contractor at Research Triangle Park, NC, will handle logistics of shipment and equipment preparation maintenance. Mr. Michael Hatfield (UAF) is responsible for flight operation of his UAV.

Table B-1. Site and Project Personnel

NAME	RESPONSIBILITY
Mr. Michael Walsh, CRREL	Principal Investigator on the SERDP project
Dr. Brian Gullett, EPA/ORD	Lead, Air Sampling Team
Dr. Johanna Aurell, UDRI	Lead Field Sampler
Mr. Bill Mitchell, EPA/ORD	In-field electronics
Mr. Dale Greenwell, EPA/ORD	Power technician
Dr. Dahman Touati, ARCADIS	Logistics, equipment transportation.
Mr. Bill Squier, EPA/ORD	Field Trolley system for sampler
Ms. Libby Nessley, ARCADIS	ARCADIS QA
Mr. Paul Groff, EPA/ORD	EPA QA manager
Mr. Dennis Tabor, EPA/ORD	Chemist, sample transmittal methods
Mr. Michael Hatfield, UAF	UAV coordination

2.1 Project Schedule and Milestones

Project milestones are given in **Table B-2**. These are planned milestones and will vary depending on test site conditions. The results will be documented in a report and, at the Principal Investigator's preference, a paper or journal article(s). The report will undergo review according to the procedures of the respective organization. Results may be presented by any participant with mutual approval at related symposia or in peer review journal formats.

Table B-2. Milestones

MILESTONE	DATE
Submit QAPP for review	1/15/15
QAPP approval	2/3/15
Equipment departure from RTP	1/14/15
Equipment arrival at JBER, AK	2/3/15
Personnel arrival, JBER, AK	2/5/15
JBER schedule commences (Ref. Attachment A, "Schedule" sheet, row 19)	2/11/15
Sampling complete, equipment packed	2/18/15
Personnel departure for RTP	2/18/15 PM
Equipment return to RTP	3/11/15
Data analysis complete	6/30/15
Report to CRREL - draft	7/15/15
Report finalized	9/1/15

3. Scientific Approach

3.1 Experimental Design

The Tests and Schedule are within the Appendix under the folders of the same names. In brief, five detonations of two blocks of C4 will occur, all at the same location, spread out over three days. These will be followed by two detonations of 81-mm projectiles to take preliminary data for anticipated subsequent testing FY16. To develop a better correlation between the two methods, single rounds will be detonated in the field in such a way as to enable the collection of both sets of data for the same event. A round will be set up on a snow and ice covered impact range and detonated using a fuze simulator (Figure B-2). The air sampling equipment will then be able to sample the residues in the air corresponding to the residues in the detonation IDA on the ground, enabling a direct comparison of the two methods.

Figure B-2. Set up of detonation point. Fuze adapter shown in inset photo.

A pole/cable and trolley system will be set up in advance at a location downwind of the detonation along which the air sampler ("Flyer") will traverse (**Fig. B-3**). This will be supplemented with a second trolley system, designed to both provide additional sample and to further ensure against missing the IDA due to wind shifts.

Figure B-3. Trolley system with Flyer

The downwind set up location of the poles will be determined upon observation of the wind roses for the pre-test days. If the wind roses result in fairly stable wind directions, both pole systems will be placed in parallel, downwind of the detonation point at a starting distanced determined on-site with the PI. The trolley will be remotely controlled and will be moved along the wire cable in an effort to maximize the sample catch in the plume. The air sampler will also be remotely controlled to minimize dilution with background sample and to preserve battery power.

It is difficult to a priori estimate the amount of plume volume that will have to be sampled in order to exceed the detection limits of the target energetics (PM collection is not viewed as problematic). Previous tests were conducted on RDX-based emissions (the primary explosive type in C4 blocks) at Tooele, Utah in June, 2012. Sampling during these tests was accomplished with the Flyer lofted by an aerostat. While the sampling and plume loft/dispersion scenarios are anticipated to be quite distinct, these data offer the only comparison basis. Data from seven Tooele tests were examined for a potential relationship between the amount of carbon (as CO_2, above background) sampled (an indication of the amount of the energetic sampled from the plume) versus the ratio of the RDX concentration to detection limit (**Fig. B-4).** No confidence-inspiring trend is noted. However, the lowest RDX emission factor was 1.7 ng RDX/mg C and the lowest C concentration noted was 10 mg/m^3.

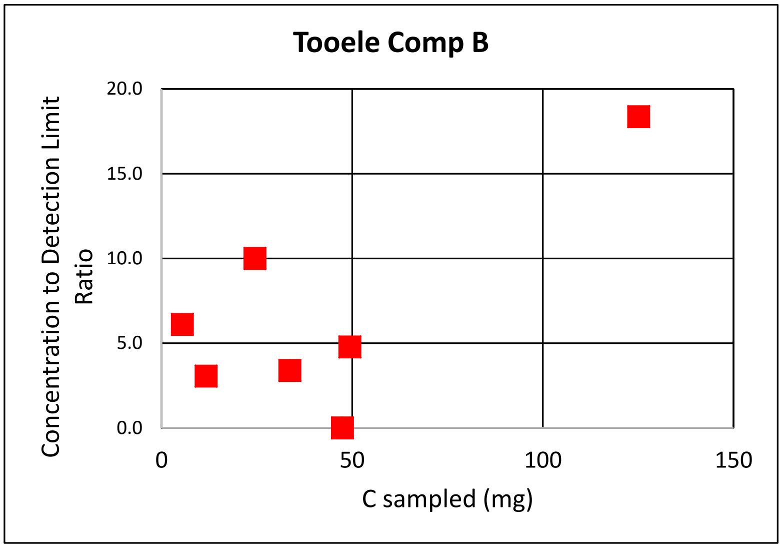


Figure B-4. Past results showing effect of sample size (carbon mass) on RDX concentration

With an RDX detection limit of 18 ng we need about 10 mg C to exceed the detection limit or 1 m^3 at the dilute concentration of 10 mg/m^3. Since the Flyer samples at a rate of about 1200 L/min (with the filter only, no sorbent), about 50 sec of sampling should be sufficient. Doubling the sampling rate with a second Flyer and increasing the plume concentration by being much closer than the Tooele Flyer both will help to ensure that we exceed the RDX detection limit. We will target a minimal carbon (CO_2) collection amount of 30 mg C. The Flyers each have CO_2 summation counters, allowing us to monitor mass over sampling time. In addition, we will have the opportunity to take composite samples using the same sampling media (filter) in order to reach the desired carbon collection mass, making the overall number of replicate samples uncertain, as discussed below. See also photo in Figure B-5.

Figure B-5. Residues deposition pattern after detonation

3.2 Test Matrix

The tests consist of five detonations of two blocks of C4 each and two detonations of 81-mm ordnance (Table B-3).

Table B-3. Test Matrix

DATE	ORDNANCE
February 11 (Wednesday)	Two blocks of C4
February 12 (Thursday)	Two blocks of C4
	Two blocks of C4
February 13 (Friday)	Two blocks of C4
	Two blocks of C4
February 16 (Monday)	81-mm
	81-mm

4 Measurements and the Flyer Sampler

The aerostat-lofted instrument platform (the "Flyer") was developed for sample collection of plumes from open area sources such as prescribed burning (**Fig. B-6)**. Interchangeable sampling instruments allow for continuous CO_2, CO, temperature, global positioning, 3D wind velocity, black carbon, and PM measurements as well as batch sampling of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), PM_{10} and $PM_{2.5}$, Cl species, PM-borne metals, and organic matter. An on-board computer and camera system allow for wireless control of the samplers and data and image transfer to the ground. For this work the Flyer will only use sampling for energetics, CO, CO_2, and PM (Table B-4). Location and GPS data are solely for informational purposes and are not critical measurements.

Figure B-6. The EPA Flyer sampling system

Table B-4. Measurements and methods

Measurement	Device/Method	Targets
CO_2	Li-COR IR	
$PM_{2.5}$	SKC filter cassette, Teflon	PM mass and metals via XRF
PM_{10}	SKC filter cassette, Teflon	PM mass and metals via XRF
CO	Electrochemical cell	
SVOC	Quartz filter	Energetics
PM	DustTrak	Optional instrument
Temperature	thermistor	
Location/altitude	GPS	

Completion of the test array will result in the sample numbers presented in **Table B-5** below.

Table B-5. Amount of samples

	Number of samples, type*			
Measurement	C4	81-mm	Background Samples	Method
Energetics	1-5, batch	1-2, batch	1, batch	Quartz filter
$PM_{2.5}$	5, batch	1-2, batch	1, batch	SKC filter cassette, PTFE
PM_{10}	5, batch	1-2, batch	1, batch	SKC filter cassette, PTFE
PM by size (optional)	5, batch	1-2, batch	1, batch	TSI, Inc. DustTrak
CO_2	5, continuous	1-2, continuous	1, continuous	Li-Cor IR
CO	5, continuous	1-2, continuous	1, continuous	Electrochemical cell, e2V
Temperature	5, continuous	1-2, continuous	1, continuous	Thermistor, Omega, Inc.

*These may be composite samples, depending on our ability to meet the C collection criterion.

5 Measurement Procedures

5.1 Carbon Dioxide (CO2)

CO_2 is continuously measured using non-dispersive infrared (NDIR) instrument (LI-820 model, LI-COR Biosciences, USA). These units are configured with a 14 cm optical bench, giving it an analytical range of 0-20,000 ppm with an accuracy specification of less than 3% of reading. The LI-820 calibration range is set to 0- 3,000 ppm, the LICOR is calibrated in accordance with EPA Method 3A [**B-5**]. A particulate filter precedes the optical lens. The LI-820 CO_2 concentration will be recorded on the onboard computer using the FlyerDAQ program, a LabView generated data acquisition and control program. The LI-820 will be calibrated for CO_2 on a daily basis according to US EPA Method 3A [**B-5**].

Table B-6. Continuous measurement of CO_2

Target Compound	Measurement/ Analytical Method	Sampling Rate	QA/QC Check Procedure	QA/QC Check Frequency	Acceptance Criteria/ DQIs	Reference Standard	Corrective Action	Preservation / Storage
Carbon dioxide	NDIR CEM LICOR 820/U.S. EPA Method 3A	Every second	3 point zero & calibration drift test	1 per sample, daily in field	±5% of span	Certified CO_2 calibration gases	Re-calibrate monitor	L: drive storage
Carbon dioxide	NDIR CEM DX6210 or DX6220/U.S. EPA Method 3A **[B-5]**	Every second	3 point zero & calibration drift test	1 per sample, daily in field	±5% of span	Certified CO_2 calibration gases	Re-calibrate monitor	L: drive storage

5.2 Carbon Monoxide (CO)

The CO sensor e2V EC4-500-CO is an electrochemical gas sensor (SGX Sensortech, United Kingdom) that measures CO concentration by means of an electrochemical cell through CO oxidation. The E2v CO sensor has a CO detection range of 1-500 ppm with resolution of 1 ppm and sensitivity of 55-85nA/ppm. The temperature and RH humidity operating range is -20 to +50°C and 15 to 90% RH, respectively. The responds time is less than 30 seconds. The sensor will be calibrated for CO on a daily bases in accordance with U.S. EPA Method 3A **[B-5]**. The sensor has a weight of approximately 5 g. The storage life of the CO sensor is 6 months. (Table B-7)

Table B-7. Continuous measurement of carbon monoxide (CO)

Target Compound	Sampling/Measure-ment/Analytical Method	Sampling Rate	QA/QC Check Frequency	QA/QC Check Procedure	Acceptance Criteria/ DQIs	Reference Standard	Corrective Action	Storage
Carbon monoxide	CEM/E2v EC4-500-CO Electrochemical cell /US EPA Method 3A **[B-5]**	Every second	1 per sample, daily in field	3 point zero & calibration drift test	±5% of span	Certified CO calibration gases	Re-calibrate monitor	L: drive storage

5.3 Particulate Matter (PM)

$PM_{2.5}$ and PM_{10} by filter, Table B-8 and B-9. $PM_{2.5}$ and PM_{10} will be sampled with SKC impactors using 47 mm or 37 mm tared Teflon filter with a pore size of 2.0 µm via a Leland Legacy sample pump (SKC Inc., USA) with a constant airflow of 10 L/min. PM will be measured gravimetrically following the procedures described in 40 CFR Part 50 **[B-6]**. Particles larger than 10 µm in the PM_{10} impactor (or larger than 2.5 µm in the $PM_{2.5}$ impactor) will be collected on an oiled 37 mm impaction disc mounted on the top of the first filter cassette. The particulate matter collected on the Teflon filters can also be used to determine metal concentrations through analysis by energy dispersive x-ray fluorescence spectrometry (ED-XRF) according to U.S. EPA Compendium Method IO-3.3 **[B-7]** or via Inductively Coupled Plasma according to U.S. EPA Compendium Method IO-3.4 **[B-8]**.

Table B-8. $PM_{2.5}$ and PM_{10} measurements

Target Compound	Sampling / Measurement/ Analytical Method	Sampling Rate	Sample Handling	Preservation/ Storage	Hold Time	Laboratory
$PM_{2.5}$ and PM_{10}	47 mm Teflon Filter/gravimetric/40 CFR Part 50 Appendix J **[B-6]**	10 L/min	1 filter in one petri dish/ sample	desiccator	30 d	EPA

Table B-9. $PM_{2.5}$ and PM_{10} measurements quality assurance check

Measured Parameter/Method	QA/QC Check Procedure	Reference Standard(s)	QA/QC Check Frequency	Acceptance Criteria/ DQIs	Corrective Action
$PM_{2.5\ \&\ 10}$ Particulate Concentration/ EPA IP-10A, analytical balance	Gas pump flow calibration with Gilibrator, filter blanks, balance calibration	Bubble flow meter, ASTM Class 1 wts.	1 per sample, 1 per test series, 4 per sampling trip	100 ug	Re-calibrate gas pump, check for contamination, re-calibrate balance

The Leland Legacy Sample pump will be calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, USA). For Leland Legacy pump operating instructions, see Operating Instructions: http://www.skcinc.com/instructions/38010.pdf.

The analytical balance used to weigh filters shall be suitable for weighing the type and size of filters and have a readability of ±10 µg. All sample filters used shall be conditioned to 20-23 °C and 30-40 % RH for a minimum of 24 h immediately before both the pre- and post-sampling weighing. Both the pre- and post-sampling weighing should be carried out on the same analytical balance, using an effective technique to neutralize static charges on the filter. The pre-sampling (tare) weighing shall be within 30 days of the sampling period. The post-sampling conditioning and weighing shall be completed within 30 days after the end of the sample period. Sampled filters are returned to the filters' petri dish and sealed with Teflon tape. The petri dishes are stored in separate Zip-Lock bags with desiccant. The Zip-lock bags are marked with the sampling information e.g. filter number, petri-dish number, and sampling date. Filter samples are shipped to the laboratory separate from bulk samples.

5.4 Continuous PM

The TSI DustTrak DRX Model 8533, **Tables B-10 and B-11**, measures light scattering by aerosols as they intercept a laser diode and has the capability of simultaneous real time measurement (every second) of PM_1, $PM_{2.5}$, Respirable (PM_4), PM_{10} and Total PM (up to 15 µm). The aerosol concentration range for the DustTrak DRX is 0.001-150 mg/m^3 with a resolution of ±0.1% of reading. The flow accuracy is ±5% of internal flow controlled. Concurrently, an enclosed, 37-mm pre-weighed filter cassette provides a simultaneous TSP gravimetric sample. The total flow rate is 3 L/min where 1/3 of the flow rate is used for the continuous measurements and 2/3 is used for the gravimetric sample. The enclosed gravimetric sample is used to conduct a custom photometric calibration factor (PCF) for the Total PM.

Table B-10. Continuous PM measurement monitors

Measured Parameter	Measurement/ Analytical Method	Aerosol size	Aerosol concentration range	Sampling Rate	Sample Handling	Storage
TSI DustTrak DRX 8533	Particle size distribution/ Laser Particle Counter - light scattering	Simultaneously TSP, PM_{10},PM_4, $PM_{2.5}$, PM_1	0.001-150 mg/m^3	Every second, 1 L/min	NA	L: drive storage
TSI DustTrak DRX 8533	37 mm Teflon Filter/gravimetric, 40 CFR Part 50 Appendix J **[B-7]**	Total PM, PM_{10} or $PM_{2.5}$*	NA	2 L/min	1 filter in 1 petri dish / sample	desiccator
TSI DustTrak 8520	Particle size distribution/ Laser Particle Counter - light scattering	PM_{10}, $PM_{2.5}$ or PM_1	0.001-100 mg/m^3	Every second,1.7 L/min	NA	L: drive storage

* Total PM if no PM_{10} or $PM_{2.5}$ impactor plate is used. NA – not applicable

The DustTrak DRX is factory calibrated to the respirable fraction, with a PCF value of 1.00. A custom PCF is conducted as per manufacturer's recommendations for $PM_{2.5}$ and PM_{10} using the simultaneously sampled $PM_{2.5}$ and PM_{10} by filter impactor concentrations (averaged continuous $PM_{2.5}$ (or PM_{10}) concentration divided by $PM_{2.5}$ (or PM_{10}) by filter mass concentration). This factor is applied to scale the real time data. A zero calibration will be performed before each day using a zero filter which comes with the DustTrak DRX and a flow calibration will performed before each day with a Gilibrator flowmeter, following procedures in Operation and Service Manual Model 8533/8534 (P/N 6001898, Revision F, January 2011). The DustTrak inlet will be cleaned after each use/day by a cotton swab, and the internal filter will be replace when indicated by the main screen filter error indicator on the DustTrak.

The TSI DustTrak Model 8520, Table B-10-Table B-11, is a light-scattering laser photometer which measures mass fraction of PM_1, $PM_{2.5}$, or PM_{10} (depending on the chosen impactor plate and nozzle size) every second. It is an older model than the 8533 above, but it is less bulky and therefore may have to be used on the space-limited Flyer. The measurement range for DustTrak 8520 is 0.001-100 mg/m3. The zero stability is ±0.001 mg/m^3 over 24 hours. The DustTrak 8520 is factory calibrated to the respirable fraction, with a PCF value of 1.00. A custom PCF are conducted as per manufacturer's recommendations for $PM_{2.5}$ and PM_{10} using the simultaneously sampled $PM_{2.5}$ and PM_{10} by filter impactor concentrations (averaged continuous $PM_{2.5}$ (or PM_{10}) concentration divided by $PM_{2.5}$ (or PM_{10}) by filter mass concentration). This factor is applied to scale the real time data. A zero calibration will be performed before each day using a zero filter which comes with the DustTrak 8520 and a flow calibration will performed before each day with a flowmeter that comes with the DustTrak 8520, following procedures in Operation and Service Manual Model 8520 (1980198, Revision S, June 2010) found at: http://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Manuals/1980198S-8520.pdf The DustTrak inlet will be cleaned after each use/day by a cotton swab.

Table B-11. Continuous PM measurements quality assurance check

Measured Parameter/Method	QA/QC Check Procedure	Reference Standard(s)	QA/QC Check Frequency	Acceptance Criteria/ DQIs	Corrective Action
Particle size distribution/ TSI DustTrak DRX 8533/Laser Particle Counter - light scattering	Factory calibration	Precision beads	Permanent unless damaged	Per manufacturer's recommendations	Manufacturer's re-calibration
Particle size distribution/ TSI DustTrak 8520/Laser Particle Counter - light scattering	Factory calibration	Precision beads	Permanent unless damaged	Per manufacturer's recommendations	Manufacturer's re-calibration

5.5 Energetics

Energetics are sampled using a low voltage Windjammer brushless direct current blower (AMETEK Inc., USA). The blower is triggered by the CO_2 concentration set points using the FlyerDAQ program or started from the ground by the operator via wireless control. The flow rate is measured by a 0-622 Pa pressure differential transducer (Setra, Model 265, USA) across a Herschel Standard Venturi tube. The Venturi tube is specially designed to meet the desired sampling rate for the target compound. The Venturi tube is mounted on the outlet of the Windjammer blower. The voltage equivalent to this pressure differential is recorded on the onboard PC using the FlyerDAQ program, which is be calibrated with a Roots meter (Model 5M, Dresser Measurement, USA) in the U.S. EPA metrology laboratory before sampling effort. A temperature thermistor is measuring the air temperature exiting the venturi.

In accord with previous experience, all of the energetics are believed to be capture on the quartz microfiber filter prior to the blower. The Flyer has battery capacity for about one hour of sampling at 1200 L/min. The filters will be removed, folded, folded into aluminum foil, bagged, and tagged prior to transferring to the PI for analysis **(Table B-12, B-13)**. Trip and field blanks will be collected and analyzed.

Table B-12. Energetics sampling.

Target Compound	Sampling/Measurement / Analytical Method	Sampling Rate	Sample Container/Handling	Preservation/ Storage	Hold Time	Laboratory
Energetics	Modified TO-9A / quartz microfiber filter / HRGC / HRMS	1200 L/min	Store in jar in cool, dark place (15°C)	Refrigerator (4°C)	60 d	CRREL

Table B-13 Quality assurance for energetic sampling.

Measured Parameter/Method	QA/QC Check Procedure	Reference Standard(s)	QA/QC Check Frequency	Acceptance Criteria/ DQIs	Corrective Action
Energetics/ Venturi	Gas pump flow calibration	Roots meter in Met Lab, spiked filter standards	Before and after field tests	±10%	Re-calibrate gas pump

Samples will initially be processed at CRREL's field laboratory on JBER. The filters containing the solids will be partially air-dried if necessary and stored in wide-mouth 120 mL amber jars in a refrigerator **[B-2]**. The samples containing the organic explosives residues will be shipped to CRREL's analytical laboratory in Hanover, NH, for final processing. Following completion of the drying process, the solids on the filters will be extracted with AcN using a shaker table (18 h). The AcN extracts will be mixed 1/3 v/v with reagent-grade water prior to analysis. Extraction of the analytes from the solid fraction will be performed at the analytical laboratory using standard methods **[B-9, B-10, B-11]**. Analyses for energetics will be conducted using high-pressure liquid chromatography (HPLCUV) following EPA method 8330B with some of the higher concentrations diluted to confirm concentrations **[B-9]**. Detection limits were 0.02 mg/L for the three compounds in the acetonitrile extracts.

There are several quality assurance steps that are taken to estimate error originating from the initial processing procedures. Filtered water blanks will be run through the process to check on any analyte carryover, and prior to changing out the wash water for the glassware, a filtered water blank will be run through the last washed glassware. Spiked samples are run through the SPE to gauge the retention efficiency of the cartridges combined with the efficiency of the elution process **[B-2]**.

5.6 Temperature

Ambient temperature at the Flyers will be measured using thermistors **(Table B-14)**. The data will be logged at 10 Hz using the FlyerDAQ program.

Table B-14. Temperature and relative humidity measurements.

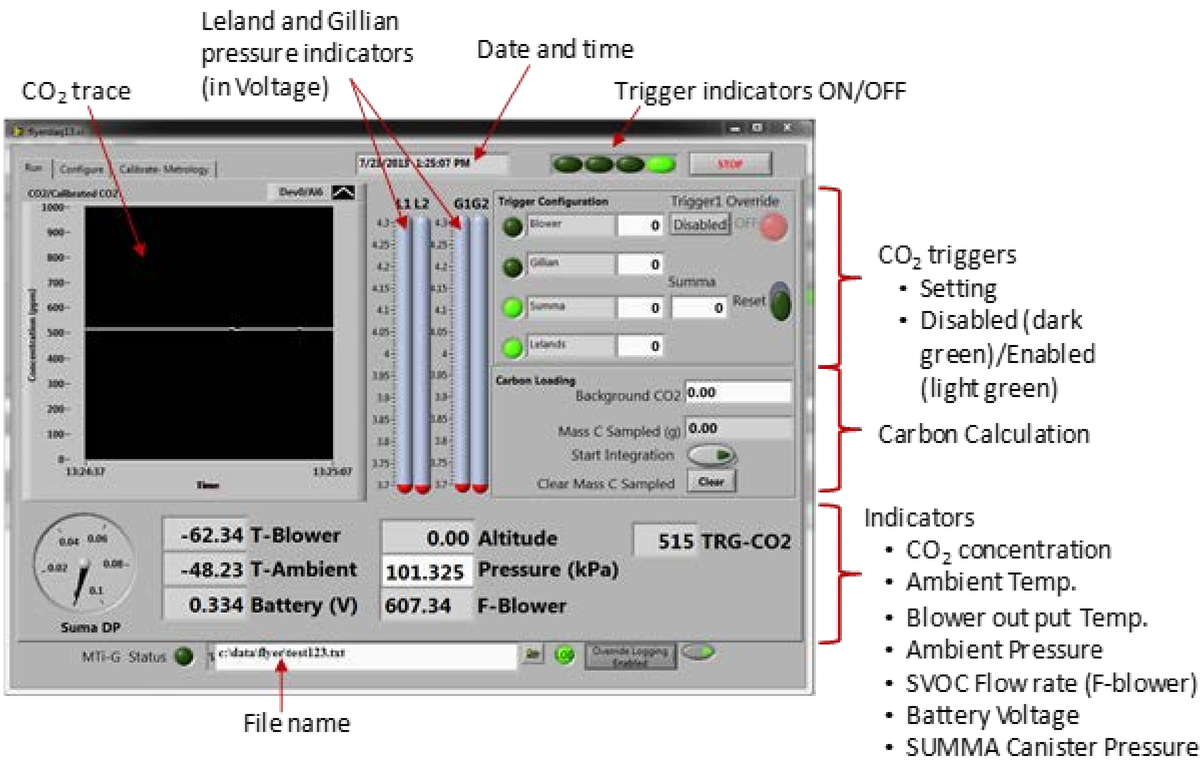
Measured Parameter	Measurements/Method	Sampling rate	Temperature / humidity range	Accuracy	Drift / Stability	Storage
Temperature	T-type thermocouple Super MCJ	Every millisecond	-100°C to 350°C	1.1°C at 25°C	0.05mV / °C	L: drive storage

5.7 FlyerDAQ Program

Data will be acquired using a multi component data acquisition system (DAS). The DAS consists of an onboard USB based data acquisition (DAQ) card controlled by an onboard computer running "FlyerDAQ", a Labview generated data acquisition and control program. Also included in the DAS is a ground based computer which can be used to view data being logged in real time and control the onboard computer via a wireless remote desktop connection if necessary (see Figure B-).

The USB DAQ card is a Measurement Computing USB-2537 data acquisition (DAQ) board. The USB-2537 has 32 differential analog input channels, 24 configurable digital input/output (DIO) channels, and 4 analog output channels. The differential analog input channels are used to measure signals in the form of voltages from sensors and instruments on the flyer. Currently four DIO channels are used to trigger the SUMMA Canister, Sensidyne pumps (2), Leland Legacy pumps (3), and the Windjammer for SVOCs based on the CO_2 concentration. The SVOCs blower can also be manually triggered from the ground. Two additional DIO channels are used to indicate and momentarily stop data logging.

The onboard computer uses FlyerDAQ, a Labview generated data acquisition and control program to configure and log data from the USB-2537 and MTi-G AHRS sensor. Additionally, FlyerDAQ is capable of plotting real time data, multipoint nth order calibrations, and performing on the fly calculations to estimate the total amount of gaseous carbon sampled for the SVOC sample. The FlyerDAQ interface consists of three different windows: Run, Configuration and Calibrate-Metrology **(Figs. B-7, B-8, and B-9)**. All data (raw, calibrated, and calculated) will be logged at a rate of 10 Hz. Data files are in tab delimited text files and are thus easily imported into common spreadsheet/database analysis programs (e.g. MS Excel and Origin).



CO₂ trace

Leland and Gillian pressure indicators (in Voltage)

Date and time

Trigger indicators ON/OFF

CO_2 triggers
- Setting
- Disabled (dark green)/Enabled (light green)

Carbon Calculation

Indicators
- CO_2 concentration
- Ambient Temp.
- Blower out put Temp.
- Ambient Pressure
- SVOC Flow rate (F-blower)
- Battery Voltage
- SUMMA Canister Pressure

File name

7/23/2013 1:25:07 PM

Background CO2 0.00

Mass C Sampled (g) 0.00

-62.34 T-Blower

-48.23 T-Ambient

0.334 Battery (V)

0.00 Altitude

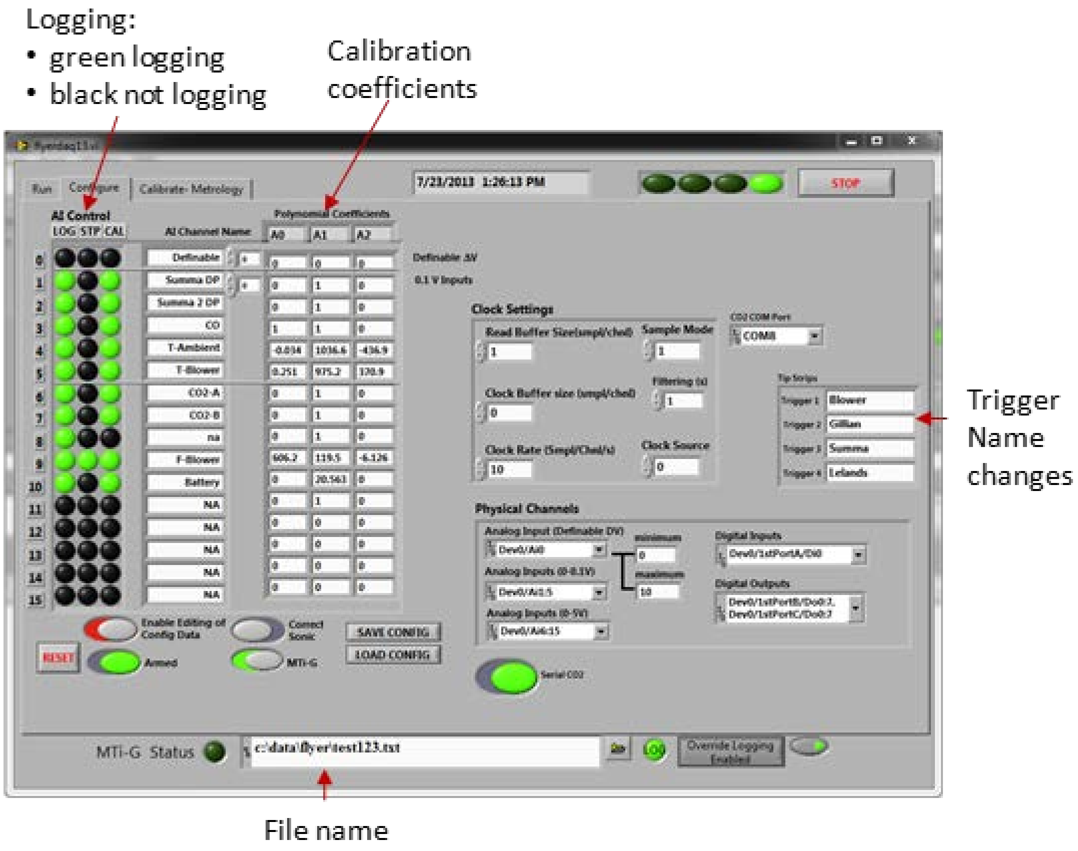
101.325 Pressure (kPa)

607.34 F-Blower

515 TRG-CO2

c:\data\flyer\test123.txt

Figure B-7. FlyerDAQ V.13 interface, Run window



Logging:
- green logging
- black not logging

Calibration coefficients

Trigger Name changes

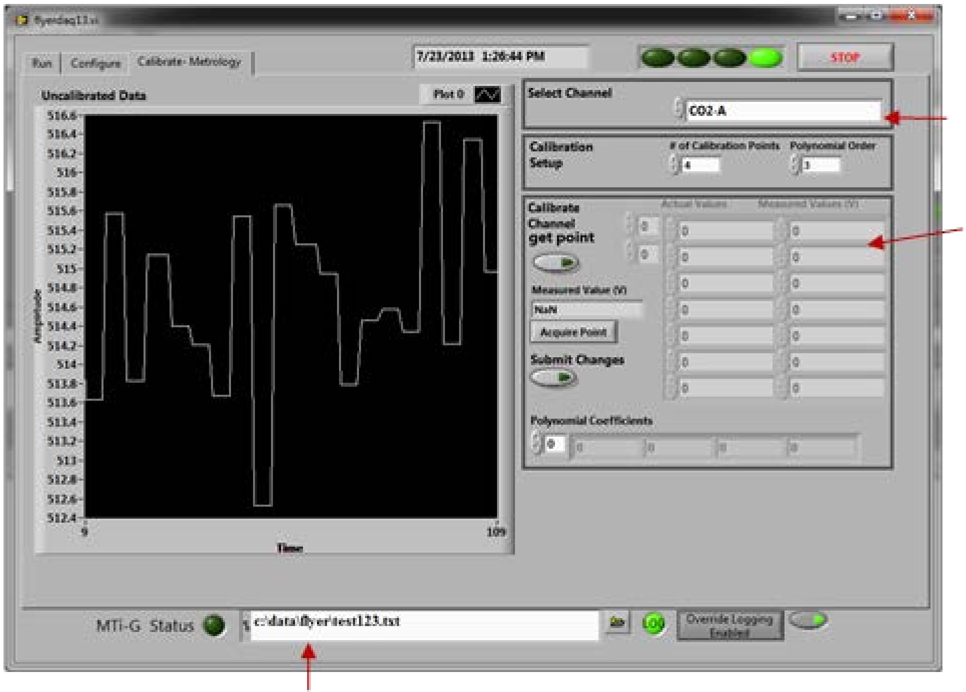
File name

7/23/2013 1:26:13 PM

CO2 COM Port COM8

c:\data\flyer\test123.txt

Figure B-8. FlyerDAQ V 13 interface, Configure window



7/23/2013 1:26:44 PM

Select Channel: CO2-A

Calibration Setup: # of Calibration Points 4; Polynomial Order 3

Measured Value (V): NaN

c:\data\flyer\test123.txt

Calibration channel

Calibration points

File name

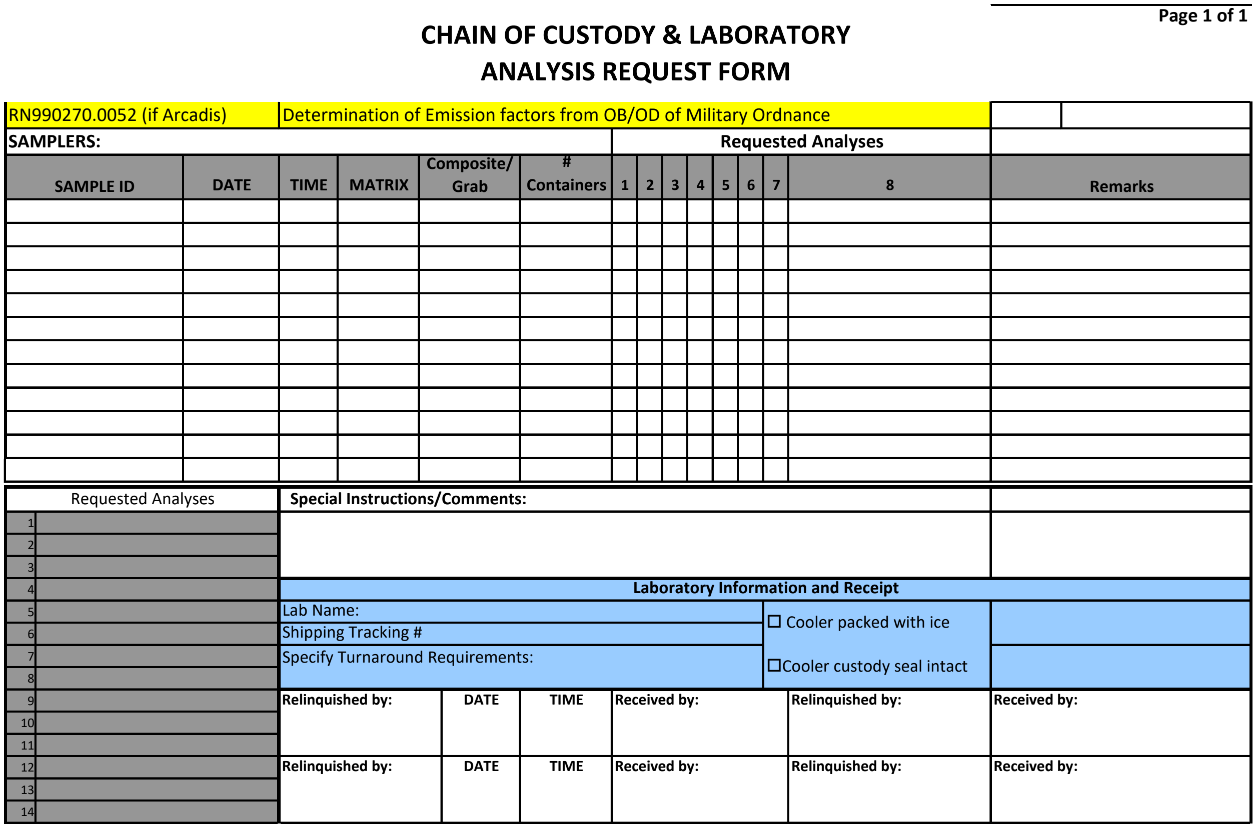
Figure B-9. FlyerDAQ v13 interface, Calibrate-Metrology window

6 Sample Identification

Each sample data sheet and sample fraction will be given an identifying code number that will designate the run number. The codes and code sequence will be explained to the field team and laboratory personnel to prevent sample mislabeling. Proper application of the code will simplify sample tracking throughout the collection, handling, analysis, and reporting processes. The sample coding to be used in this study is described in **Table B-15**. For each target compound a chain of custody sheet will be generated (**Fig. B-10**).

Table B-13. Sample Coding

AA-CC-DD-MMDDYY-EE	Sample Code	Code definition
AA	TB	Test condition (TB = Trip blank, PL = Plume Sample, BS = Background Field Sample
CC	C4 or 81	Type of test
DD	FT	Sampling Media (FT = Filter, PM = Particulate Matter Filter)
MMDDYY	071510	Date Field, month/day/year
EE	01	Sample Number (01, 02, 03, etc.)



Page 1 of 1

CHAIN OF CUSTODY & LABORATORY
ANALYSIS REQUEST FORM

RN990270.0052 (if Arcadis)	Determination of Emission factors from OB/OD of Military Ordnance												
SAMPLERS:						**Requested Analyses**							
SAMPLE ID	**DATE**	**TIME**	**MATRIX**	**Composite/ Grab**	**# Containers**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Remarks**

Requested Analyses	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	

Special Instructions/Comments:

Laboratory Information and Receipt

Lab Name:
Shipping Tracking #
Specify Turnaround Requirements:

☐ Cooler packed with ice
☐Cooler custody seal intact

Relinquished by:	**DATE**	**TIME**	**Received by:**	**Relinquished by:**	**Received by:**
Relinquished by:	**DATE**	**TIME**	**Received by:**	**Relinquished by:**	**Received by:**

Figure B-10. Chain of custody sheet

7. Sample Storage and Transportation

PM filters will be held in hard plastic petri dishes and double-sealed in plastic bags. Quartz filters will be folded, wrapped in aluminum foil, and packed in a plastic bag. The filter media will be shipped in coolers to and from the field via airplane.

8. Data Analysis, Interpretation, and Management

The emission ratio of each species of interest will be calculated from the ratio of background-corrected pollutant concentrations to background-corrected carbon dioxide concentrations. Emissions factors will be calculated using these emissions ratios following the carbon balance method (**Burling et al., 2010**), shown in **Equation B-1**.

$$EF_i = f_c \frac{ER_i}{\sum_j \frac{\Delta C_j}{\Delta CO_2}}$$

Eq. B-1

where EF_i is the emission factor of species i in terms of gram effluent per kilogram fuel , f_c is the fraction of carbon in the fuel, ER_i is the mass emission ratio of species i, ΔCO_2 is the background-corrected mass concentration of CO_2, ΣCj is the background corrected mass concentration of carbon in major carbon emissions species j. The majority of the carbon emissions will be emitted as carbon dioxide. With this assumption, carbon dioxide is the only carbon-containing compound that is required to be measured at each measurement location

Field data will be transferred from the data loggers to external hard drives via a laptop computer with a USB port. Electronic data and pictures will be posted in the folder L:\Lab\NRML_Public\GullettResearchUpdates\ on the EPA network share drive upon return from the field or as they are generated or received.

9. Reporting

Deliverables:

- CRREL will provide energetics analyses.
- UDRI will provide Flyer data (PM, CO, CO2) and emission factors.
- EPA (Gullett) will provide data report to CRREL and participate in product writing with CRREL lead.

Products:

- Data report with results of the sampling and analysis of the air emissions

10. References

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[B-3] Walsh, M.R., M.E. Walsh, C.A. Ramsey, S. Taylor, D. Ringelberg, J. Zufelt, S. Thiboutot, G. Ampleman, and E. Diaz (2013) “Characterization of PAX-21 insensitive munition detonation residues,” Propellants, Explosives, Pyrotechnics, 38:399-409.

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[B-5] U.S. EPA Method 3A (2012). Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure). 1989. http://www.epa.gov/ttn/emc/promgate/m-03a.pdf. Accessed November 21, 2012

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[B-9] US EPA (2006). Nitroaromatics and Nitramines by High-Pressure Liquid Chromatography, EPA SW846 Method 8330B, 2006, US Environmental Protection Agency, Washington, DC (http://www.epa.gov/osw/hazard/testmethods/pdfs/8330b.pdf).

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Appendix C. Alkaline Hydrolysis of IMX-101 Analytes

DNAN, like other nitroaromatics, is susceptible to alkaline hydrolysis (Sunahara et al. 2009). At pH 13 (25°C) DNAN has a half-life of 10 hours with the formation of 2,4-dinitrophenol and Meisenheimer complexes as minor products (Sviatenko et al. 2014). Meisenheimer complexes tend to be highly colored, a characteristic that has been exploited for colorimetric tests of nitroaromatic compounds and may be responsible for some of the color associated with the 155-mm M1122 IMX-101 samples. Salter-Blanc et al. (2013) demonstrated the significance of increases in pH from 11 to 12 on the decrease in DNAN concentration at 25 °C **(Figure C1).** Loss of DNAN coincided with the formation of Meisenheimer complexes, 2,4-dinitrophenol, and 2,4-dinitrophenolate.

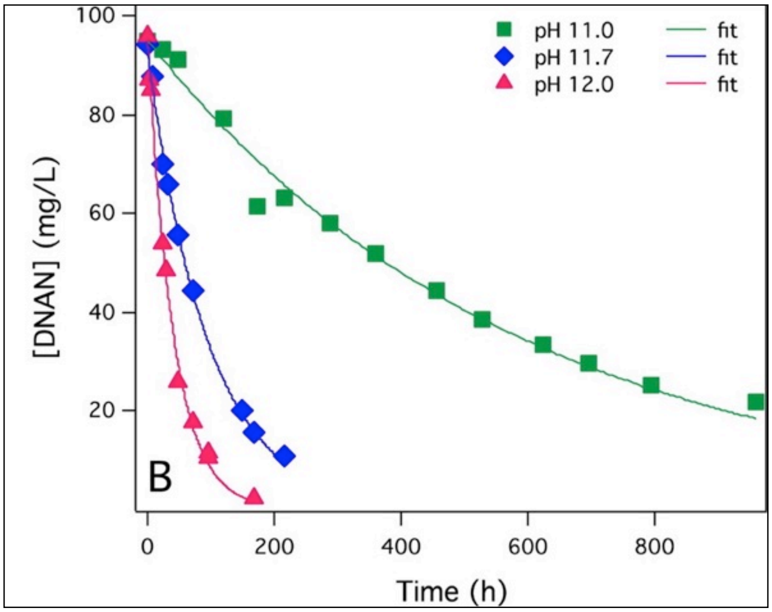

Figure C1. Loss of DNAN between pH 11 and 12 at 25°C (Salter-Blanc et al. 2013)

Nitroguanidine is also documented to undergo alkaline hydrolysis. At pH 12 (25°C) nitroguanidine has a half-life of 55 hours and the hydrolysis products are nitrourea and ammonia (Spanggord et. al. 1985). After we discovered that the concrete had such a major effect on the pH of the 155-mm M1122 IMX-101 samples, we plotted NQ concentrations in the aqueous fractions from the 155-mm M1122 IMX-101 samples versus pH. There is a downward trend in concentration with increasing pH **(Figure C2)**.

The rate of alkaline hydrolysis depends on temperature and is slower at lower temperatures. The 155-mm M1122 samples were maintained at cold temperatures (<4°C) except during the following processing steps: the aqueous samples were warmed to room temperature prior to removal of a designated volume with a pipet; the solid samples were air-dried a room temperature; the extraction analytes from the solids (soot and debris) with solvent took place a room temperature; and the extracts that were prepared for analysis were contained in autosampler vials on the instrument. We discovered that there was a problem with the 2017 samples during a test to see if the NQ was nearing saturation of the aqueous fractions at cold temperatures. Some of the samples from Shot 1 were warmed to room temperature and rotated on a platform shaker for 2 days. Reanalysis of the samples revealed a marked decrease in the NQ concentration but not NTO (**Table C1**). We had previously verified the stability of NQ and NTO in melted snow samples, and again analyzed two samples from 2014 that were stored in the refrigerator. No concentration change was found. The difference between the 2014 samples and the 2017 samples was the pH. The 2014 samples were neutral and the 2017 samples were highly alkaline. The collection method used in 2017 resulted in the co-collection of concrete, which we hypothesize caused the pH change, resulting in the loss of NQ and DNAN in our samples.

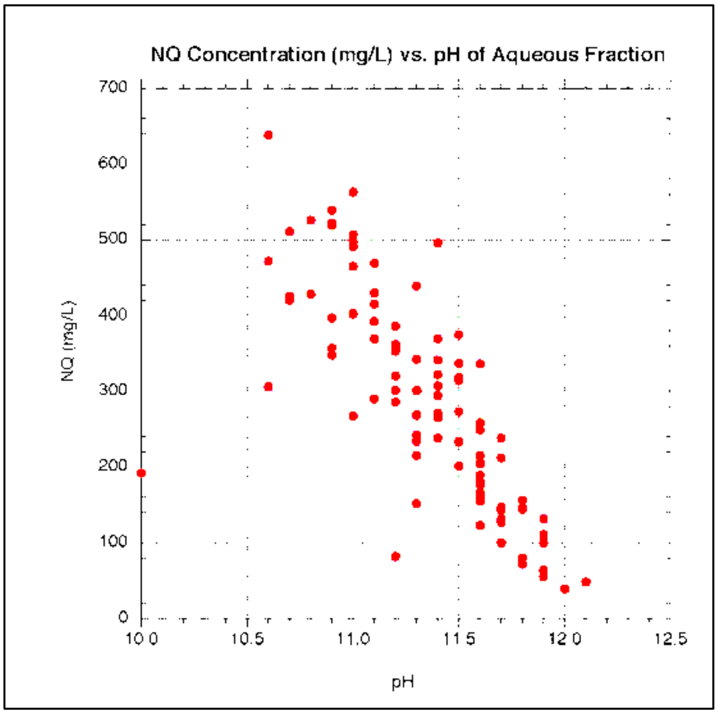

Figure C2. NQ concentrations in aqueous fractions versus pH.

Table C1. Initial and subsequent concentrations (mg/L) of NQ and NTO in aqueous samples from 2017 and 2014.

	NQ (mg/L)		NTO (mg/L)		
Sample	Initial Analysis	After 2 Days at ~22°C	Initial Analysis	After 2 Days at ~22°C	pH
17FRAP145	350	30	290	270	11.2
17FRAP147	390	29	390	400	11.1
17FRAP153	340	10	200	200	11.4
17FRAP154	340	16	280	260	11.3
	Initial Analysis	After 3 years at ~4°C	Initial Analysis	After 3 years at ~4°C	pH
14FRA37	71	72	12	12	neutral
14FRA38	73	73	11	11	neutral

Fortunately for this project, NTO is not degraded at high pH. Researchers at the Stevens Institute evaluated treatment options for wastewater containing DNAN, nitroguanidine, and/or NTO. They found that:

> "Alkaline hydrolysis was effective in destroying DNAN and the efficiency of the process increases with increasing temperature. The product of the alkaline hydrolysis appears to be 2,4-dinitrophenol, which has a strong yellow color.

> Conversely, NTO was not susceptible to alkaline hydrolysis." (Stevens Institute 2010)

In summary, the mass estimates for NQ and DNAN are underestimates of the mass remaining after the detonations of the 155-mm M1122 IMX-101 rounds due to the co-collection of concrete that raised the pH of the samples. Evidence of NQ degradation was the decrease in concentration with time for the 2017 samples. Evidence of DNAN degradation was that 2,4-DNP was detected a concentrations higher than DNAN in the debris sample-extracts; the pH of the extracts were 11.2 to 11.4. Detonation efficiency based on NTO should be used for comparison to the previous data.

References:

Salter-Blanc, Alexandra J. Eric, J. Bylaska, Julia J. Ritchie, and Paul G. Tratnyek. Mechanisms and Kinetics of Alkaline Hydrolysis of the Energetic Nitroaromatic Compounds 2,4,6-Trinitrotoluene (TNT) and 2,4-Dinitroanisole (DNAN) Environmental Science & Technology 47 (2013), 6790-6798 DOI: 10.1021/es304461t

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