INTERIM REPORT

Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Interim Report 2

ESTCP Project ER-1481

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Michael R. Walsh
Marianne E. Walsh
Alan D. Hewitt
Charles M. Collins
Susan R. Bigl
Kelsey Gagnon
ERDC

Guy Ampleman
Sonia Thiboutot
Isabelle Poulin
Sylvie Brochu
André Marois
Annie Gagnon
Denis Gilbert
Defence R&D Canada

Aurélie Bellavance-Godin
Richard Martel
Geneviève Bordeleau
Institut National de la Recherche Scientifique Centre

Peter Woods
British Army Training Unit Suffield (BATUS)

Jeffrey N. Bryant
Bering Sea Environmental LLC

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US Army Corps of Engineers®
Engineer Research and Development Center

Strategic Environmental Research and Development Program ER-1481 (Phase 2)

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Michael R. Walsh, Guy Ampleman, Sonia Thiboutot, Marianne E. Walsh, Isabelle Poulin, Aurélie Bellavance-Godin, Richard Martel, Geneviève Bordeleau, Sylvie Brochu, Alan D. Hewitt, André Marois, Annie Gagnon, Charles M. Collins, Denis Gilbert, Peter Woods, Jeffrey N. Bryant, Susan R. Bigl, and Kelsey Gagnon

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COVER: Night firing of 105-mm Leopard C2 Main Battle Tank at CFB Valcartier, February 2009. (Photo by Canadian Defence Forces)

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Michael R. Walsh, Marianne E. Walsh, Alan D. Hewitt, Charles M. Collins, Susan R. Bigl, and Kelsey Gagnon

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

Guy Ampleman, Sonia Thiboutot, Isabelle Poulin, Sylvie Brochu, André Marois, Annie Gagnon, and Denis Gilbert

Defence R&D Canada-Valcartier
2459 Pie-XI Blvd North
Québec, Quebec G3J 1X5 CANADA

Aurélie Bellavance-Godin, Richard Martel, and Geneviève Bordeleau

Institut National de la Recherche Scientifique
Centre Eau, Terre, et Environnement
290, de la Couronne
Québec, Québec G1K 9A9 CANADA

Peter Woods

British Army Training Unit Suffield (BATUS)
Canadian Force Base, Suffield
Alberta, CANADA

Jeffrey N. Bryant

Bering Sea Environmental LLC
4300 B Street, Suite 402
Anchorage, AK 99503

Prepared for Strategic Environmental Research and Development Program
Arlington, Virginia 22203

Abstract: The Cold Regions Research and Engineering Laboratory and Defence Research and Development Canada–Valcartier have partnered to improve the understanding of the distribution and fate of propellant residues on military training ranges. Field studies were conducted to estimate the propellant residue mass deposited per round fired from various munitions as well as residues from the field disposal of excess training propellants. Experiments were conducted to measure the rate of release of nitroglycerin and dinitrotoluenes after deposition. United States and Canadian installations were examined to determine the mass and distribution of residue accumulation. Profile sampling was conducted to document the depth to which these residues had penetrated the ground. Column studies were conducted with nitroglycerin, nitroguanidine, potassium perchlorate, and diphenylamine from intact and expended propellants to document transport rates for solution-phase propellant constituents and to develop process descriptors for use in models to enable prediction of fate and transport for these constituents. Gaps were filled in other areas of energetics residues deposition, rounding out a holistic overview of training impacts on military ranges. Testing of propellant burn structures was begun, and we continue to promote multi-increment sampling for energetics. Major accomplishments are presented for Environmental Restoration Project 1481, Phase II.

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This report was prepared by the U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory (ERDC–CRREL), and represents the collaboration of researchers from ERDC–CRREL in Hanover, New Hampshire, and the Defence Research and Development Canada-Valcartier (DRDC-Valcartier) of Quebec, Canada. The research was sponsored by the Strategic Environmental Research and Development Program (SERDP) of Arlington, Virginia, under Environmental Restoration Project Number ER-1481 (extension). Mr. Bradley P. Smith was Executive Director for SERDP, with Dr. Jeff Marqusee as Technical Director, and Dr. Andrea Leeson was Project Monitor.

The principal investigator was Mr. Michael R. Walsh, Engineering Resources Branch (ERB) at ERDC–CRREL, with co-principal investigators Dr. Guy Ampleman and Dr. Sonia Thiboutot, research chemists at DRDC-Val.

Various chapters of this report were reviewed by Dr. Clarence L. Grant, Professor Emeritus, University of New Hampshire; Marianne E. Walsh, Michael R. Walsh, Dr. Susan Taylor, Dr. Thomas F. Jenkins, Dr. Thomas A. Douglas, and Susan R. Bigl from ERDC-CRREL; Dr. Sonia Thiboutot from DRDC-Valcartier; and Charles A. Ramsey from Envirostat.

The manuscripts for this report were edited, organized, and assembled by Susan R. Bigl and Kelsey Gagnon, Biogeochemical Branch (BCB), ERDC–CRREL.

At the time this work was performed, Colonel Gary E. Johnston was Commander and Executive Director of ERDC, and Dr. James R. Houston was Director.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
inches	0.0254	meters
microns	1.0 E-06	meters
miles (U.S. statute)	1,609.347	meters
pints (U.S. liquid)	0.473176	liters
pounds (mass)	0.45359237	kilograms
quarts (U.S. liquid)	9.463529 E-04	cubic meters
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters

This report may be cited as one document or by chapters as follows:

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M.R. Walsh, G. Ampleman, S. Thiboutot, M.E. Walsh, I. Poulin, A. Bellavance-Godin, R. Martel, G. Bordeleau, S. Brochu, A.D. Hewitt, A. Marois, A. Gagnon, C.M. Collins, D. Gilbert, P. Woods, J. Bryant, S.R. Bigl, and K. Gagnon.

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M.R. Walsh

Nomenclature

ACGIH	American Conference of Governmental Industrial Hygienists
AcN	acetonitrile
AEC	Army Environmental Center
Ald	aldehydes
APFSDS	armor piercing fin stabilized discarding sabot
ATR	attenuated total reflectance
BATUS	British Army Training Unit, Suffield
BEI	backscattered electron imaging mode
BIP	blow in place
BLP	blind loaded plug
BTC	breakthrough curve
BTEX	benzene, ethylbenzene, toluene, and xylene (o, m, p)
CBI	clean burning igniter
CCME	Canadian Council of the Ministry of Environment
CEA	Camp Ethan Allen
CEC	cation exchange capacity
CFB	Canadian Forces Base
CFB/ASU	Canadian Forces Bases/Area Support Unit
CFU	colony-forming unit
CI SQFT	Centre d’Instruction du Secteur du Quebec de la Force Terrestre
CN	total cyanide
CRREL	Cold Regions Research and Engineering Laboratory
DAD	diode array detector
DND	Department of National Defence
DNG	dinitroglycerine
DNT	dinitrotoluene
DoD	Department of Defense
DPA	diphenylamine
DRDC	Defence Research and Development Canada
DTA	Donnelly Training Area (formerly Fort Greely), Alaska
DU	decision unit
EC	ethyl centralite (diethyl diphenyl urea)
EDX	energy dispersive x-ray analysis

EM	energetic material
ERF	Eagle River Flats
EOD	explosives ordnance disposal
EPA	Environmental Protection Agency
ER	Environmental Restoration (program)
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
FP	firing point / firing position
FT-IR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GPS	global positioning system
HE	high explosive
HESH	high explosive squash head
HMX	high melting explosive 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine cyclotetramethylene-tetranitramine octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine
HPLC	high-performance liquid chromatography high-pressure liquid chromatrography
IC/ESI/MS/MS	ionic chromatography/electrospray ionization tandem mass spectrometry
ICP-AES	inductively coupled plasma – atomic emission spectroscopy
ICP/MS	inductively coupled plasma/mass spectrometry
INRS	Institut National de la Recherche Scientifique
INRS-ETE	Institut National de la Recherche Scientifique – Eau, Terre, et Environnement
KClO4; KP	potassium perchlorate
k_d	adsorption coefficient ($cm^3\ g^{-1}$)
LC/MS/MS	liquid chromatography/tandem mass spectrometry
LLE	liquid-liquid extraction
LOD	limit of detection
LP	launch position
METC	Munitions Experimental Test Center
MG	machine gun
MIS	multi-increment sampling
MMR	Massachusetts Military Reservation
MWS	model water sample

NaBr	sodium bromide
NATO	North Atlantic Treaty Organization
NC	nitrocellulose
NCSM	Notre Commandant Sa Majesté
nd	not detected
NIOSH	National Institute for Occupational Safety and Health
NG	nitroglycerin
NQ	nitroguanidine
NSN	NATO stock number
OM	organic matter
OSHA	Occupational Safety and Health Administration
OTP	outside the plume
PAH	polycyclic aromatic hydrocarbon
PCDD	polychlorodibenzo-p-dioxin
PCDF	polychlorodibenzofurane
PE	polyethylene
PM	particulate matter
PTFE	polytetrafluoroethylene
PV	pore volume
PVDF	polyvinylidene fluoride
QA	quality assurance
QC	quality control
RDDC	Recherche et Développement pour la Défense Canada
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
RfC	reference concentration (US EPA)
RPD	relative percent differences
RP-HPLC	reverse-phase high-performance liquid chromatography
RSD	relative standard deviation
SAW	squad automatic weapon (a machine gun)
SE	secondary electron (imaging mode)
SEM	scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
SH	squash head
SH/P-T	squash head/practice – tracer
SLLE	salting-out liquid–liquid extraction

SPE	solid-phase extraction
SPHz	self-propelled howitzer
SPME	solid-phase microextraction
SRTPDS	short range target practice discarding sabot
SVOC	semi-volatile organic compound
TCC	total cell count
TDR	time domain reflectometry
TEF	toxic equivalency factor
TEQ	toxic equivalent quantity
TLV	threshold limit value
TNB	Trinitrobenzene
TNT	2,4,6-trinitrotoluene
TOC	total organic carbon
TPFSDS	target practice fin stabilized discarding sabot
TPRAP	target practice rocket assisted projectiles
TSP	total suspended particulate
USAGAK	U.S. Army Garrison Alaska
USARAK	U.S. Army Alaska
UTM	universal transverse mercator
UV/VS	ultraviolet/visible spectrum
UXO	unexploded ordnance
VOC	volatile organic compound
WP	white phosphorus

1 Introduction

Michael R. Walsh

1.1 Background

Live-fire training is a necessary component to ensure readiness for the armed forces of the United States and Canada. To sustain the long-term use of military training ranges, installations must comply with environmental regulations that protect human health and the environment. In particular, the U.S. Department of Defense (DoD) must ensure that compounds in residues produced by live-fire training do not migrate beyond installation boundaries at concentrations that impair the use of ground and surface water resources utilized by surrounding communities. Currently, the liability posed by off-site migration of energetic residues from military ranges is not fully known. Little or no environmental data exist for residues from newer composite energetic formulations and uncertainty remains in the understanding of the fate of some compounds and stabilizers in more conventional energetic formulations such as nitrocellulose (NC)-based propellants. Assessing the deposition, accumulation, fate, and transport of residues associated with energetic compounds at training ranges will further the Army's goal of quantifying potential contaminants of concern and enhance their ability to adapt range practices to best prevent limitations on the use of critical range facilities.

1.2 The need for a holistic examination of potential contaminant sources

Prior to 1990, little research had been conducted on energetic residues resulting from training activities on military ranges. That all changed with the closure of training ranges at Fort Richardson, Alaska, in 1990 (Racine et al. 1992) and the Massachusetts Military Reservation (MMR) in 1997 (Clausen et al. 2004). Although limited use of these facilities has resumed, severe limitations on the use of both ranges have been imposed. It became clear to the military that more needed to be known about the impact of training with live munitions on the environment, and several agencies and entities got involved. In the United States, site investigations and research at impact areas and firing points was sponsored by the Army Environmental Center (AEC), the U.S. Army Garrison, Alaska (USAGAK), the DoD's Strategic Environmental Research and Development Program (SERDP), and the National Guard Bureau at MMR. In Canada, the Canadian Government funded research through the Department of National Defence (DND), Canada.

Initial studies concentrated on the characterization of impact areas, as that was where most of the energetic compounds were directed (Jenkins et al. 2001, Brochu et al. 2006). Research results indicated that high-order detonations of the most commonly used munitions resulted in very little energetics residues. Although the characterization work was quite useful, studies were also conducted to gather data related to the amount of detonation residues produced on a per-round basis (Hewitt et al. 2003, Walsh 2007) to enable the modeling of source term input as well as to determine energetics loading on ranges resulting from live-fire training. As an adjunct to these studies and the ongoing characterization studies, firing points were examined (Walsh et al. 2001, Jenkins et al. 2004). These sites were found to contain energetic residues, sometimes at high levels, and as they tend to be fixed locations, accumulation of energetic residues was a concern. Observing training exercises resulted in the discovery of another potential source of propellant residues, the expedient field disposal of excess propellants (Walsh et al. 2006). At this point, a more holistic approach to examining military training activities for possible sources of energetics residues was obvious.

Many military activities have been or are now being examined for possible energetics compounds loading of the environment. Sites include artillery impact areas, firing points, propellant disposal sites, open burn / open detonation munitions disposal sites, demolitions training ranges, and small arms ranges. Each site has its characteristic activity, sometimes more than one, that will potentially lead to a range of energetics residue sources. Adjunct activities on these ranges have also been examined, including blow-in-place (BIP) of dudded munitions and the field disposal of excess propellants. The scope of research has expanded to include metals as well as energetic materials. In every case, new source terms have been identified and quantified, allowing for a better understanding of the impacts of military training and other activities on ranges.

1.3 Scope of project

This project was designed to acquire data for estimating mass and concentration of propellant residues in the source zone, as well as process descriptors for mass transportation from the surface to groundwater, all data required for use in risk assessments. In addition, some data gaps are addressed with the completion of deposition studies of BIP operations and the effect of close proximity detonations on unexploded ordnance (UXO). Solutions to propellant burn contamination are included in the scope as well as an effort to disseminate and promote related sampling and sample processing methods developed through earlier SERDP- and ESTCP-funded research.

1.4 Research objectives

The main thrust for this project is the characterization and fate of propellant residues resulting from military activities on testing and training ranges. In addition, several tasks included in the scope of work relate to other non-propellant energetic compounds. The tasks are as follows: propellant deposition and characterization studies at firing points; large-column studies on the fate and transport of surface-deposited propellant compounds; characterization of, deposition due to, and solutions to the open burning of excess propellants; effect of close-proximity detonations on legacy UXO on impact ranges; completion of characterizing residues from small-quantity field disposal (BIP) of UXO; and dissemination and promotion of the use of multi-incremental sampling for the characterization of energetic residues on military ranges. The overarching goal is to increase our understanding of the environmental effects of training with energetic compounds on military lands.

1.5 An overview of progress to date

The characterization and deposition studies of propellant residues at firing points are a continuation of research started under SERDP ER-1155. This work formed the basis of the original SERDP ER-1481 under Dr. Thomas Jenkins. For the current extension of ER-1481, the primary goal is to continue deposition, characterization, fate, and transport studies for weapon systems and propellants not addressed in the previous projects. Thus, we are filling some critical data gaps and expanding some existing work in areas we foresaw as critical to the overall effort.

To date, we have completed deposition studies on four weapon systems. All four tests looked only at firing points and a limited distance downrange because of the danger involved in sampling the impact points. Two types of shoulder-fired rockets have been tested, the U.S. AT4 (Chapter 2: Walsh et al.) and the Canadian M-72 (Chapter 3: Thiboutot et al.). For the AT4 test, the area behind the firing position was also characterized the following spring prior to any further use of the site. Propellant debris from the firing was collected during both time periods and optically examined. The third weapon system test completed was the firing of a Canadian Leopard 105-mm gunned tank (Chapter 4: Thiboutot et al.). Tests have been completed on the British 155-mm AS-90 self-propelled howitzer (SPHz) utilizing tripe-based propellant (nitrocellulose [NC], nitroglycerine [NG], and nitroguanadine [NQ]), but results are preliminary and thus not included in this report. These tests were conducted in association of the British Army Training Unit, Suffield, Canada (BATUS). DRDC has also completed characterization work on a legacy shoulder-fired rocket range at Carpiquet (Chapter 5: Thiboutot et al.). Soil profiling and surface sampling were conducted at Carpiquet to determine infiltration of energetic compounds in the soil column.

A series of large-column tests have been completed at Institut National de la Recherche Scientifique – Eau, Terre et Environnement. The columns were topped off with firing point soils containing double-base (NC and NG) propellant residues from a shoulder-fired rocket training area. The columns were subjected to an accelerated 2-yr climatic regime to derive fate, transformation, and transport parameters (Chapter 6: Bellavance-Godin et al.). A new series of column studies has been initiated using different source term soils.

A new effort initiated under the ER-1481 extension was the study of propellant residues resulting from the field-expedient disposal of excess propellants from howitzers and mortars. Preliminary deposition rate studies under the original ER-1481 project indicated that percent-level energetic residues may remain after expedient field disposal under certain climatic conditions. Under the extension, studies were conducted using single-base (NC) howitzer propellant and double-base mortar propellant. Results indicated that high levels of energetic residues will remain under certain climatic conditions, but that burning within a semi-enclosed structure will improve disposal efficiencies by two orders of magnitude (Chapter 7: Walsh et al.). During the investigation of propellant disposal residues in

Canada, DRDC discovered the presence of dioxins and furans. These were found to result from the disposal initiation protocol, which has now been changed for the Canadian Forces nationwide (Chapter 8: Poulin et al.). Two burn tests of triple-base propellants have been conducted by CRREL at Canadian Forces Base (CFB) Suffield following the BATUS 155-mm SPHz tests. Results will be written up for the ER-1481 project final report. Two types of burn disposal structures are currently under development as part of the SERDP project extension. A fixed burn pan structure has been designed, built, and tested in Canada by DRDC with very good results. Canadian Forces will be mandated to use the final version of this structure for propellant disposal pending completion of testing. In the United States, a mobile burn pan structure has been designed, is currently being built, and will be field tested by CRREL. The U.S. Army Alaska (USARAK) and Canadian Forces have both expressed interest in testing this structure upon completion of preliminary tests to be conducted this spring in Canada. Results will be reported in the final report for this project.

Another new effort under the ER-1481 extension is the close-proximity detonation tests. Final preparations are currently underway. Rounds have been procured and an initiation device designed and built. The initiator will be tested in February prior to use in the tests, currently scheduled for March 2011. CRREL, DRDC, and USARAK are all scheduled to participate in the tests to be held on the Eagle River Flats (ERF) impact range on Fort Richardson, AK. The effect of a close proximity detonation on an unexploded round will be examined. The breaching of UXO has been found to be the most readily available source of significant quantities of energetic compounds on impact areas. With the initiation of this project, in association with work funded by AEC and SERDP on dissolution of energetic materials from corroded rounds and exposed explosives, we will have a much better understanding of this large source term.

Wrapping up an effort started in January 2004, two series of BIP tests were conducted at the ERF impact range in Alaska. Sixty- and 120-mm high-explosive (HE) mortar rounds were detonated on snow covered ice with blocks of C4 explosive (91% RDX) and the residues collected and analyzed (Chapter 9: Walsh et al.). This completes the suite of deposition rate tests for detonation and BIP residues for common HE artillery and mortar rounds. The next step will be to consolidate the results in a readily available spreadsheet, along with results of our firing point tests. Work has already begun on this effort, and a preliminary spreadsheet is presented in Chapter 10 (Walsh).

The final task in the ER-1481 extension scope of work is the dissemination, promotion, and demonstration of the multi-increment sampling (MIS) strategy and U.S. Environmental Protection Agency (EPA) Method 8330B. The MIS protocol, developed in part through the SERDP program by CRREL and Envirostat, is a new method of sampling for non-homogeneously distributed contaminants, specifically energetic residues, with the primary goal of site characterization. This protocol is included as an appendix to Method 8330B, the first time a sampling protocol has been included as part of an EPA Method. Resistance to the new sampling method was stiff to begin with, but through workshops, field demonstrations, and conference presentations, acceptance is now strong and growing. The MIS protocol has caught the attention of our North Atlantic Treaty Organization (NATO) allies, and Defence Research and Development Canada (DRDC) gave a field demonstration to the U.K. Ministry of Defence in 2008. Other NATO countries, especially Norway and the Netherlands, have adopted aspects of MIS, and several other countries are very interested in learning how to implement the protocol. As a result of our research, both Canada and the United States have been requested to participate in a NATO workgroup on the environmental impact of military training on ranges. Both the SERDP-generated characterization and deposition work as well as MIS are to be topics of the workgroup.

Results for the completed studies described above are summarized in the final chapter of this report (Chapter 10: Walsh). We also discuss the current state of work-in-progress and data gaps not covered by the current scope of work that we uncovered over the course of the project.

1.6 References

Brochu, S., E Diaz, S. Thiboutot, G. Ampleman, A.D. Hewitt, S.R. Bigl, M.E. Walsh, K. Bjella, T. Ranney, M.R. Walsh, S. Taylor, C. Ramsey, D. Lambert, and N.Perron (2006) Assessment of 100 years of military training in Canada: The case of Canadian Forces Base Petawawa. In *Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 6*. ERDC TR-06-12. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Clausen, J., J. Robb, D. Curry, and N. Korte (2004) A case study of contaminants on military ranges: Camp Edwards, Massachusettes, USA. *Environmental Pollution* 129:13–21.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Karn (2003) *Estimate for Explosives Residue from the Detonation of Army Munitions.* ERDC/CRREL TR-03-16. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren (2001) *Characterization of Explosives Contamination at Military Firing Ranges*. ERDC TR-01-05. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, and K.L. Bjella (2004) *Representative Sampling for Energetic Compounds at as Antitank Firing Range.* ERDC/CRREL TR-04-7. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Racine, C.H., M.E. Walsh, B.D. Roebuck, C.M. Collins, D.J. Calkins, L.R. Reitsma, P.J. Buchli, and G. Goldfarb (1992) White phosphorus poisoning of waterfowl in an Alaska salt marsh. *Journal of Wildlife Diseases*, 28(4): 669–673.

Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney (2001) *Sampling for Explosives Residues at Fort Greely, Alaska: Reconnaissance Visit July 2000.* ERDC/CRREL TR-01-15. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari. 2006. *Energetic Residues Deposition from 60-mm and 81-mm Mortars.* ERDC/CRREL TR-06-10. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M.R. (2007) *Explosives Residues Resulting from the Detonation of Common Military Munitions: 2002–2006.* ERDC/CRREL TR-07-2. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

2 Propellant Residues Deposition from Firing of AT4 Rockets

*Michael R. Walsh, Marianne E. Walsh, Sonia Thiboutot, Guy Ampleman, and Jeffrey N. Bryant**

2.1 Abstract

Military live-fire training missions utilize a variety of energetic materials that are never completely consumed during firing. In March 2009, tests were conducted at Fort Richardson, Alaska, to determine the residues related to the firing of AT4 anti-armor shoulder-fired rockets. Six rockets were fired from the same firing position on the snow-covered range. Replicate multi-increment samples were collected from the snow surface behind and downrange of the firing point in each of eight decision units. Samples were analyzed and results composited to derive an estimate of the mass of unreacted energetic materials. Total estimated per-round deposition rate of nitroglycerin (NG) for the M136 AT4 rocket is 95 g/round, or 73% of the original NG load. This indicates that the propellant burn efficiency for the AT4 is poor, with much propellant not consumed during firing. In subsequent May 2009 samples, we found approximately one-third of the NG had leached out of the propellant fragments since March. Large propellant strip segments collected in May contained 67% of the nominal NG of the original propellant, and we hypothesize that even more had leached from the more numerous, smaller segments. Canadian tests of the similar Carl Gustav rocket also indicate high rates (> 14%) of unburned propellants.

2.2 Preface

This study was conducted for the Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) under Environmental Restoration Program Project ER-1481. Dr. Andrea Leeson was the program manager.

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This report was prepared by: Michael R. Walsh, Engineering Resources Branch (ERB), at the U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), in Hanover, New Hampshire; Marianne E. Walsh, Biogeochemical Branch, CRREL; Dr. Sonia Thiboutot and Dr. Guy Ampleman, Energetics Materials Section, Defence Research and Development Canada–Valcartier (DRDC), Val Belair, Quebec, Canada; and Jeffrey N. Bryant, Bering Sea Environmental LLC of Anchorage, Alaska.

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The Commander and Executive Director of the Engineer Research and Development Center is Colonel Gary E. Johnston. The Director is Dr. James R. Houston.

2.3 Introduction

Use of munitions during live-fire training is a necessary component for a well-trained military. The environmental impacts of the energetic materials associated with these munitions were not fully known until relatively recently. That knowledge was accelerated with the closure of ranges in Alaska (Eagle River Flats on Fort Richardson) and Massachusetts (Massachusetts Military Reservation), and subsequent research into the characterization of contaminants on those ranges (Racine et al. 1992; Clausen et al. 2004).

Initially, research emphasis was on the impact areas, where detonation of the projectiles had the potential to introduce large quantities of energetics into the environment. Characterization and deposition studies indicated that a properly functioning munition will not deposit appreciable amounts of energetics during training (Hewitt et al. 2005; Jenkins et al. 2006; Walsh, M.R. 2007). In the process of examining impact areas, the focus expanded to include the characterization of firing points (Walsh, M.E. et al 2001, 2007; Walsh, M.R. et al. 2005a, 2005b, 2007a). When firing positions for shoulder-fired rockets were characterized, high concentrations of propellant residues were found in the surface soils (Thiboutot et al. 1998; Jenkins et al. 2006; Wingfors et al. 2006).

The examination of firing points (FPs) as a source of energetic residues is a recent thrust in range sustainability research. Starting in 2000, studies funded by U.S. Army Alaska (Soil and Water Quality Monitoring Fund) at Fort Wainwright's Donnelly Training Area (DTA) indicated propellant-related energetic compounds were accumulating at heavily used indirect-fire and direct-fire FPs (Walsh, M.E. et al. 2001). Further research in 2001 and 2002 reinforced the original indications, with the propellant constituents nitroglycerin (NG) and 2,4-dinitrotoluene (DNT) recovered at several FPs (Walsh et al. 2004). The State of Alaska lists DNT as a hazardous substance.

In 2002, the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) funded research at Fort Richardson, Alaska, to estimate high-explosives (HE) residue deposition (RDX, HMX, and TNT) from the live-fire detonation of 105-mm and 81-mm HE projectiles. Following the firing of the 105-mm howitzers, propellant residues containing DNT were collected from the snow-covered area in front of one of the guns (Walsh et al. 2004). Results indicated concentrations of energetic residues four orders of magnitude higher for the firing points than found at the impact areas (Hewitt et al. 2003; Walsh et al. 2005b; Walsh, M.E. et al 2007).

The ease of sample collection on snow and the straightforward processing of these samples led us to consider further investigations at winter firing points as an adjunct to the impact area research we were then conducting for SERDP. The methodology for the collection of samples on snow originally developed by Jenkins et al. (2000a, 2000b, 2002) was optimized by M.R. Walsh et al. (2005a, 2007b), making sampling much more efficient and repeatable.

Trials have been conducted on several common weapon systems including howitzers (M.R. Walsh et al 2005b; Diaz et al 2008), mortars (M.R. Walsh et al. 2005c, 2006), small arms (M.R. Walsh et al 2007a; Brochu et al. 2009), and tanks (Ampleman in prep.). Results of studies conducted at shoulder-fired rocket positions on training ranges indicated concentrations of NG up to 1,400 mg/kg. When comparing that finding to that of 500 mg/kg for heavily-used small arms ranges and <10 mg/kg for artillery positions, it was clear that more information was required on the impacts of the shoulder-fired rockets (Jenkins et al. 2007).

Canadian researchers at the Defence Research and Development Canada (DRDC) had conducted deposition trials in 2007 for the Carl Gustav shoulder-fired rocket and in 2008 for the M72 LAW rocket, indicating moderate to high levels of residues (Thiboutot et al. 2008a, 2008b). Additional work on U.S.-inventoried shoulder-fired rockets thus was deemed necessary.

2.4 Objectives

Because of the need for continued training with live ammunition at military ranges, the need for Army Range Officers to manage residues from such training lands, and the identified problems with depositions from the use of shoulder-fired rockets, further investigations of residues from the firing of shoulder-fired rockets were initiated, including the deposition of unburned propellants resulting from the firing of these weapons (Thiboutot et al. 2007).

This report details a propellant residues deposition test conducted at Fort Richardson, Alaska, in March 2009. This report documents follow-on work to the previous studies by examining the propellant residue deposition rate for the U.S. Army’s M136 AT4 shoulder-fired rocket.

The objective of this work is to provide data and results that can be used by the range community to assess the environmental impact of training with the AT4 rocket. This information then can be used to develop an integrated training lands management plan.

2.5 Approach

Testing for AT4 propellant residues was conducted in 2009 during two deployments. We first visited the Fort Richardson, Alaska, 40-mm/AT4 Range (40/90 Range)[*] for live firing of the weapons systems in March 2009. We returned to the same site in May 2009 to resample the area behind the winter firing position in order to gauge the natural decomposition of the depositions from exposure to weather.

It was our original intent to sample downrange all the way to the target, but evidence of unauthorized use of the target by 40-mm grenade gunners prohibited traveling downrange beyond a few meters of the parking area. The snow cover masked prior activities and rendered this task unsafe.

Processing of the March samples was performed at a CRREL field laboratory located in our logistics building on Fort Richardson, prior to final processing and analysis at CRREL's analytical laboratory in Hanover, NH. Processing of the snow samples in Alaska greatly reduced the quantity of sample material that needed to be shipped to the analytical laboratory. The soil samples collected in May were shipped directly to the CRREL laboratory in Hanover for processing and analysis. Sections 2.9 and 2.11 of this chapter provide details for the sampling procedures and the processing and analyses of those samples.

It is important to note there were no baseline samples of the soils in the area taken prior to snowfall, so we are uncertain if NG was present at the location prior to our test.

2.6 Field site and conditions

No activity had occurred at the Fort Richardson range during the winter immediately prior to our test. For the March test, the parking area had been plowed, but a recent snowfall had deposited 3 cm of snow on the surface. We set the firing position on the top of the up-range snow berm that was formed during the several snow clearing operations of the parking area. The FP configuration was designed to minimize snow displacement and mixing from the backblast of the rocket firing. The snow surface behind the firing position sloped away for 3 m, leveled out for about 10 m,

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[*] The location and time of the first visit were chosen due to previously documented results of being able to easily collect more residues from a snowy surface (M.R.Walsh et al. 2007b).

then sloped abruptly down less than a meter to the natural grade (Figure 2-1). Forward of the firing position, the area was flat for 18 m before encountering the opposite snow berm. The temperature at the time of testing was around –7 °C with winds out of the north variable at around 4 m/sec. The sky was heavily overcast at the start of the test, clearing as the day progressed. Snow depth was less than 40 cm outside the berms and 3 cm on the plowed parking area. Berm height was approximately 1.5 m.

Figure 2-1. Looking at backblast area from snow berm near firing position.

Following the natural snow melt, the site in May 2009 was revealed to consist of two areas – one-half of the sampled area was a gravel pad, the remainder was brush-covered soil (Figure 2-2). Weather was not a factor during this second sampling because we were not firing rockets but only were collecting soil samples from the previous test in March.

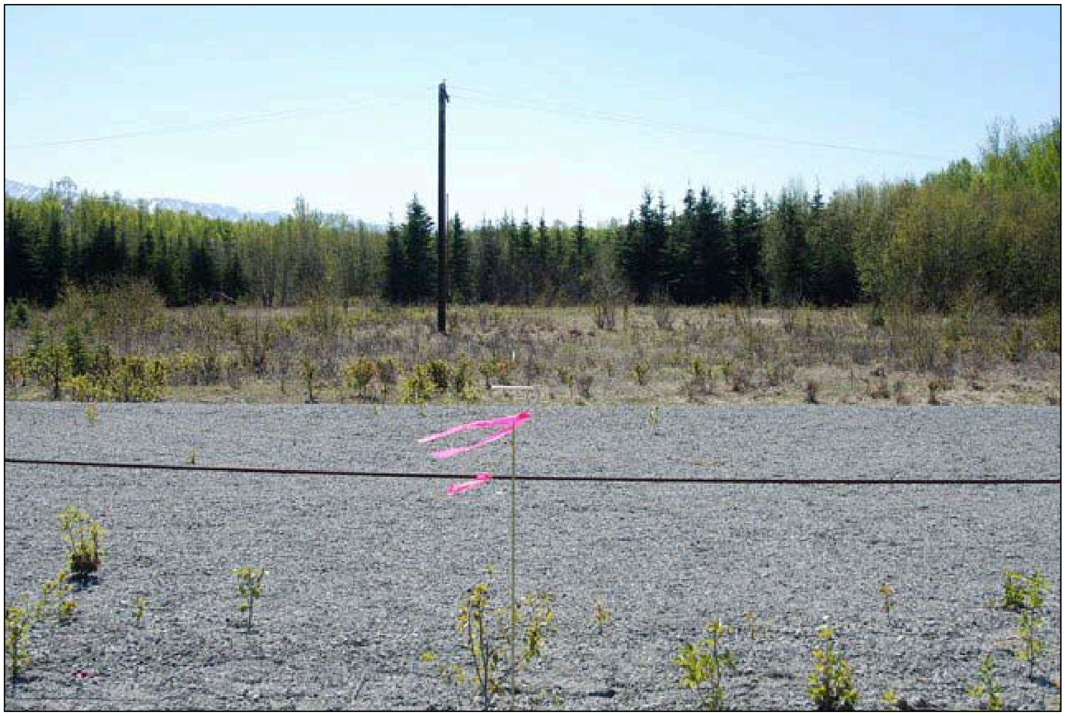


Figure 2-2. Backblast area in May 2009 prior to sampling.

2.7 Munitions tested

The munitions tested were M136 AT4 shoulder-fired rockets, drawn from stock at Fort Richardson ammunition supply point by soldiers of the 716th Explosive Ordnance Disposal (EOD) detachment (Table 2-1). Each weapon system consisted of a launcher and an 84-mm high-explosive anti-tank (HEAT) round. The round contained 355 g of AKB 204 propellant configured in 200 strips 15-mm thick by 167-mm long. The propellant is double-base, with a nominal composition of 61% nitrocellulose (NC), 37.5% nitroglycerin (NG), and 1.5% ethyl centralite (EC), a stabilizer and waterproofing agent. (Appendix 2-A contains complete munitions data for this test.)

Table 2-1. Propellant constituent for munition used during firing point test.

Weapon	Munition (Mil / DODIC)	Propellant	Constituent	Constituent Load (g / % of total load)
AT4 Shoulder-fired Rocket	M136 / C995 (HEAT)*	AKB 204	NG	133 / 37.5%
*HEAT: high-explosive anti-tank warhead				

2.8 Rocket firing test

Rocket firing was conducted the morning of 16 March 2009. As previously stated, we were assisted by soldiers of the 716th EOD detachment. Range access was granted for the full day by the U.S. Army Alaska Range Office.

Prior to the firing, a background snow sample was collected from the backblast area behind the designated FP. (A detailed description of the sampling method is in the following section of this chapter.)

Traffic around the firing points was kept to a minimum and restricted to established paths. The snow berm surrounding the parking area was utilized to minimize the effect of the backblast on the sampling surface by elevating the firing position above most of the surrounding snow surface (Figure 2-3). The weapons were fired when the wind slacked to minimize dispersion of the propellant residues.

We were unable to follow our original intent to sample downrange all the way to the target, because of evidence of unauthorized use of the target by 40-mm grenade gunners. This prohibited traveling downrange beyond a few meters of the parking area, as the snow cover could mask prior activities and rendered this part of the task unsafe.

Following the firing of the rockets, decision units (DUs) were set up for sampling. A total of eight DUs were demarcated, three behind the firing position and five downrange (Figure 2-4). The plume areas were demarcated by packing a path through the snow around the extent of propellant residues visible on the snow surface, a procedure known as visual demarcation. The outside-the-plume (OTP) sampled areas were 0-3 and 3-6 m from the plume periphery. Where the front and back plume met, the OTP annuli were truncated. Two 3- × 10-m transects were located 40- and 50-m downrange from the firing position. The plumes and transects were recorded using a Trimble GPS Pathfinder Pro XR system (±1-m) supplemented with hand measurements taken with a tape. Areas of the DUs are given in Table 2-2.

Figure 2-3. AT4 Firing position on snow berm.

Table 2-2. Decision unit areas – March 2009.

Decision Unit	Area (m³)
Back Plume – Plume	410
Back Plume – 0-3 m OTP*	250
Back Plume – 3-6 m OTP	270
Front Plume – Plume	390
Front Plume – 0-3 m OTP	240
Front Plume – 3-6 m OTP	260
Downrange Transect FPT-1	27
Downrange Transect FPT-2	25

*OTP: Outside the plume – An annular area outside the demarcated plume

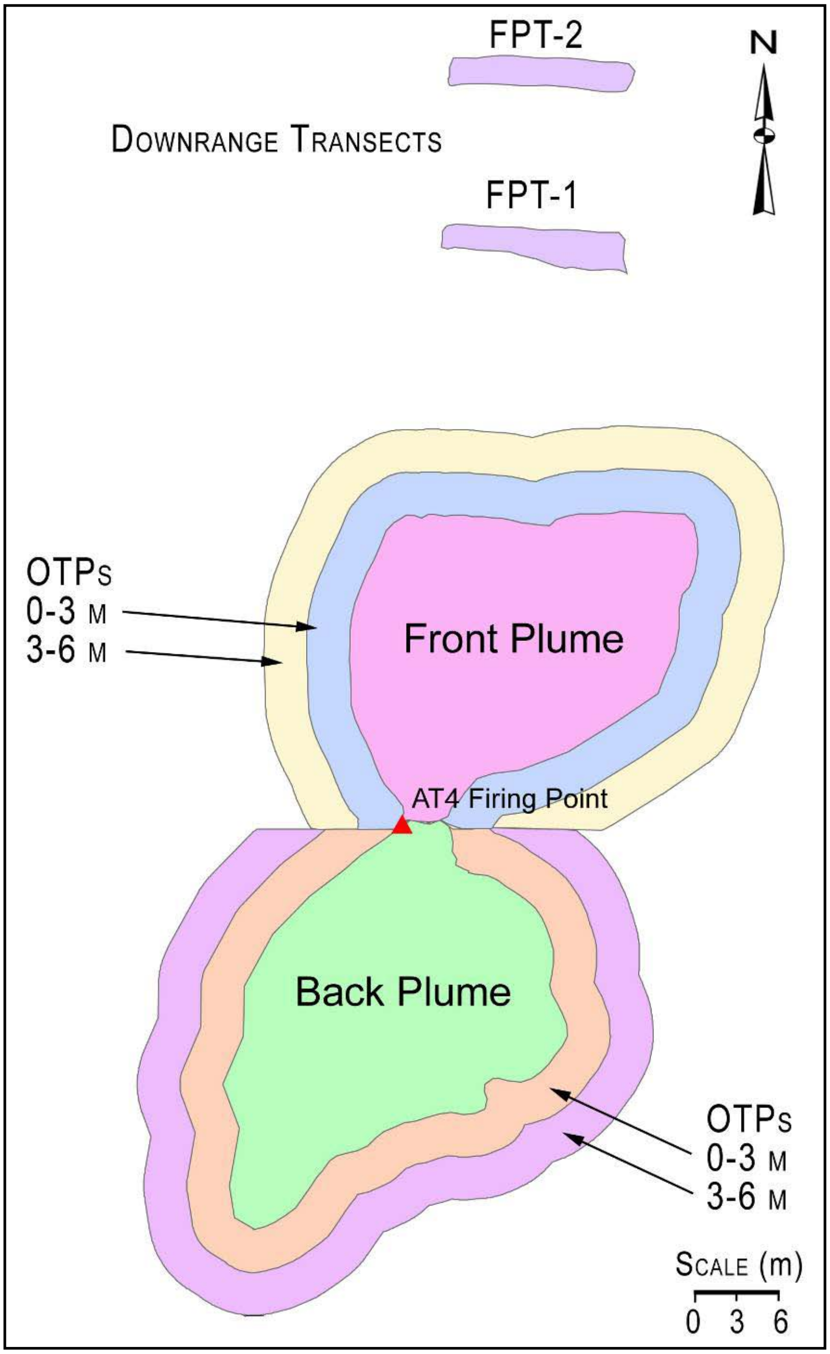


Figure 2-4. Sampling decision units for AT4 test – March 2009.

Follow-up sampling was conducted in May 2009. A 30 × 30 m DU was created in the back plume region behind the AT4 firing position (Figure 2-5). A set of three systematic-random multi-increment samples were taken from this area to determine residue loads. Because no background samples of the soils in the area were taken prior to our test in March, this sampling will characterize the site rather than give us rigorous depositional information.

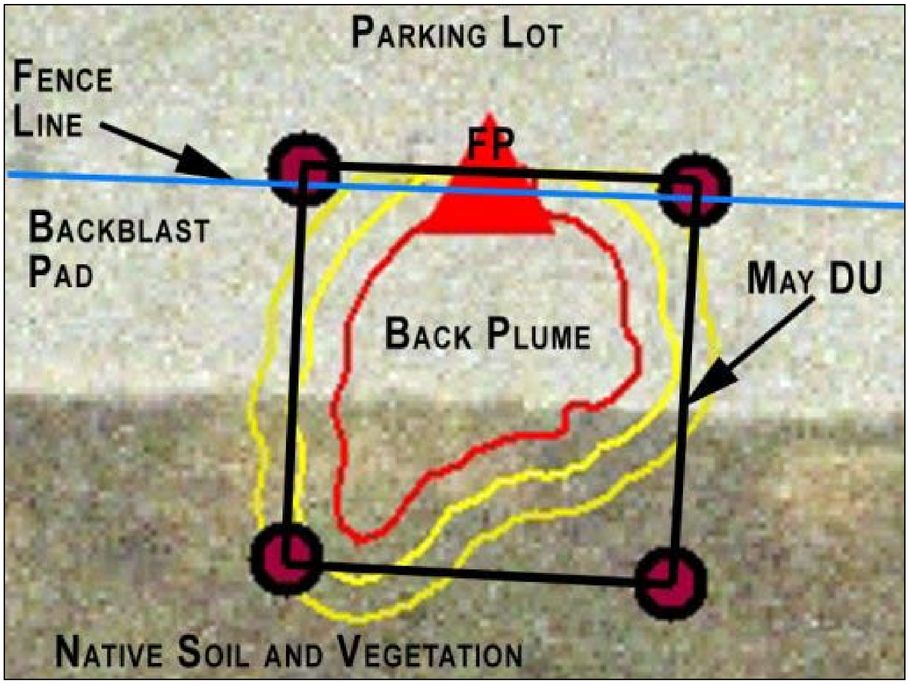


Figure 2-5. May 2009 decision unit (DU) superimposed over March DUs (red and yellow outlines).

2.9 Sampling method

The March sampling was done on a fresh snow surface following the multi-increment sampling (MIS) protocol established by M.R. Walsh, et al. (2007b). Briefly, 30 to 100 increments of surface snow were collected with a 10 × 10-cm scoop, to a depth of 2.5 cm, to make up a single sample within a DU (inside the demarcated plume, outside the plume, within transects, etc.), until the area is representatively sampled. The increments for a given sample are collected in a single clean polyethylene bag to make up the MIS. MIS allowed us to test and compensate for uncertainty derived from the small total area collected from within each decision unit, typically less than 1 m^2.

To estimate the depositional mass of energetic residues, we needed to know the area over which the energetic material is deposited and the average concentration for that area. A critical assumption is that the visible plume represents the major area of deposition. The plume is composed of deflagration products, and its depositional pattern will be affected by wind. However, because there is no other way to estimate the area of deposition, we assume that most residues are deposited within the plume. This assumption was tested by taking multi-increment samples from concentric annuli outside the demarcated plume. The objective of OTP sampling is to determine how much, if any, of the unconsumed energetics are measurable outside of the plume. Replicate samples were obtained for the two 3 m annuli for both the front and back plumes. The 10 × 10-cm scoops were used to a depth of 2.5 cm for each increment.

Subsurface samples were also taken to estimate how much residue was missed by sampling only the top 2.5 cm of snow. A sample increment was first taken with a 20 × 20-cm scoop. From the center of the sampled area, a 2.5-cm deep sample was taken with a 15 × 15-cm scoop, thus obtaining a "subsurface" sample. These subsurface increments were deposited into a clean bag as a separate sample.

In the spring, soil samples were taken from the backblast area behind the AT4 firing position. Systematic-random MIS was used to characterize the site (M.E. Walsh 2005; Jenkins et al. 2005). The 30 × 30-m decision unit was broken down into ten 3-m wide lanes. The location of the starting point was randomly selected for each of the three samples from within the first 3 × 3-m "cell" and an increment systematically taken in each of the remaining 99 cells based on the starting increment location. The area consisted of two types of soils, so two different sampling tools were used. On the gravel pad directly behind the firing position, #2 stainless steel scoops (AMS #428.02) were used to collect unconsolidated material from an area approximately 3 × 3-cm to a depth of 2 cm. In the area containing cohesive soils, a 3-cm CRREL multi-increment sampling tool was used to collect 3-cm diameter by 2.5-cm deep cores (Figure 2-6). Both types of increments were deposited in the same bag to construct a sample.

Figure 2-6. Sampling backblast area in May 2009.

2.10 Propellant segment samples

Following the cessation of firing in March, a few large segments (≈1 cm long) of what appeared to be propellant strips on the snow surface in the backblast area were collected for analysis. Several small segments were also collected from the snow surface and stored in a refrigerator at the field lab for later chemical and optical analysis as well as for future dissolution tests. A snow sample that contained a large amount of propellant debris was collected from the back plume area (Figure 2-7), specially packed for transport, and sent for further analysis and study at the analytical laboratory in Hanover (CRREL). Meanwhile, at the field laboratory on Fort Richardson, one of the large segments was dried and tested with an Expray kit (Plexus Scientific, Alexandria, VA) for NG.

Figure 2-7. Propellant debris on snow in back plume following rocket firing. Edge of scoop is 10 cm long.

In May, a cursory visual search of the backblast area near the firing point was conducted to collect propellant previously present on the snow surface after the winter firing. Most of the debris observed in the winter was <0.5 cm, small enough to fall between the cobbles on the gravel backblast pad immediately behind the firing position. However, two large (>1 cm) segments were found after a brief search and placed in plastic bags for the dissolution study and chemical analysis at CRREL's analytical laboratory.

2.11 Sample processing and analysis

2.11.1 Snow samples

The samples of snow were transferred to a laboratory at the Fort Richardson cantonment area for processing. Upon arrival, the samples were transferred from the field bags to clean bags, double-bagged, and placed in clean polyethylene tubs for thawing. Placing the samples in clean bags reduces the chances of cross-contamination from contact with adjoining bags and residues on the exterior of the sample bags. Double-bagging and the tubs were necessary because of the inclusion of sharp pieces of debris collected with the snow samples. Otherwise, gravel particles or plant stems could pierce the sample bags, allowing the thawed sample to leak.

Samples were shifted from warmer to cooler areas of the lab's logistics bay to prevent over-warming (temperatures >10 °C) after melting. The samples were then processed based on completion of melting and the sampled area they were taken from. Samples anticipated to have the least residues were processed first and those anticipated to be more contaminated were done last to reduce the possibility of cross-contamination.

Processing involved filtering the melted samples using a vacuum system to separate the particle (solids) fraction from the aqueous fraction (Figure 2-8). The particle fraction was collected on filter papers (Whatman glass microfiber 90 mm ∅ grade GF/A). Following filtering, the papers were placed in a clean amber jar, dried, and stored in a refrigerator at <5°C. The aqueous fraction was recorded prior to mixing and decanting of two or four 500-mL aliquots into glass amber bottles. (Two bottles were the normal number collected for analysis; four were collected for a laboratory quality assurance procedure.)

Figure 2-8. Snow sample filtration setup at the CRREL analytical laboratory.

One (or three) 500-mL aliquot of the filtrate was pre-concentrated by passing it through a Waters Porpak RDX (Sep-Pak, 6-cm^3, 500-mg) solid-phase extraction (SPE) cartridge and eluted with 5 mL of acetonitrile (AcN), resulting in a 100:1 concentration of the analytes (Walsh and Ranney 1998). The concentrate was split into two aliquots, 3.5 mL for analysis and 1.5 mL for archiving. When processing was completed, the 3.5-mL splits and the filters were shipped to CRREL's analytical chemistry laboratory in Hanover, NH, for final processing and analysis.

The filters containing the solids were extracted after shaking for 18 hours using AcN. The AcN extracts from the solid phase extraction of the melted snow and of the solid residue on the filters were analyzed by high-performance liquid chromatography (HPLC). Analyte concentrations were determined following the general procedures of SW 846 Method 8330B to determine nitroaromatics, nitrate esters, and nitramines by HPLC (USEPA 2006). The HPLC method has an analytical error that is very small, about 2% relative standard deviation (RSD) for replicate injections.

To prepare for the HPLC analysis, 1 mL of each AcN extract was mixed with 3 mL of reagent-grade water. Determinations were made on a modular system from Thermo Electron Corporation (Waltham, MA) composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength ultraviolet/visible absorbance detector set at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15 cm × 3.9 mm (4 µm) NovaPak C_8 column (Waters Chromatography Division, Milford, MA) at 28 °C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference materials were 8095 Calibration Mix A (1 mg/mL) and a single-component solution of NG (1 mg/mL). A spike solution at 1 mg/L was prepared from 8095A Calibration Mix and the single-component solution of NG. Spiked water samples at 0.002 mg/L were prepared by mixing 1.0 mL of the spike solution to 500 mL of water in a volumetric flask. Following SPE, the extract target concentration was 0.20 mg/L for each analyte.

To calculate the mass of unreacted energetics deposited on the snow, we calculated the mass of the samples (mg) by multiplying the extract concentration (mg/L) by the volume of AcN (L) for the extraction (soot fraction) or the volume (L) of water from the snowmelt (aqueous fraction). These masses were then divided by the actual area sampled with the scoops (m^2) to get a surface concentration in mg/m^2. This value was multiplied by the measured area of the DU to derive our estimates of the mass within the area sampled (mg) (Jenkins et al. 2002; Hewitt et al. 2003). For the HPLC, the detection limit was 0.05 mg/L for NG in the AcN extract. Values below this limit are labeled as “ND” in the data, indicating “no detectable” analyte.

2.11.2 Soil samples

Soil samples were double-bagged and shipped to CRREL’s analytical laboratory for processing and analysis. The samples were opened and spread out to dry on aluminum foil covered trays to dry at room temperature. The dried material was then sieved under a hood with a #10 sieve to separate out the <2-mm fines from the larger material. The fines were ground using a Lab-Tech Essa LM-2 puck mill equipped with a B800-mm metal bowl, processing 500 g of material or less for five 60-second grinds with a 2-min minimum cool-down time between grinds. The ground material (< 75 µm) was then spread in a 1 cm layer over clean aluminum foil and 30 increments taken by spatula using MIS to obtain a 10-g subsample, which was placed in a 2-oz. wide-mouth jar. AcN was added to the subsample and the jar agitated for 18 hrs on a shaker. Prior to analysis, 1.0 mL of extract was mixed with 3.0 mL of MilliQ water and filtered. The HPLC separations were achieved using a 15 cm × 3.9 mm (4µm) NovaPak C_8 (Waters Millipore) column eluted with 1.4 mL/min 15:85 isoproponol:water at 28 °C. The oversize fraction (>2 mm) was processed using whole-sample extraction with AcN. Detection was by ultra-violet (UV) light at 210 nm for NG.

2.11.3 Propellant samples

After collecting the debris samples from behind the firing position in March, the propellant segments were tested at our field laboratory for the presence of NG using an Expray kit. A large segment of debris was placed on a filter paper and sprayed with reagent to indicate the presence of NG. The resultant red coloration indicated a high content of NG within the larger debris (Figure 2-9). The remaining discrete debris pieces, as well as the debris contained in the snow sample collected for later analysis, were assumed to be unburned propellant particles worthy of further analysis and testing at CRREL’s analytical laboratory. The remaining particle samples were left in sealed jars and stored on site in a refrigerator, and the snow sample was stored in a chest freezer pending later analyses.

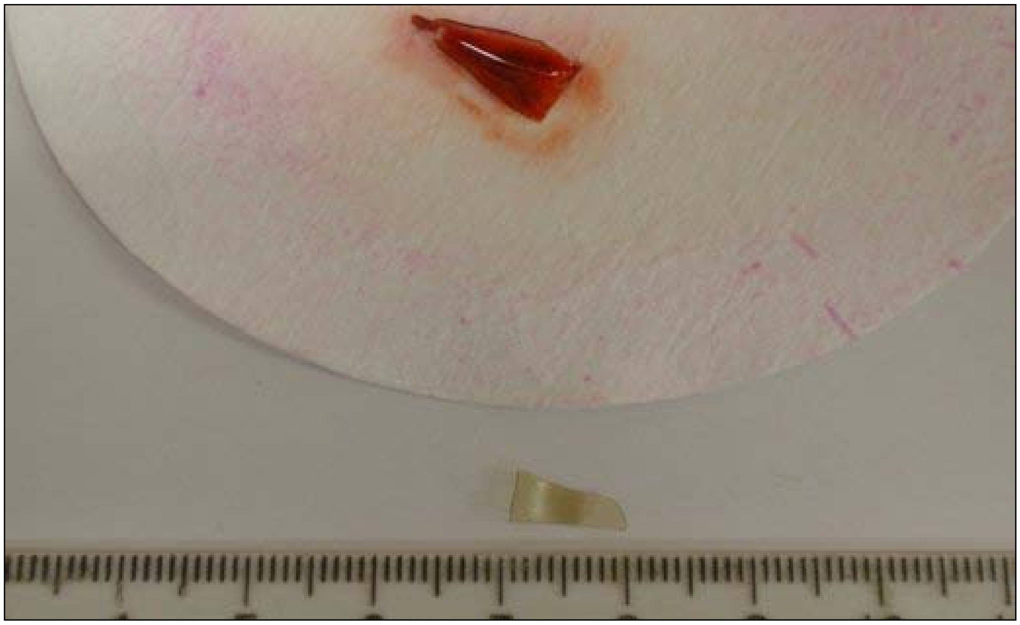


Figure 2-9. Pieces of propellant found in backblast area following firing. The top segment was sprayed with Expray reagent (Red = NG) – March 2009.

At CRREL's analytical lab, the large propellant pieces collected in March and May were photographed (Appendix 2-D). The small snow sample was placed in a filtration unit and the melting snow was filtered through a glass fiber filter using a vacuum filtration system (Section 2.11.1) to separate the propellant debris from the melted snow (Figure 2-10). The aqueous volume was measured and stored for later analysis. The solids were air-dried for another study related to this research. The two weathered pieces collected in May, seven of the larger pieces collected in March, and the aqueous fraction from the stored snow sample were all analyzed using the HPLC setup and procedure described above.

Figure 2-10. Setup at CRREL's laboratory for filtering propellant debris from March snow sample.

2.12 Quality control procedures

Quality control (QC) procedures were conducted both in the field and in the laboratory. Field QC, noted previously, included replicate sampling within the residue plumes, sampling outside the demarcated plumes, and sampling beneath the sampling points in the back plume for one sample. In the processing laboratory, blank samples consisting of filtered water from a reagent water filtration system were periodically run through a filter assembly and SPE setup for later analysis at the laboratory. This procedure was designed to determine whether cross-contamination from the sample filtering apparatus was occurring. Water fractions for several samples were divided into three aliquots and run through the SPE to determine whether recovery rates from the SPE procedure were consistent. SPE spikes were run to determine cartridge filter retention and recovery. These processes are described in greater detail in Walsh (2007). One background sample was taken in March to determine the concentration of the analyte in the areas to be sampled prior to the test.

2.13 Results

The background sample collected from the downrange FP area prior to firing contained no detectable nitroglycerin, indicating a clean test area.

2.14 Deposition rate

A total of 21 multi-increment samples, composed of 1,035 increments over a combined area of 1,872 m^2 in eight DUs, were taken to determine the deposition and distribution of NG from the firing of six rockets. The winter DUs ranged from 25 m^2 for the downrange transect FPT-2 to over 400 m^2 for the backblast plume. The large back plume is the result of the open-ended recoilless design of the shoulder-fired rocket. The propellant is mostly burned prior to the projectile leaving the launch tube; thus, much of the gas and residues are directed behind the firing position. A test area map from GPS data was shown (Figure 2-4).

Analytical data averaged for the replicate samples are given below in Table 2-3. The largest estimated average mass of NG residues was within the backblast plume, and the remaining areas contained less than an order of magnitude of additional residues. In the backblast area, the subsurface and OTP masses were not significant. For the downrange area, the OTPs were significant, but the transects were not.

Table 2-3. NG Residue mass for test decision units.

Decision Unit	DU Area (m^2)	Sampled Area (m^2)	Replicates	Est. Average Mass NG (mg)
Backblast Areas				
Back Plume	410	1.0 (0.24%)	4	530,000
Plume subsurface	410	0.70 (0.17%)	1	1,200
OTP 0-3 m	250	0.39 (0.16%)	2	1,300
OTP 3-6 m	270	0.46 (0.17%)	2	360
Downrange Areas				
Front Plume	390	0.50 (0.12%)	3	34,000
OTP 0-3 m	240	0.40 (0.17%)	2	3,800
OTP 3-6 m	260	0.40 (0.15%)	2	2,100
Transect FPT-1	27	0.38 (1.4%)	2	0.19
Transect FPT-2	25	0.40 (1.6%)	2	–ND–

An analysis of these results is given in Table 2-4. The results were composited as meta-decision units (MDUs) for comparison. For the first MDU, the surface mass of the back plume is 530,000 mg. This constitutes 99% of the NG mass in the backblast area MDU and 92% of the total mass over all DUs. There are 88 g of NG per round in the back plume, which is 67% of the original NG load for each round. The subsurface sample taken in the back plume indicates that 1,200 mg of NG lies beneath the sampled depth of the plume. This constitutes 0.23% of the total mass for MDU #1 and also of the plume, and 0.21% of the NG mass for the whole test. The contribution to the deposition rate is only 0.2 grams/round (g/rnd) or 0.15% of the total NG residue mass per round. Downrange, the 0–3 m OTP had a total estimated mass of 3,800 mg NG, constituting 9.5% of the total for the MDU, 11% of the mass of the front (downrange) plume, and 0.7% of the mass for the whole test. This contributes 0.63 g/rnd or 0.41% to the total deposition rate. Although significant for the downrange MDU, its contribution is not significant to the overall deposition rate estimate. The downrange transects contribute very little to the totals; they are not significant on a per-round basis and likely not significant overall.

Table 2-4. Contributional analysis of the results.

Meta DU (MDU)	Decision Unit (DU)	Est. Avg. NG Mass (mg)	Mass for MDU (mg)	For MDU Only	As a % of the MDU Plume	As a % for Whole Test	Deposition Rate	
							(g /rnd)	(%)
	Background	——						
MDU #1								
Backblast	Plume B/S	530, 000		99%	——	92%	88	67%
	Plume B/U	1,200		0.23%	0.23%	0.21%	0.20	0.15%
	OTP B: 0-3 m	1,300		0.25%	0.25%	0.24%	0.22	0.17%
	OTP B: 3-6 m	360		0.07%	0.07%	0.06%	0.060	0.05%
	Total: Backblast		**530,000**			**93%**	88	**67%**
MDU #2								
Downrange	Plume D/S	34,000		85%	–	6.0%	5.6	4.3%
	OTP D: 0-3 m	3,800		9.5%	11%	0.7%	0.63	0.48%
	OTP D: 3-6 m	2,100		5.4%	6.3%	0.4%	0.36	0.27%
	Total: Downrange		**40,000**			**7.0%**	6.6	**5.0%**
MDU #3								
Transects	FPT-1	0.19				0.000034%	<0.001	<0.01%
	FPT-2	-ND-				0.00%	0.00	<0.01%
	Total: Transects		**0.19**			**0.000034%**	<0.001	**<0.01%**
Totals	**All Plumes**	**560,000**			**99%**		**93**	**71%**
	All DUs	**570,000**			——		**95**	**73%**

Overall, MDU #1 (the backblast area) contained 93% of all the NG residues, amounting to a little over 88 g/round or 67% of the initial NG load of the round. Downrange, MDU #2 contained 7% of the NG residues or 6.6 g/rnd, 5.0% of the rocket's initial NG load. This totals 95 g or 73% of the original NG load for each rocket. This total is an order of magnitude higher deposition rate than we have seen for the scores of tests conducted over the last 10 years on various weapon systems.

To verify the validity of these numbers, we looked at the mass of the solids material recovered from the melted snow samples. The backblast area contained 93% of the NG residues so we will examine that data. The solids portion of the samples contained over 96% of the recovered NG (see Appendix 2-B). The mass of solids residues on the filters averaged 4.72 g for the four surface samples (Table 2-5). Using the mean NG content of the propellant (36.5%), the average theoretical NG content of the solid mass should be 1.72 g. The average recovered is 1.31 g. This is 76% of the expected mass of NG in the residues, if we assume that all the residues are raw propellant. From an examination of the material on the filters based on color and geometry of the particles, we estimated about 80% of the material was unburned propellant (Figure 2-11). Using this estimate, we get an average 95% agreement between what the analyses determined and what the filter mass indicates.

Table 2-5. NG mass estimate for filter residues prior to processing and analysis.

Sample	Solid Residue on Filter (g)	Theoretical NG on Filter (36.5% NG)	Estimated NG on Filter (g)	Agreement Est. : 36.5%	Agreement: Assume Solids 80% Propellant
Back Plume 1	5.25	1.92	1.37	71%	91%
Back Plume 2	4.62	1.69	1.29	76%	95%
Back Plume 3	4.98	1.82	1.41	77%	97%
Back Plume 4	4.01	1.47	1.16	79%	99%
Average:	**4.72**	**1.72**	**1.31**	**76%**	**95%**

Figure 2-11. Filtered mass from back plume sample. Beige material is propellant. Filter paper is 90 mm in diameter.

2.15 May site characterization

Three multi-increment, surface soil samples (2.5 cm deep) were collected from within the backblast area in May 2009, two months after the firing test. The DU encompassed the entire back plume and the first OTP (0–3 m) as well as significant portions of the 3–6 m OTP area (Figure 2-4). The overall area of the May DU was 900 m^2. The three MIS were composed of 100, 100, and 101 increments. The average concentration of NG in the samples was 13 µg/g (Appendix 2-C). The estimated mean mass in the 30 × 30 m^2 DU was 250 g. If all the residues present in the DU are from the winter firing, the average mass of NG per round is 42 g/rnd, or 48% of the estimated mass in the area from the winter firing. No baseline sample was taken from the soil in the backblast area in the fall prior to our tests, so it is unknown what the NG levels were prior to our test.

2.16 Analysis of propellant segments

Analyses of the propellant debris collected in March and May confirmed the qualitative indication (given by the Expray test) that the material on the snow surface was mostly raw propellant. The five “fresh” particles collected from the snow surface immediately after the test in March contained on average 99% of the expected amount of NG for an unburned piece of AKB 204 propellant with a nominal NG content of 36.5% (95% if the NG content is 38%). This agrees with the results depicted in Table 2-5 for 36.5% NG propellant content. The "weathered" particles collected 61 days later in May contain 66% of the NG load for 36.5% content (Table 2-6). This is an approximate 33% loss of NG over the time period.

Table 2-6. Results of unburned propellant analyses.

Date Collected	ID	Propellant Mass (mg)	Nominal (36.5%) NG Mass (mg)	Mass of NG Detected (mg)	Recovery
18-May-09	Weathered 1	46	17	11	65%
18-May-09	Weathered 2	36	13	8.6	66%
Average					66%
16-Mar-09	Fresh 1	16	5.8	5.9	102%
16-Mar-09	Fresh 2	10	3.8	3.7	97%
16-Mar-09	Fresh 3	11	4.1	4.0	98%
16-Mar-09	Fresh 4	13	4.7	4.6	98%
16-Mar-09	Fresh 6	71	26	26	100%
Average					99%

2.17 Discussion

As mentioned earlier, the deposition rate of energetic residues for the AT4 was significantly higher than that found for any other weapon system we have tested. Table 2-7 summarizes the results of testing we have done with mortars, howitzers, a tank, and small arms. Those results are then compared to the AT4 results presented here and to results from the M72 LAW and Carl Gustav rockets tested by DRDC in Canada. The results are generalized to the propellant constituents of concern, NG and DNT.

Table 2-7. Comparison of various firing point residues loads.

Weapon System	Propellant	Analyte	Load/ Rnd (g)	Residues/ Round (mg)	Residues/ Load
Howitzers					
105-mm	M1-I & II	DNT	42	34	8 x 10^{-2} %
155-mm	M1	DNT	275	1.2	5 x 10^{-4} %
Mortars					
81-mm	M9	NG	30	1,000	3.5%
120-mm	M45	NG	26	350	1.4%
Leopard Tank[2]					
105-mm (MIS)	M1	DNT	300	6.7	2.2x10^{-3}%
105-mm (Trays)	M1	DNT	300	7.8	2.7x10^{-3}%
Small Arms					
5.56-mm Rifle	WC844	NG	0.16	1.8	1.10%
5.56-mm MG[1]	WC844	NG	0.16	1.3	0.79%
7.62-mm MG	WC846	NG, DNT	0.27	1.5	0.56%
9-mm Pistol	WPR289	NG	0.040	2.1	5.44%
12.7-mm MG[1]	WC860 & WC857	NG	1.5	11.	0.73%
Shoulder-fired Rockets					
84-mm Carl Gustav[3]	AKB 204	NG	140	20,000	14%
66-mm LAW[4]	M7	NG	22	42	0.1%
84-mm AT4	AKB 204	NG	130	95,000	73%

[1] Averages loads and residues from ball and tracer rounds in linked ammunition.

[2] Preliminary results. (Ampleman et al. in prep)

[3] Thiboutot et al. (2008a)

[4] Thiboutot et al. (2008b)

In the past, we have found weapon systems with longer barrels, rifled barrels, or larger propellant loads generally have a lower percentage of their propellant deposited as residues. This is likely due to the higher temperatures and pressures generated in these types of armaments. By contrast, a recoilless design such as the shoulder-fired rockets has a short, non-rifled, open-ended design, meaning pressures and temperatures can only build up within the rocket motor.

It is interesting to note that for the DRDC's tests of the M72 LAW rocket, the residue-per-round deposition rate is two orders of magnitude lower than for the AT4. The M7 propellant of the LAW rocket contains up to 8% ammonium perchlorate, a strong oxidizing agent. The propellant is obviously burning much more efficiently than propellant used with the AT4 which contains no oxidizing agent. A strong oxidizer may be required for efficient propellant consumption in a recoilless weapon design. There may be some problems associated with this inefficient burning process such as unreliability and the failure to hit a target.

Looking at results from the May sampling, the estimated mass in the DU is about half what we found directly after firing the rockets. The two large segments recovered in May had lost 33% of the NG they originally contained. Smaller propellant particles are likely to more readily leach NG as compared to larger particles, especially for unburned particles, because the smaller particle's surface area-to-mass ratio is higher. The majority of the residues were smaller particles; thus, the diffusion of NG from the estimated mass in May is likely higher on average than reflected in the 33% value obtained for the larger segment and the 52% reduction in NG over the backblast area is plausible. It is important to note that we did not take a baseline sample of the test location area prior to snowfall, so we are uncertain if NG was present on the soil below the snow cover prior to our test.

2.18 Conclusions

Training with the AT4 shoulder-fired rockets will result in significant deposition and accumulation of nitroglycerin residues behind the firing position. Our tests indicated that more than 70% of the propellant is not consumed during operation of the weapon. On AT4 ranges with fixed firing positions, the propellant residues may build up to hazardous levels, an issue that will have to be addressed by range managers. Furthermore, leaching of NG from the unburned propellant may cause a groundwater contamination problem. Developing a rocket motor that burns propellant more efficiently would result in less energetic residue mass. Additional testing of rockets in the U.S. Army arsenal is warranted based on the results of this test.

2.19 Nomenclature

AcN	acetonitrile
C4	91% RDX, 9% oil
CA	Canadian Army
Composition B	60% RDX, 39% TNT, 1% wax
CRREL	Cold Regions Research and Engineering Laboratory
DNT	dinitrotoluene (2,4-dinitrotoluene)
DoD	U.S. Department of Defense
DRDC	Defence Research and Development Canada
DU	decision units
EC	ethyl centralite
EOD	explosive ordnance disposal
EPA	Environmental Protection Agency
ER	Environmental Restoration
ERDC	Engineer Research and Development Center
FP	firing point
GPS	global positioning system
HEAT	high-explosive anti-tank
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high-performance liquid chromatography
LCS	laboratory control spike; laboratory control sample
MDU	meta-decision unit
MI	multi-increment
MIS	multi-increment sample
MMR	Massachusetts Military Reservation
MMRP	Military Munitions Response Program
MS	matrix spike
MSD	matrix spike duplicate
NC	nitrocellulose
NG	nitroglycerin
OTP	outside-the-plume

PE	polyethylene
PETN	pentaerythritol tetranitrate
QA	quality assurance
QC	quality control
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RSD	relative standard deviation
SERDP	Strategic Environmental Research and Development Program
SPE	solid-phase extraction
TNT	2,4,6-trinitrotoluene
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UXO	unexploded ordnance

2.20 References

Ampleman, G., S. Thiboutot, M.E. Walsh, M.R. Walsh, A. Gagnon, and A. Marois (in prep) *Energetic residues from the firing of a Leopard main battle tank*. Technical Report DRDC Valcartier (number pending). Val-Bélair, QC: Defence Research and Development Canada (DRDC)-Valcartier.

Brochu, S., I. Poulin, D. Faucher, E. Diaz, and M.R. Walsh. 2009. *Environmental assessment of small arms live firing: Study of gaseous and particulate residues*. Poster presentation, 237th ACS National Meeting, Salt Lake City, UT. 22-26 March 2009.

Clausen, J., J. Robb, D. Curry, and N. Korte. 2004. A case study of contaminants on a military range: Camp Edwards, MA, USA. *Environmental Pollution* 129:13-21.

Diaz, E., D. Gilbert, D. Faucher, A. Marois, and A. Gagnon. 2008. *Gun propellant residues dispersed from static artillery firings of LG1 Mark II and C3 105-mm howitzers*. Technical Report DRDC Valcartier TR 2007-282. Val-Bélair, QC: DRDC-Valcartier.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Kern. 2003. *Estimates for explosives residues from the detonation of army munitions*. ERDC/ CRREL TR-03-16. Hanover, NH: USACE Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL).

Hewitt, A.D., T.F. Jenkins, M.E. Walsh, M.R. Walsh, and S. Taylor. 2005. RDX and TNT residues from live-fire and blow-in-place detonations. *Chemosphere* 61:888-894.

Jenkins, T.J., T.A. Ranney, P.H. Miyares, N.H. Collins, and A.D. Hewitt. 2000a. *Use of surface snow sampling to estimate the quantity of explosives residues resulting from land mine detonations*. ERDC/CRREL TR-00-12. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL).

Jenkins, T.J., T.A. Ranney, M.E. Walsh, P.H. Miyares, A.D. Hewitt, and N.H. Collins. 2000b. *Evaluating the use of snow-covered ranges to estimate the explosives residues that result from detonation of army munitions*. ERDC/CRREL TR-00-15. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL).

Jenkins, T.J., M.E. Walsh, P.H. Miyares, A.D. Hewitt, N.H. Collins, and T.A. Ranney. 2002. Use of snow-covered ranges to estimate explosives residues from high-order detonations of army munitions. *Thermochimica Acta*, 384: 173–185.

Jenkins, T.J., A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, and K.L. Bjella. 2005. Representative sampling for energetic compounds at military training ranges. *Environmental Forensics* 6: 25–55.

Jenkins, T.J., A.D. Hewitt, C.L. Grant, S. Thiboutot, G. Ampleman, M.E. Walsh, T.A. Ranney, C.C. Ramsey, A.J. Palazzo, and J.C. Pennington. 2006. Identity and distribution of residues of energetic compounds at army live-fire training ranges. *Chemosphere* 63:1280-1290.

Jenkins, T.J., A.D. Hewitt, S.R. Bigl, S. Taylor, D.J. Lambert, D.K. MacMillan, J.L. Clausen, and N.M. Perron. 2007. Sampling of various types of firing point areas for propellant residues at several military reservations. Chapter 3 in T.F. Jenkins et al. *Characterization and fate of gun and rocket propellant residues on testing and training ranges: Interim Report 1*. ERDC Technical Report TR-07-1. Vicksburg, MS: USACE Engineer Research and Development Center (ERDC). Available at: http://libweb.wes.army.mil/uhtbin/hyperion/ERDC-TR-07-1.pdf (accessed Oct. 2009).

Racine, C.H., M.E. Walsh, C.M. Collins, D.J. Calkins, B.D. Roebuck, and L. Reitsma. 1992. *Waterfowl mortality in Eagle River Flats, Alaska: The role of munitions residues*. CRREL Report 92-5. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL).

Thiboutot, S., G. Ampleman, A. Gagnon. A. Marois, T.F. Jenkins, M.E. Walsh, P.G. Thorne, and T.A. Ranney. 1998. *Characterization of antitank firing ranges at CFB Valcartier*. WATC Wainwright, and CFAD Dundurn. DREV-R-9809. Val-Bélair, QC: DRDC-Valcartier.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of gun propellant residues from 84-mm Carl Gustav rocket firing*. DRDC Valcartier TR 2007-408, Unclassified. Valcartier, Quebec, Canada: Defence Research and Development Canada.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon. D. Gilbert, V. Tanguay, and I. Poulin. 2008a. Energetic residues deposition from 84-mm Carl Gustav antitank live-firing. In *Characterization and fate of gun and rocket propellant residues on testing and training ranges: Final report*. T.F. Jenkins and S.R. Bigl, eds. Technical Report ERDC TR-08-1. Vicksburg, MS: USACE Engineer Research and Development Center. Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/ERDC-TR-08-1.pdf.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, and D. Gilbert. 2008b. Deposition of nitroglycerin from the live firing of M72 A5 66-mm rockets. In *Proceedings of the 2008 SERDP & ESCP Partners in Environmental Technology Technical Symposium and Workshop*, Washington, DC, 2-4 December 2008.

U.S. Army. 1994. *Army ammunition data sheets: Artillery ammunition (FSC 1310, 1315, 1320, 1390)*. Technical Manual TM 43-0001-28. Washington, DC: U.S. Government Printing Office.

U.S. Environmental Protection Agency (USEPA). 2006. Nitroaromatics, nitroamines, and nitrate esters by HPLC. SW846 Method 8330B Washington, DC: USEPA Office of Solid Waste. Revision 2, October 2006. Available at (accessed Oct. 2009): www.epa.gov/epawaste/hazard/testmethods/pdfs/8330b.pdf .

Walsh, M.E., and T.A. Ranney. 1998. *Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and GC-ECD*. USA CRREL Special Report 98-2. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL).

Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney. 2001. *Sampling for explosives residues at Fort Greely, Alaska*. ERDC/CRREL Technical Report TR-01-15. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-01-15.pdf.

Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A.B. Gelvin, T.A. Douglas, N. Perron, D.J. Lambert, R.N. Bailey, and K. Meyers. 2004. *Range characterization studies at Donnelly Training Area, Alaska: 2001 and 2002* ERDC/CRREL Technical Report TR-04-3. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-04-3.pdf.

Walsh, M.E., C.A. Ramsey, C.M. Collins, A.D. Hewitt, M.R. Walsh, K.L. Bjella, D.J. Lambert, and N.M. Perron. 2005. *Collection methods and laboratory processing of samples from Donnelly Training Area firing points, Alaska 2003*. ERDC/CRREL Technical Report TR-05-6. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-05-6.pdf.

Walsh, M.E., C.M. Collins, C.A. Ramsey, T.A. Douglas, R.N. Bailey, M.R. Walsh, A.D. Hewitt, and J.L. Clausen. 2007. *Energetic residues on Alaskan training ranges*. ERDC/CRREL Technical Report TR-07-9. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-07-9.pdf.

Walsh, M.R. 2007. *Explosives residues resulting from the detonation of common military munitions: 2002-2006*. ERDC/CRREL Technical Report TR-07-2. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at: http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-07-2.pdf (accessed Oct. 2009).

Walsh, M.R., M.E. Walsh, C.A. Ramsey, and T.F. Jenkins. 2005a. *An examination of protocols for the collection of munitions-derived explosives residues on snow-covered ice*. ERDC/CRREL Technical Report TR-05-8. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at: http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-05-8.pdf (accessed Oct. 2009).

Walsh, M.R., S. Taylor, M.E. Walsh, S.R. Bigl, K. Bjella, T.A. Douglas, A.B. Gelvin, D.J. Lambert, N.M. Perron, and S.P. Saari. 2005b. *Residues from live-fire detonations of 155-mm howitzer rounds*. ERDC/CRREL Technical Report TR-05-14. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-05-14.pdf.

Walsh, M.R., M.E. Walsh, C.M. Collins, S.P. Saari, J.E. Zufelt, A.B. Gelvin, and J.W. Hug. 2005c. *Energetic residues from live-fire detonations of 120-mm mortar rounds*. ERDC/CRREL Technical Report TR-05-15. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-05-15.pdf.

Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari. 2006. *Energetic residues deposition from 60-mm and 81-mm mortars*. ERDC/CRREL Technical Report TR-06-10. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at: http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-06-10.pdf (accessed Oct. 2009).

Walsh, M.R., M.E. Walsh, S.R. Bigl, N.M. Perron, D.J. Lambert, and A.D. Hewitt. 2007a. *Propellant residues deposition from small arms munitions*. ERDC/CRREL Technical Report TR-07-17. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-07-17.pdf.

Walsh, M.R., M.E. Walsh, and C.A. Ramsey. 2007b. *Measuring energetics residues on snow*. ERDC/CRREL Technical Report TR-07-19. Hanover, NH: USACE Engineer Research and Development Center (ERDC-CRREL). Available at (accessed Oct. 2009): http://libweb.wes.army.mil/uhtbin/hyperion/CRREL-TR-07-19.pdf.

Wingfors, H., C. Edlund, L. Hägglund, A. Waleij, J. Sjöström, R.-M. Karlsson, P. Leffler, U Qvarfort, M. Ahlberg, S. Thiboutot, G. Ampleman, R. Martel, W. Duvalois, A. Creemers, and N. van Ham. 2006. *Evaluation of the contamination by explosives and metals in soils at the Alvdalen Shooting Range – Part II: Results and discussion*. Scientific Report FOI-R-1877-SE. Stockholm, Sweden: FOI/Swedish Defence Research Agency.

Appendix 2-A: Munitions Data

Table 2-A1 contains information relevant to the munitions used during the test covered in this report. Propellant loads for the analytes of concern are given in Table 2-1.

Table 2-A1. Munitions data.

NSN	DODIC	Nomenclature	Lot No.	Drawn for tests
1315-01-245-4950	C995	Cartridge, 84 Millimeter: M136 (AT4) and Launcher	FFV89C001-045B	6

Note: Munitions were drawn from inventory, Ammunition Supply Point, Fort Richardson, AK.
Ref.: US Army (1994).

Figure 2-A1. Unexploded AT4 projectile fired in March found downrange of target.

Appendix 2-B: Analytical Results - March

Table 2-B1 contains sampling data for the test conducted on snow at the 40MM/AT4 (40/90) range at Fort Richardson on 16 March 2009. Table 2-B2 contains the results of the analyses.

Table 2-B1. AT4 firing point sampling data.

Sample	Scoop Size (cm / side)	Sample Type	# of Increments	Samplers' Initials	Filtrate Vol. (mL)	# of Filters	Notes
FRA09-01	10	**Background**	36	MRW	1,180	1	
FRA09-02	10	FPT-2	40	AG/JB	1,840	1	Rep 1
FRA09-03	10	FPT-2	40	AG/JB	1,857	1	Rep 2
FRA09-04	10	FPT-1	38	AG/JB	1,650	1	Rep 1
FRA09-05	10	FPT-1	38	AG/JB	1,710	1	Rep 2
FRA09-06	10	OTP-D:3-6	40	MRW/ST	1,590	2	Rep 1: 3-6
FRA09-07	10	OTP-D:3-6	40	MRW/ST	1,522	1	Rep 2: 3-6
FRA09-08	10	OTP-D:0-3	40	MRW/ST	1,370	1	Rep 1: 0-3
FRA09-09	10	OTP-D:0-3	40	MRW/ST	1,300	1	Rep 2: 0-3
FRA09-10	10	OTP-B:3-6	46	MRW/ST	2,030	1	Rep 1: 3-6
FRA09-11	—	**BLANK 1**	—	MRW	1,000	1	
FRA09-12	10	OTP-B:3-6	46	MRW/ST	2,045	1	Rep 2: 3-6
FRA09-13	10	OTP-B:0-3	39	MRW/ST	1,810	1	Rep 1: 0-3
FRA09-14	10	OTP-B:0-3	39	MRW/ST	1,800	1	Rep 2: 0-3
FRA09-15	**15**	Plume B/U	31	MEW/GA	2,620	1	Subsurface
FRA09-16	10	Plume D/S	50	MRW/ST	1,000	1	Rep 1
FRA09-17	10	Plume D/S	50	MRW/ST	1,015	1	Rep 2
FRA09-18	10	Plume D/S	51	MRW/ST	1,140	1	Rep 3
FRA09-19	10	Plume B/S	100	MEW/GA	4,270	1	Rep 3
FRA09-20	10	Plume B/S	100	MEW/GA	4,180	1	Rep 1
FRA09-21	10	Plume B/S	100	MEW/GA	4,635	1	Rep 2
FRA09-22	**20**	Plume B/S	31	MEW/GA	4,380	1	Rep "4"
FRA09-23	—	**BLANK 2**	—	MRW	1,000	1	
End of Samples							

Codes:
B: Backblast area behind the firing point
Background: Background sample of surface snow prior to tests;
BLANK: Blank ultra-filtered water "sample"
D: Downrange of firing point
FPT: Firing Point Transect
OTP: Outside The demarcated Plume (X-Y m)
Plume: The visually demarcated main Plume
S: Surface sample
U: Subsurface sample

Table 2-B2. Sample analytical results (NG) for AT4 firing point.

	NG Mass in Sample					NG Mass in Plume	
	Filtrate Portion			*Filter Portion*			
Sample	Total (mg/L)	Total (mg)	Calculated (mg/m^2)	Total (mg)	Calculated (mg/m^2)	Total (mg)	Average (mg)
FRA09-01	*-ND-**	—	—	*-ND-*	—	—	
FRA09-02	*-ND-*	—	—	*-ND-*	—	—	
FRA09-03	*-ND-*	—	—	*-ND-*	—	—	*-ND-*
FRA09-04	*-ND-*	—	—	0.0054	0.014	0.39	
FRA09-05	*-ND-*	—	—	*-ND-*	—	—	0.19
FRA09-06	0.02	0.029	0.071	5.8	14.6	3,800	
FRA09-07	0.02	0.024	0.060	0.69	1.7	470	2,100
FRA09-08	0.35	0.48	1.2	0.052	0.13	320	
FRA09-09	0.52	0.67	1.7	11	28	7,200	3,800
FRA09-10	0.1	0.18	0.40	0.31	0.66	290	
FRA09-11	*-ND-*	—	—	*-ND-*	—	—	
FRA09-12	0.1	0.20	0.42	0.55	1.2	440	360
FRA09-13	0.17	0.31	0.79	3.2	8.1	2,100	
FRA09-14	0.25	0.45	1.2	0.43	1.1	540	1,300
FRA09-15	0.26	0.67	1.0	1.4	2.0	1,200	1,200
FRA09-16	4.7	4.7	9.4	49	98	42,000	
FRA09-17	3.9	4.0	8.0	29	59	26,000	
FRA09-18	4.3	4.9	10	40	78	34,000	34,000
FRA09-19	12	49	49	1,400	1,400	580,000	
FRA09-20	12	50	50	1,300	1,300	540,000	
FRA09-21a	12	54	54	1,400	1,400	600,000	
-21b	13	60	60				
-21c	12	55	55				
-21 Avg.	12	56	56	1,400	1,400	600,000	570,000
FRA09-22	11	49	39	1,100	900	380,000	530,000
FRA09-23	*-ND-*	—	—	*-ND-*	—	—	

*ND: Not detected during sample analysis

Appendix 2-C: Analytical Results - May

Table 2-C1 contains the analytical results for the May 2009 samples obtained in the backblast area. The results in Table 2-C1 are for NG, the major constituent of concern recovered from the samples. The decision unit (DU) area was 30 x 30 m, or 900 m^2.

Table 2-C1. Analytical results for May 2009 backblast area samples.

	09FRA04	09FRA05	09FRA06	Mean
Sample Mass <2-mm size fraction	1,900 g	1,500 g	960 g	1,500 g
Sample Mass >2-mm size fraction	1,400 g	1,100 g	61 g	1,000 g
Total Sample Mass	3,300 g	2,700 g	1,600 g	2,500 g
NG Conc. in <2-mm fraction: Lab Rep 1	17 µg/g	13 µg/g	9.0 µg/g	13 µg/g
NG Conc. in <2-mm fraction: Lab Rep 2	16 µg/g	12 µg/g	10 µg/g	13 µg/g
NG Conc. in <2-mm fraction: Mean of Reps	16 µg/g	12 µg/g	9.0 µg/g	13 µg/g
NG Conc. in >2-mm fraction: Mean of Reps	0.18 µg/g	0.14 µg/g	0.66 µg/g	0.33 µg/g
NG Mass Recovered in Sample: <2-mm fraction	31,000 µg	19,000 µg	9,000 µg	20,000 µg
NG Mass Recovered in Sample: >2-mm fraction	257 µg	160 µg	400 µg	270 µg
Total Mass of NG in Sample	31 mg	19 mg	94 mg	20 mg
Estimated Area Sampled	710 cm^2	710 cm^2	710 cm^2	710 cm^2
Mass / Unit Area	430 mg/m^2	270 mg/m^2	130 mg/m^2	280 mg/m^2
Estimated NG Mass in 30-m x 30-m Decision Unit	390,000 mg	240,000 mg	120,000 mg	250,000 mg

Appendix 2-D: Images of Propellant Segments

The following images were taken of segments of the AKB 204 propellant strips that fuel the AT4 rockets. These segments were recovered following the firing point test. These images were taken with a camera through a microscope. Images from March 2009 were of segments recovered directly after the firing test. The May 2009 images are of segments recovered following resampling of the area after two months. Weathering effects on the segments are obvious, with color change and leaching evident at the edges. Further electron- and photo-micrograph work by Dr. Susan Taylor of CRREL will be done with these particles as part of her SERDP project on propellants.

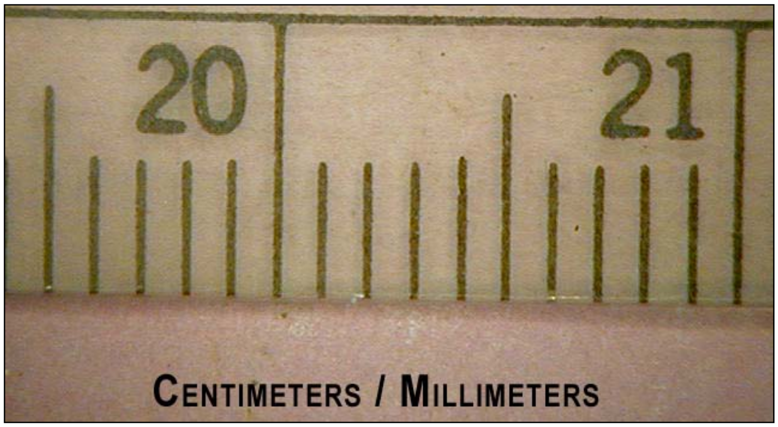
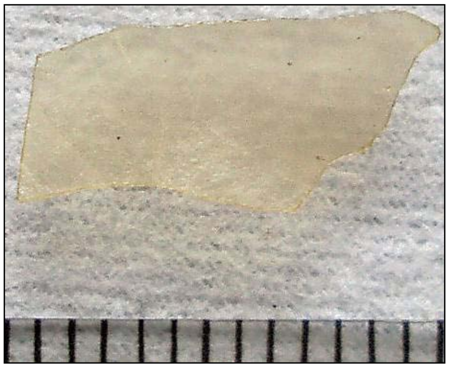


Figure 2-D1. Scale for 6x magnifications.

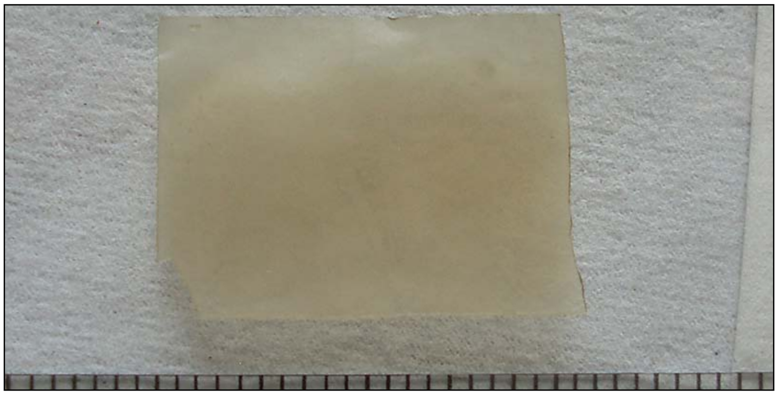
a. Propellant segment image with 6x magnification.



b. Propellant segment image taken without microscope (mm scale).

Figure 2-D2. Images of post-firing fresh propellant segment #4 collected in March 2009.

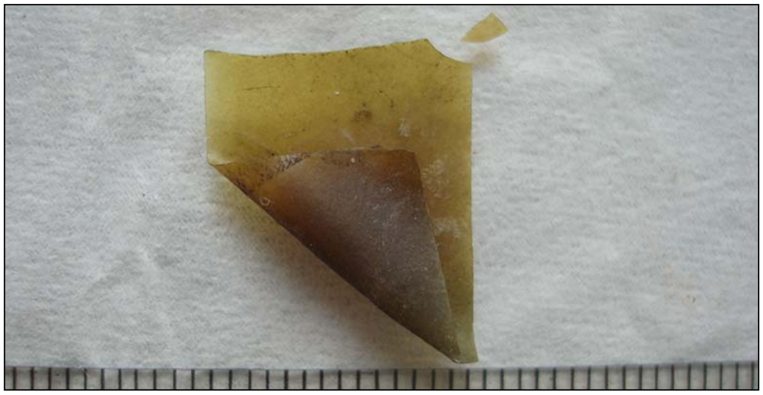
a. Propellant segment image taken with 6x magnification.



b. Propellant segment image taken without microscope (mm scale).

Figure 2-D3. Images of post-firing fresh propellant segment #6 collected in March.

a. Propellant segment image taken with 6x magnification.



b. Propellant segment image taken without microscope (mm scale).

Figure 2-D4. Images of weathered propellant segment #1 collected in May from backblast area.

a. Propellant segment image taken with 6x magnification.

b. Propellant segment image taken without microscope (mm scale).

Figure 2-D5. Images of weathered propellant segment #2 collected in May from backblast area.

3 Energetic Residues Deposition from 66-mm Antitank Rockets

Sonia Thiboutot, Guy Ampleman, André Marois, Annie Gagnon, and Denis Gilbert[*]

3.1 Abstract

The environmental impact of live-fire military training needs to be assessed to train our troops in a sustainable manner. Propellant residues have been detected around firing positions of training ranges and the source term per round has to be defined for many types of weapons. Shoulder-fired antitank weapons are used on a frequent basis, and their firing positions are contaminated by nitroglycerin (NG) residues. The deposition rate of NG from antitank live firing must be assessed. DRDC Valcartier participated in a live-firing exercise of the Royal 22e Régiment to determine the residues generated by the firing of 98 M-72 66-mm rounds. Soil samples were collected using particle traps up to 10 m in front and 30 m behind the weapons. Each round led to the deposition of 42 mg of NG (0.1 % by weight), and 92% of the residues are being deposited within the first 20 m behind the firing positions. This trial demonstrated that the burning of propellant was incomplete. In comparison, the firing of Carl Gustav 84-mm rockets leads to a dispersion rate of 14% NG by weight. Our results demonstrate that these weapons lead to the accumulation of gun propellant residues in the environment, and that the propellant formulation has a huge impact on its combustion efficiency. Other similar trials should be conducted and efforts should be dedicated to the development of better propelling charges. This work was supported by DRDC's Sustain Thrust program and the Strategic Environmental Research and Development Program (SERDP) Environmental Restoration Project 1481 follow-on.

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[*] This chapter previously published as DRDC-Valcartier TR 2009-003 (see bibliography in Chapter 10).

3.2 Introduction

Routine military training involving munitions in live-fire exercises have proven to lead to the buildup of explosives and propellant residues in the environment. Where military activities are essential to maintain troop combat readiness, it is imperative to better understand the specific impact of each type of live-firing activity, which will allow better management of these ranges to minimize adverse environmental effects and future development of a more environmentally friendly generation of weapons. This study of propellent residues will lead to recommendations for minimizing the adverse environmental or human health impact of actual weapons, without reducing the training tempo.

Numerous live-fire ranges have been characterized over the last several years [1-7]. Past studies conducted at antitank ranges demonstrated that both target impact areas and firing points (FPs) contain high concentrations of explosive and propellant residues in the soil surfaces [8, 9]. The explosive cyclotetramethylene-tetranitramine (HMX) accumulates at the target area, while high levels of NG have been detected near the FP. The delineation of FPs in training ranges has shown that propellant residues were dispersed not only in front of the firing line but behind it as well because the rear of the launcher is open to eliminate the recoil effect. In Figure 3-1, for example, firing of a Carl Gustav 84-mm shows the projections both behind and in front of the muzzle. The dispersion of HMX, which has been studied extensively in the past, is due to the high dud rate of antitank weapons. The accumulation of NG at the FP has been attributed to the projection of unburned propellants that are never completely consumed. These HMX and NG residues have the potential to contaminate the soil surfaces and the underlying groundwater.

Figure 3-1. Live firing with a shoulder antitank weapon.

A recent study of the deposition of propellant residues from the live firing of Carl Gustav 84-mm antitank rockets [10] demonstrated that as much as 20 g of NG was deposited per round, or 14% w/w. The study also showed that most of the deposition occurred behind the firing line.

M-72 66-mm antitank rockets are another antitank weapon fired frequently on Canadian antitank ranges. They are shoulder-launched and use a double-base propellant composed of NG dispersed in a nitrocellulose (NC) matrix, in which a proportion of potassium perchlorate (KP) is also dispersed. The objective of the study reported here was to examine the mass loading of propellant residue at FPs for the M-72 weapon. The pertinent information generated on the source term of propellant residues will enable further modeling studies. It will also allow the evaluation of time required for propellant residues to accumulate to levels of concern on a given site, based on the frequency of its use. The work described in this chapter was conducted in June 2008.

3.3 Experimental methods

3.3.1 Field work

The live firing was conducted at the Liri antitank range, located within the Garrison Valcartier training area, on 5-6 June 2008. The left- and right-hand sides of Figure 3-2, respectively, show an aerial view of the Liri antitank range firing point and the target impact area. This site has been in use since 1986 (22 years) by the Canadian Forces for live-fire training with antitank weapons. The range has many target tanks located in a relatively flat area approximately 3 m lower than the FP. In contrast with the Arnhem antitank range where the Carl Gustav study was conducted [10], the Liri range is highly vegetated with limited access for safety reasons. A 10-m area in front of the firing line was swept for the potential presence of unexploded ordnance (UXO) to allow for the installation of particle traps. A tree line located 35 m behind the firing line prevented the installation of particle traps any farther in that direction. The site has two launch positions (LPs) located 40 m away from each other (Figure 3-2).

Figure 3-2. Liri antitank firing range firing point (left) and target impact area (right).

The sampling effort was conducted during a training exercise of the Royal 22e Régiment under the instruction of the “Centre d’Instruction du Secteur du Québec de la Force terrestre” (CI SQFT). We collected particles ejected during the firing of 66-mm rockets using particle traps installed only at the LP located at the left-hand side of the range (Figure 3-2). This limitation was to minimize the disturbance of the firing exercise at the request of the military unit. On 5 June, a total of 65 rounds of 66-mm were fired; on 6 June, 33 rounds were fired. The installation of the particle traps in front of and behind the LP was done in the early morning, prior to the arrival of the units. For both days, the prevailing meteorological conditions were very light rain and light winds that blew rearwards from the firing line. Those conditions were optimum to avoid losing particles; the light winds did not dilute the plume, and the mist contributed to pulling particles down into the traps.

Firing instructions, safety briefing, and explanation on the aim of our sampling study were given to the military group prior to the exercise (Figure 3-3). The live firing was conducted by groups of four students that fired in teams of two at both LPs (Figure 3-4). Each student fired a minimum of two 66-mm rounds and a few groups fired more than four rounds per LP. The number of rounds fired at the left-hand LP was recorded by our team in collaboration with Lieutenant Voyer, the officer in charge of the exercise.

Figure 3-3. Briefing to unit prior to firing exercise.

Figure 3-4. Ready to fire.

3.4 Material

Past studies on particles collection from detonation events or live firing have mostly used either aluminum witness plates [11] or snow cover as the receptacle for particles [12-16]. Witness plates were not considered for this study due to their flat aluminum surface and their poor retention of solid particles in a highly turbulent situation. The use of snow as a pristine media for the collection of a contamination plume has many advantages and has been used successfully in past trials. However, this method generates large snow samples that cause sample handling, conservation, and processing constraints. Moreover, using snow as a receptacle for particles would not be practical for a trial in June. Commercially available aluminum containers described as particle traps, into which distilled water was poured, were successfully used in a previous study on the dispersion of perchlorate [17] as well as for the Carl Gustav 84-mm deposition study [10]. The same approach was applied in the present study.

Commercially available 47.3 by 36.5 (0.173 m^2) rectangular aluminum containers were used as the receptacles for particles across the sampling area. Heavy trap holders designed to prevent losing traps due to the high turbulence that follows firing were used in this trial for the first time (Figure 3-5). Ethanol was poured into the traps to provide a surface to which particles would efficiently adhere. The traps were collected immediately after the completion of the exercise. During interruptions of the exercise, DRDC had access to the setup to inspect the traps and add ethanol if needed (Figure 3-5, right).

Figure 3-5. Particle trap and holder (left) being filled with ethanol (right).

3.5 Weapon description and propellant composition

The M-72 66-mm fired in the exercise was of type M-72 A5-C1 (Figure 3-6). The 66-mm infantry antitank gun is a U.S. design and is manufactured in Norway by Raufoss. The Light Antitank Weapon System 66-mm M-72 series is a recoilless, low-velocity weapon that is breech-loaded and percussion-fired [18]. Three versions of the weapon are in service with the

Figure 3-6. M-72 A5 – C1 used in the live-fire trial.

Canadian Forces: the M-72 A1, A3, and A5 series, which each differ slightly in the quantity of propellant and weapon design. The 66-mm M-72 A5 Lightweight Anti-armor Weapon System is a shoulder-fired, portable, single-shot disposable launcher/rocket assembly. The weapon system is issued as a single round and may be fired from either shoulder in the prone, kneeling, sitting, or standing position. The M-72 A5 weapon system (known in Norway as the NM-72) incorporates significant design and product improvements to enhance the range, accuracy, and penetration performance compared to the A1 and A3 series.

The rocket consists of three major assemblies: the warhead, the fuse, and the rocket motor assembly (Figure 3-7). The M-72 A5 rocket motor consists of an impact extruded aluminum alloy motor tube, folding fin assembly, and M7 type I double-base propellant together with an integral percussion igniter assembly. The compositions of the two types of propellants used in the M-72 66-mm A5 series and the Carl Gustav 84-mm round are presented in Table 3-1, for the sake of comparison. The M-72 66-mm A5 is propelled by 122 g of type I M7 propellant, which is included in the weapon as 37 sticks of M7 tubular propellant (Figure 3-8). Each stick is between 142 and 147 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm.

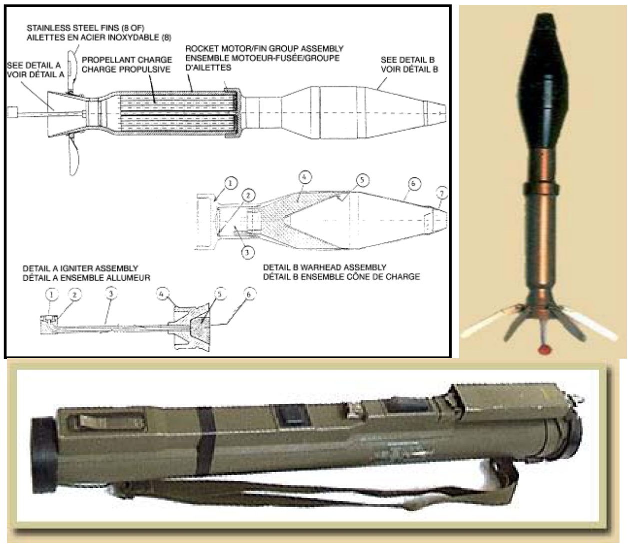

Figure 3-7. M-72 66-mm weapon.

Ninety-eight 66-mm rounds were fired in two events (65 on day 1 and 33 on day 2). As a result, a total of 7,930 g of propellant containing 2,815 g of

NG were fired on 5 June; 4,026.0 g of propellant containing 1,429.3 g of NG were fired on 6 June.

Table 3-1. M7 propellant formulations.

Propellant	% NC	% NG	% KP	% Carbon black	% EC
66-mm: M7 Type I	54.6	35.5	7.8	1.2	0.9
84-mm: AKB DB	61	37.5	0	0	1.5

Figure 3-8. M7 propellant sticks.

3.6 Field setup

The particle traps were installed in front of and behind the firing line. The slope in front of the LP ran downward toward the flat impact area, which had a dense vegetative cover. As mentioned earlier, it was not possible to install traps farther than 10 m in front of the firing line. Due to the presence of bushes in this area, a limited number of traps could be installed; a total of five traps were placed in two lines at +5 and +10 m from the LP, wherever it was possible to put them (Figure 3-9). The red tape in Figure 3-9 delineates the safe working area, which was cleared by an explosive ordnance disposal (EOD) expert, Mr. Boucher from METC Valcartier.

Behind the LP, six trap lines were set up perpendicular to the line of fire. Traps were placed at respective distances of -5, -10, -15, -20, -25, and -30 m from the firing line and covered a width of 10 m (Figure 3-10). As mentioned earlier, the presence of a tree line limited the sampling template to 30 m behind the LP. For the six rows behind the LP, five traps were used per row: the center trap installed directly behind the LP and four traps placed 2.5 and 5 m away in each direction. Three traps were also placed in a small water stream, which was considered to be a sensitive ecological receptor, located parallel to the line of fire, behind and 6 m to the left of the LP (Figure 3-11). The field setup used is illustrated in Figure 3-12.

Figure 3-12 shows the trap locations as well as the areas that were integrated by our sampling pattern (highlighted in corresponding colors). The total surface of each represented area is given in the right-hand column, with a color code identical to the area that it represents. Three field blanks were installed approximately 60 m west from the FP, along a tree line. The total area covered by the sampling template was 400 m^2, which was considered limited, but the Liri range could not offer a wider sampling surface. The area covered by the traps themselves represented 2% of this area.

Figure 3-9. Particle traps in front of firing line.

Figure 3-10. Rows of particle traps behind the firing line.

Figure 3-11. Particle traps in the stream adjacent to the firing range.

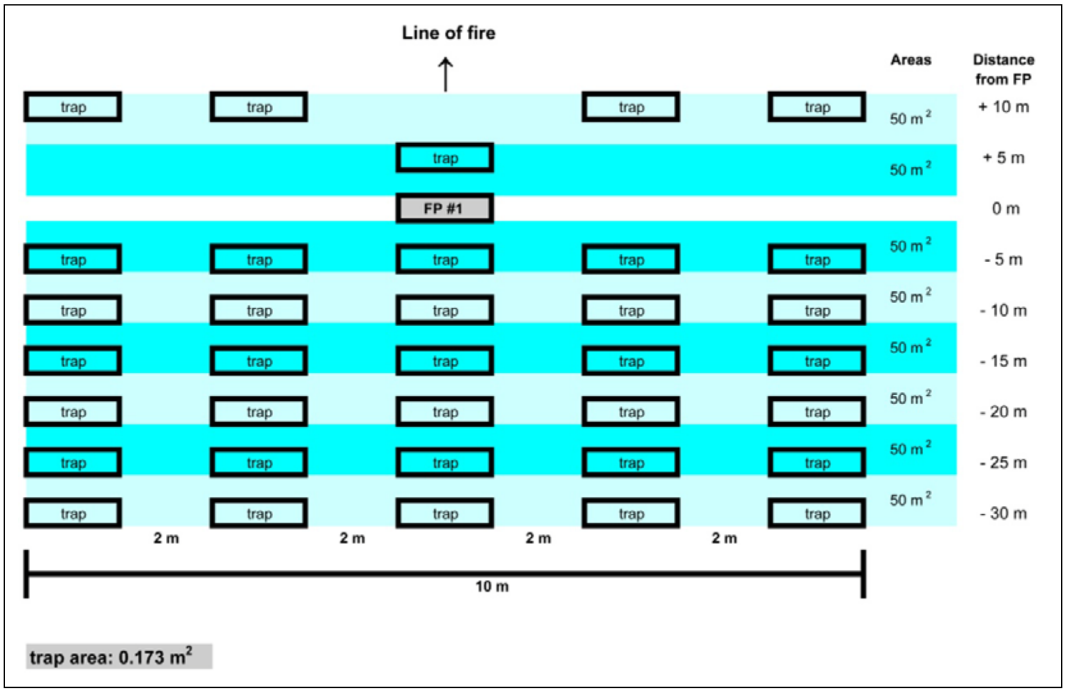

Figure 3-12. Field setup.

3.7 Sample processing

At the end of the live firing, the traps were brought back to the firing pads for processing. The very short timeframe between the end of firing and our departure required our team to combine the samples per row.

The ethanol was poured into wide-mouth 1-L jars, and the traps were rinsed four times with ethanol to ensure that all particles were effectively collected. A total of 21 samples were collected, including three field blanks that were collected in the same manner. Samples were taken back to the laboratory and processed the same day.

3.8 Extraction and analysis

The glass jars were opened under a hood for 72 hours to allow evaporation of the ethanol. A known volume of acetonitrile (AcN) was added to allow a freestanding solution (approximately 200 mL). The exact volume of AcN used for the extraction of each sample was carefully noted and served for the subsequent estimations of the mass deposited. Jars were placed on a wrist-action shaker table for 1 hour and then transferred to an ultrasonic bath for 18 hours. Finally, a quantity of the final solution (between 700-800 µL) was transferred with an Eppendorf pipette into a 3-mL Luer-Lok syringe fitted with a 0.45-µm filter. The resulting solution was diluted with the same quantity of distilled water and filtered into a 2-mL amber vial. Samples were analyzed (20 µL injection) using Reverse Phase High Performance Liquid Chromatography (RP-HPLC). The chromatograph was equipped with an ultraviolet diode array detector monitoring at 210, 220, and 254 nm. The column used was a Supelcosil LC-8 column 25 cm × 3 mm × 5 µm eluted with 15:85 isopropanol/water (v/v) at a flow rate of 0.75 mL/min. The concentrations measured by HPLC allowed us to determine the amount of deposited NG and the concentration deposited in a given area, which was calculated depending on the number of traps that were combined to build each sample.

3.9 Results and discussion

3.9.1 Test setup

The test setup used was appropriate to collect propellant residues. However, the presence of soil residues in a few traps might indicate possible cross-contamination from pre-existing residue deposition at the FP. This might lead to an overestimation of the deposition rate, a weakness of our setup. The soil was wet due to the rain, which helped minimize soil movement. The newly designed trap holders proved to be successful, since no traps were lost due to the rearward blast. The total area covered by our sampling pattern was 400 m^2, which seemed appropriate, based on the absence of NG detected at the limit of the boundary of the area sampled. However, due to time constraints, a limited number of traps were used; also, combining them by rows increased the uncertainty in the corresponding results. The small unit area of the traps and, consequently, the proportion of the deposition area sampled are also considered to be a weakness of this trial.

3.9.2 Particle size, distribution and type

The particle size, distribution, and type did not vary with distance and location as opposed to the Carl Gustav trial. Behind the firing line, a few traps showed evidence of propellant residues as yellowish glassy particles, which were mixed with dust and particles from the soil surface transported by the blast (Figure 3-13). Distribution was quite homogeneous near the LP, with a few visible propellant particles per trap; however, no visual propellant particles were observed farther than 15 m away. No propellant particles were observed in the traps located in front of the LP.

Figure 3-13. Particles collected in the middle trap at -5 m.

3.9.3 Estimate of the mass of nitroglycerin deposited

Results of the mass of NG deposited are presented in Table 3-2. A few samples were diluted to obtain a result in the linear region of the calibration curve.

The total amount of NG dispersed is approximated to be 4.1 g for the two days. Ninety-eight rounds were fired; each round contained 122 g of propellant and was composed of 35.5 % NG leading to 4244.38 g of NG fired. Therefore, 4.1 g of NG represents 0.1 % w/w of NG deposited on the surface soil; in other words, 42 mg of NG was deposited per round of M-72 A5 as unreacted residue. In terms of residue deposited in front versus behind the LP in the first trial day, 2.226 g was projected behind, while 0.191 g was projected in front, meaning that 92% of the residues are projected behind the LP. On Day 2, 99% of the residues were detected behind the LP. In both cases, most of the material was projected toward the rear; 92% was located in the first 20 m for Day 1, while more than 99% was located in the first 15 m for the second day. While the amount of NG dispersed in the environment is quite limited for the 66-mm, a recent study on the fate of NG from soils contaminated by propellant residues indicates that it can be desorbed from its NC matrix. Thus it is more readily leached from the M7 propellant composition than 2,4-DNT from M1 propellants commonly used with howitzer munitions [19].

Table 3-2. NG deposited.

Sample location (row)	NG in traps (mg)	Estimated mass NG in area (mg)	Estimated average mass of NG deposited per round (mg)
Day 1			
-30 m	nd	0	0
-25 m	nd	0	0
-20 m	2.31	134	2.1
-15 m	2.13	123	1.9
-10 m	11.24	650	10.0
-5 m	22.82	1319	20.3
+ 5 m	0.63	182	2.8
+10 m	0.12	9	0.1
Stream	nd	0	0
Total Day 1		**2416**	**37**
Day 2			
-30 m	nd	0	0
-25 m	nd	0	0
-20 m	0.34	20	0.6
-15 m	0.68	39	1.2
-10 m	16.81	972	29.4
-5 m	11.11	642	19.5
+ 5 m	0.02	6	0.2
+10 m	nd	0	0
Stream	nd	0	0
Total Day 2		**1679**	**51**
nd: not detected			

When we compare the results obtained for both days, they are quite similar, with 37 mg of NG deposited per round on day 1 and 51 mg on day 2. This is the only indication up to now that our setup leads to representative results. The meteorological conditions were the same for both days, and any bias that they bring is the same for both days. In both cases, more than 92% of the deposition occured behind the firing line and mostly within the first 15 m. Results obtained for the farthest samples collected at -25 m, -30 m, and +10 m tend to demonstrate that our sampling area, while limited due to site constraints, seems appropriate. The three field blanks located away from the firing positions came back non-detected.

From studies conducted thus far in Canada and in the United States, we can state that the live firing of 66-mm A5 M-72 rockets leads to deposition rates in the same order of magnitude as other weapon types. The same calculations were made for 60-, 81-, and 120-mm mortars and resulted in the respective dispersion of 0.0065, 3.5, and 1.4 % w/w of the original NG mass [13, 20]. Artillery 105- and 155-mm Howitzer firings led to the dispersion of 0.2% to 0.5% and 5 x 10^{-4} w/w of 2,4-DNT, respectively, as a residue in the environment [11, 21].

A huge discrepancy exists between the deposition rates of the 66-mm M-72 and the Carl Gustav 84-mm rockets. The Carl Gustav contains a larger quantity of propellant, so it would be logical to measure fewer residues from a larger charge since it would logically burn at higher pressure and higher temperature. However, there should not be much difference in breech pressures between these two munitions. The launchers are both open to the atmosphere, thus having the recoilless characteristic. We observed the opposite, however, with a greater deposition rate for the 84-mm, and it can be explained by the differences in the propellant formulations. The ingredient proportions are similar for both propellants (Table 3-1), with the exception that the M-72 round propelling charge includes 7.8% of KP, a strong oxidizer. It is postulated that KP leads to a more equilibrated formulation that produces better combustion efficiency. We did not analyze for perchlorate in the present study.

3.10 Recommendations and conclusion

The goal of this study was to characterize residues resulting from the firing of 66-mm anti-armor lightweight rockets. Our results demonstrate that the combustion of the propellant charge is slightly inefficient, with 0.1 %

w/w of NG being deposited as unreacted propellant residue, or 42 mg per round. Testing in live-fire exercises always presents a challenge. In our case, the main weaknesses of our trial were the relatively limited area that was sampled and the small size of the particle traps. Both factors result in a smaller sampled area and a less accurate approximation of the total mass for the plume. Moreover, the presence of soil residues in a few traps might indicate cross-contamination from pre-existing residues deposition at the FP, which might lead to an overestimation of the deposition rate.

However, it is interesting to note that there is a huge difference in the deposition rate of the two frequently used antitank weapons in Canada, the Carl Gustav 84-mm, and the M-72 66-mm A5. It would take 475 rounds of 66-mm to deposit the same amount of NG as a single 84-mm round. The 66-mm propellant includes 7.8% of KP, a strong oxidizer, which can explain the measured discrepancy between the NG deposition rates from both weapons. The oxidizer brings more oxygen into the composition, leading to a better combustion process so that fewer residues are deposited. The ignition mechanisms and the propellant charge geometry of the two weapons also differ, and may be part of the explanation. The meteorological conditions prevailing in the two trials were different (winter versus summer) and could also have an influence on the results. It is recommended to repeat the experiments on both weapons to confirm our results using the same setup and under the same meteorological conditions.

In future trials, if available, pristine snow should be used to collect the residues instead of traps, which would lead to the integration of a larger sampling area to minimize the associated errors. This method would also minimize the risk of cross-contamination from residues deposited in past firings. If pristine snow is not available, using more traps to better delineate the plume would also be appropriate since it avoids the cross-contamination problems from the contaminated snow. If time permits, the delineation of the plume should be made in both directions from the LP. Our study has demonstrated that future trials should focus on the first 20 m behind the LP. Our study also proved that previous site characterization results were correct in detecting propellant residue contamination by antitank rockets behind the FP, while results in front of the FP might represent a mixture of various activities conducted on this type of range. As an example, antitank ranges often serve for mortar training and the firings are done in front of the FP. This study reinforces the importance of managing and maintaining the soil quality at FPs to avoid creating sources of energetic residues on firing ranges. It also reinforces the need to develop better propelling systems that will minimize residue deposition. A preliminary study has recently been undertaken to assess if fire management could be used to remediate contaminated FPs. The setup of the FPs could also be modified with a protective layer underneath the mostly impacted area to prevent the leaching of contaminants towards the groundwater table.

3.11 Acknowledgements

Lieutenant Colonel R. Lavoie, CI SQFT Commander, is gratefully acknowledged for allowing our presence during the live-fire exercise. Warrant Officer Mario Lafleur from range control and Lieutenant Voyer from the National Support Element of the Royal 22e Régiment are also acknowledged for their collaboration with the trial. Mr. Firmin Boucher from Munitions Experimental Test Center is also acknowledged for the sweep he conducted in the area sampled. We are grateful to Thrust Sustain, WBE 12so04, and SERDP for their financial support.

3.12 Nomenclature

CI SQFT	Centre d'Instruction du Secteur du Québec de la Force Terrestre
DND	Department of National Defence
DNT	dinitrotoluene
DRDC	Defence Research and Development Canada
FP	firing point
HMX	cyclotetramethylene tetranitramine or high melting explosive
METC	Munitions Experimental Test Centre
NC	nitrocellulose
nd	not detected
NG	nitroglycerin
LP	launch position
R&D	research and development
RP-HPLC	reverse-phase high performance liquid chromatography
SERDP	Strategic Environmental Research and Development Program

3.13 References

1. Thiboutot, S., A. Marois, A. Gagnon, T. Gamache, and G. Ampleman. 2007. *Caractérisation de la dispersion de résidus de munitions dans les sols de surface d'un secteur d'essai*, DRDC Valcartier TR 2007-110. Val Belair, Quebec: Defence Research and Development Canada (DRDC).

2. Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, A.D. Hewitt, S. Brochu, J. Robb, E. Diaz, J. Lewis, H. Colby, R. Martel, K. Poe, K. Groff, K.L. Bjella, C.A. Ramsey, C.A. Hayes, S. Yost, A. Marois, A. Gagnon, B. Silverblatt, T. Crutcher, K. Harriz, K. Heisen, S.R. Bigl, T.E. Berry, Jr., J. Muzzin, D.J. Lambert, M.J. Bishop, B. Rice, M. Wojtas, M.E. Walsh, M.R. Walsh, and S. Taylor. 2006. *Distribution and fate of energetics on DoD test and training ranges: Interim report 6*. ERDC TR-06-12, Vicksburg, MS : U.S. Army Engineer Research and Development Center.

3. Jenkins, T.F., A.D. Hewitt, C.L. Grant, S. Thiboutot, G. Ampleman, M.E. Walsh, T.A. Ranney, C.A. Ramsey, A.J. Palazzo, and J.C. Pennington. 2006. Identity and distribution of residues of energetic compounds at Army live-fire training ranges; *Chemosphere*, 63:1280-1290.

4. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, K. Bjella, C. Ramsey, and T.A. Ranney. 2004. *Environmental conditions of surface soils, CFB Gagetown training area: Delineation of the presence of munitions related residues (phase III, final report)*, DRDC Valcartier TR 2004-205. Val Belair, Quebec: DRDC.

5. Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren. 2001. *Characterization of explosives contamination at military firing ranges*, ERDC TR-01-5. Vicksburg, MS: U.S. Army ERDC.

6. Diaz, E., S. Brochu, S. Thiboutot, G. Ampleman, A. Marois, and A. Gagnon. 2007. *Energetic materials and metals contamination at CFB/ASU Wainwright, Alberta: Phase I*. DRDC Valcartier TR 2007-385. Val Belair, Quebec: DRDC.

7. Marois, A., A. Gagnon, S. Thiboutot, G. Ampleman, and M. Bouchard. 2004. *Caractérisation des sols de surface et de la biomasse dans les secteurs d'entraînement, base des Forces canadiennes, Valcartier*. RDDC Valcartier TR 2004-206.

8. Thiboutot, S., G. Ampleman, A. Gagnon, A. Marois, T.F. Jenkins, M.E. Walsh, P.G. Thorne, and T.A. Ranney. 1998. *Characterization of anti-tank firing ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn*, DREV-R-9809.

9. Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, K.L. Bjella. 2004. *Representative sampling for energetic compounds at an antitank firing range*. ERDC/CRREL TR-04-7. Hanover, NH: U.S. Army ERDC.

10. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of gun propellant residues from 84-mm Carl Gustav rocket firing*. DRDC Valcartier TR 2007-408. Val Belair, Quebec: DRDC.

11. Dubé, P., S. Thiboutot, G. Ampleman, A. Marois, and M. Bouchard. 2005. *Preliminary assessment of the dispersion of propellant residues from the static live firing of 105-mm howitzer*; DRDC Valcartier TM 2005-284. Val Belair, Quebec: DRDC.

12. Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, J.A. Stark, and J.C. Pennington. 2001. *Use of snow-covered ranges to determine the amount of explosives residues deposited from high-order detonations of Army munitions*. Geological Society of American National Meeting, November 5-9, 2001, session 48, paper 48-0.

13. Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari. 2006. *Energetic residues deposition from 60-mm and 81-mm mortars*. ERDC/CRREL TR-06-10. Hanover, NH: U.S. Army ERDC.

14. Walsh, M.R., M.E. Walsh, G. Ampleman, S. Thiboutot, and D.D. Walker. 2006. *Comparison of Explosives residues from the blow-in-place detonation of 155-mm high-explosive projectiles*. ERDC/CRREL TR-06-13. Hanover, NH: U.S. Army ERDC.

15. Walsh, M.R., M.E. Walsh, C.A. Ramsey, and T.F. Jenkins. 2005. *An examination of protocols for the collection of munitions-derived explosives residues on snow-covered ice*. ERDC/CRREL Technical Report 05-8. Hanover, NH: U.S. Army ERDC.

16. Hewitt, A.D., T.F. Jenkins, T.A. Ranney, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Karn. 2003. *Estimates for explosives residue from the detonation of army munitions*. EDRC/CRREL TR-03-16. Hanover, NH: U.S. Army ERDC.

17. Thiboutot, S., G. Ampleman, M.C. Lapointe, S. Brochu, M. Brassard, M. Stowe, R. Farinaccio, A. Gagnon, and A. Marois. 2007. *Dispersion of ammonium perchlorate following the firing of Mk58 rocket motors, Chapter 7, SERDP annual report*, ERDC/CRREL TR 07-01. Hanover, NH: U.S. Army ERDC.

18. Ammunition and Explosive Technical Information, Light Antitank Weapon System 66 millimetre M-72 Series. 1989. Canadian Forces Technical Order, Information note #C-74-340-DAO/TA-000, December 1989.

19. Hewitt, A.D., and S. Bigl. 2005. *Elution of energetic compounds from propellants and composition B residues*. EDRC/CRREL TR-05-13. Hanover, NH: U.S. Army ERDC.

20. Walsh, M.R., M.E. Walsh, C.M. Collins, S.P. Saari, J. Zufelt, A.B. Gelvin, and J.W. Hug. 2005. *Energetic residues from live-fire detonations of 120-mm mortar rounds*. ERDC/CRREL TR-05-15. Hanover, NH: U.S. Army ERDC.

21. Walsh, M.R., S. Taylor, M.E. Walsh, S. Bigl, K. Bjella, T. Douglas, A. Gelvin, D. Lambert, N. Perron, and S. Saari. 2005. *Residues from live fire detonations of 155-mm howitzer rounds*. ERDC/CRREL TR-05-14. Hanover, NH: U.S. Army ERDC.

4 Study of the Propellant Residues Emitted During the Live Firing of 105-mm Leopard Tank Squash-Head Practice Rounds at CFB Valcartier, Canada

*Sonia Thiboutot, Guy Ampleman, André Marois, Annie Gagnon, Denis Gilbert, Michael R. Walsh, Marianne E. Walsh, and Peter Woods**

4.1 Abstract

Extensive research indicates that propellant residues accumulate at firing positions and represent a concern for the environment and human health. To better understand the impacts of live firing at firing positions, a series of characterizations was conducted to measure the deposition of propellant residues from many sources. The study reported here was conducted three times with Leopard tanks firing 105-mm tank gun ammunition. The first trial, carried out at Canadian Forces Base (CFB) Gagetown, identified no propellant residues. For validation purposes, two additional trials were conducted at CFB Valcartier. Defence Research and Development Canada (DRDC) Valcartier assessed the particles emitted, the gaseous emissions, and the particles' size distribution during these live-fire events. Gases were collected in front of and inside the tank. Results from the gaseous emissions study will be described in another report. This chapter describes results obtained on the deposition of propellant residues during tank live firings. In November 2008, the setup consisted of half circles of particle traps positioned 1, 5, 10, 15, 20, 30, and 40 m in front of the tank. Ethanol was poured inside the traps to contain the particles emitted during firing. Following the first set of firings, many traps were destroyed, some caught fire, and the experiment had to be stopped. During this event, since the gaseous collection system was deemed adequate, it was decided to continue the firing to measure the gaseous emissions. The particle collection experiment was postponed until February 2009 when a more robust setup could be put in place. During the February 2009 test, two methods of resi-

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dues collection were compared: snow collection and particle trap. For this trial, the new traps were placed in front of the tank using a square pattern at 3, 5, 10, 15, 20, 25, 30, 40, and 45 m. This time, the particle trap setup was efficient and robust enough to collect the residues. Results from both collection methods were compared. It was found that firing 105-mm tank gun ammunition leads to the accumulation of solid propellant residues in the vicinity of the gun at 0.00263% by weight of unburned 2,4-Dinitrotoluene (2,4-DNT). Similar results were obtained with both methods, confirming the validity of these results. It was also found that most of the particles were deposited 20–25 m in front of the tank. This chapter describes the sampling strategy, the laboratory procedure, and the results obtained.

4.2 Introduction

For many years, DRDC Valcartier has been involved in the evaluation of the environmental impacts of live-fire training to characterize and mitigate adverse effects on training ranges and thereby sustain ongoing military activities [1-6]. Over the years, many efforts were conducted to assess the environmental loading of explosives at most of the Canadian Forces bases. To date, these efforts have addressed mainly heavily used target areas [7-17]. Many of these studies were conducted in collaboration with the U.S. Army Corps of Engineers, Engineer Research and Development Center–Cold Regions Research and Engineering Laboratory (ERDC-CRREL) in Hanover, New Hampshire, and the ERDC Environmental Laboratory (ERDC-EL) in Vicksburg, Mississippi [4–6; 14; 18–21]. Walsh et al. [22] observed that the firing positions were also experiencing a build-up of energetic residues; since then, many studies have been dedicated to the characterization of firing positions [20; 23–26]. This research determined that nitroglycerin (NG) and/or 2,4-DNT embedded in nitrocellulose (NC) fibers are deposited in front of and around firing positions [11; 22–27]. Moreover, it is common practice in the United States and Canada to burn excess propellant bags that are removed from the munitions to adjust the ballistic parameters directly on the ground. This practice results in the incomplete combustion of the propellants, therefore leaving high concentrations of propellant compounds on the soil surface. This practice is currently being assessed by DRDC Valcartier and Director Land Environment; it is hoped the current practice will soon be replaced by an environmentally friendly alternative.

Four years ago, DRDC Valcartier assessed the dispersion of propellant residues following 105-mm artillery and tank gun firings at CFB Valcartier by placing aluminum witness plates in front of the gun muzzles [28]. At CRREL, similar trials were conducted using snow as a collection media [29]. Both studies demonstrated that propellant residues comprised of NC fibers containing 2,4-DNT were deposited in front of the muzzle of artillery guns, but in a similar test, no residues were found after firing tank ammunition in Valcartier [28]. The conditions for the trial in Valcartier were not ideal, so it was decided to repeat this trial in Gagetown [24]. During the trial in Gagetown, no residues were detected in any of the particle traps in front of the tank, but we realized that our setup was not adequate and the experiment would have to be repeated another time. Moreover, Walsh et al. studied residues at mortar firing positions and found NG at elevated concentrations for 81-mm mortars [30].

During an artillery trial in CFB Valcartier, it came to our attention that gunners often suffered from headaches after gun firing exercises [31]. Furthermore, in some cases, the headaches persisted for days. One potential explanation was the intake of airborne chemicals by the gunners during the exercise. Since then, Canada studied air emissions and particle size distribution coming from the live firing of several weapon systems. These included the 105-mm gun in the field and in a closed environment at the muffler installation in Nicolet, Lac St-Pierre, Canada; the new M777 155-mm howitzer; and the emissions around and inside the 105-mm gunned tank [25; 32–35]. All these studies were undertaken to further understand the emission of propellant particles and gases in the area where gunners normally stand while firing. Of particular interest is the size of the particles emitted during the firing, since sub-micron particles can adversely affect human health.

Considering that tank gunners can be exposed to gases inside the turret and because of the growing interest in the contamination of firing positions, it was decided to reinvestigate emissions resulting from the firing of a 105-mm gunned Leopard tank. One of the aspects covered during the tank trial in Gagetown was the collection of gases in front of and inside the tank during the firing [24; 36]. During this trial, the gaseous sampling equipment suffered extreme damage during the firing, and it was decided to repeat the air sampling during the CFB Valcartier tank trial in November 2008. During this trial, the air emission collection system was carefully protected from the blast and incurred no damage [37]. However, our setup of particle traps was inadequate to resist the blast in these winter conditions: some traps were completely destroyed, some were expelled from the site by the blast, and others caught fire. The experiment had to be stopped and postponed until February 2009.

This chapter describes the two tank trials of November 2008 and February 2009 at CFB Valcartier where particle traps were installed using different setups and where two sample collection methods were used and compared. This work was co-funded by the Sustain Thrust from DRDC and by the Strategic Environmental Research and Development Program (SERDP) of the United States through Environmental Restoration (ER) Project 1481.

4.3 Background

4.3.1 Logistics

The first trial was organized and conducted at CFB Valcartier by DRDC Valcartier in conjunction with the 12th Régiment Blindé du Canada (12th RBC) during one of their exercises in November 2008. A Leopard tank fired 105-mm practice rounds in the Termoli range and propellant residues were collected using particle traps containing ethanol to improve capture of the propellant residues.

During this trial, the soil was frozen and no snow had accumulated yet, which made the blast of the firings even stronger on the particle traps (Figure 4-1). From the very beginning of the trial, some traps were destroyed, some were expelled by the blast, and others caught on fire from the ethanol being ignited by the flame of the firings (Figure 4-2 and Figure 4-3).

It was decided to stop this experiment and postpone it until February 2009, when we installed a more robust setup of particle traps. The air emissions collectors (Figure 4-2, left) were strong enough to withstand the blast, so this part of the study continued and the results are described in another report [37]. The military offered us an opportunity to repeat our experiment outside of their busy schedule, leaving us with a Leopard tank for our specific needs.

It was decided to repeat the trial in February 2009 with a new setup of stronger particle traps. Our February 2009 trial was conducted at night due to other range priorities, leading to spectacular firings (Figure 4-4). After 90 squash head 105-mm practice rounds were fired, we collected snow and traps from 2100 hrs until collection was completed by 2300 hrs (Figure 4-5). Two methods of sampling for the particles were used, one by collecting the snow cover and the other by collecting the residues in the particle traps at the end of the firings (Figure 4-6 through Figure 4-9).

Figure 4-1. Leopard C2 firing in November 2008 trial.

Figure 4-2. November 2008 setup on fire.

Figure 4-3. Particle traps destroyed during November 2008 trial.

Figure 4-4. Leopard tank firing squash head at night.

Figure 4-5. Sampling propellant residues at night.

Figure 4-6. Collecting particles using the snow collection method.

Figure 4-7. Sampling snow at the surface and below the surface.

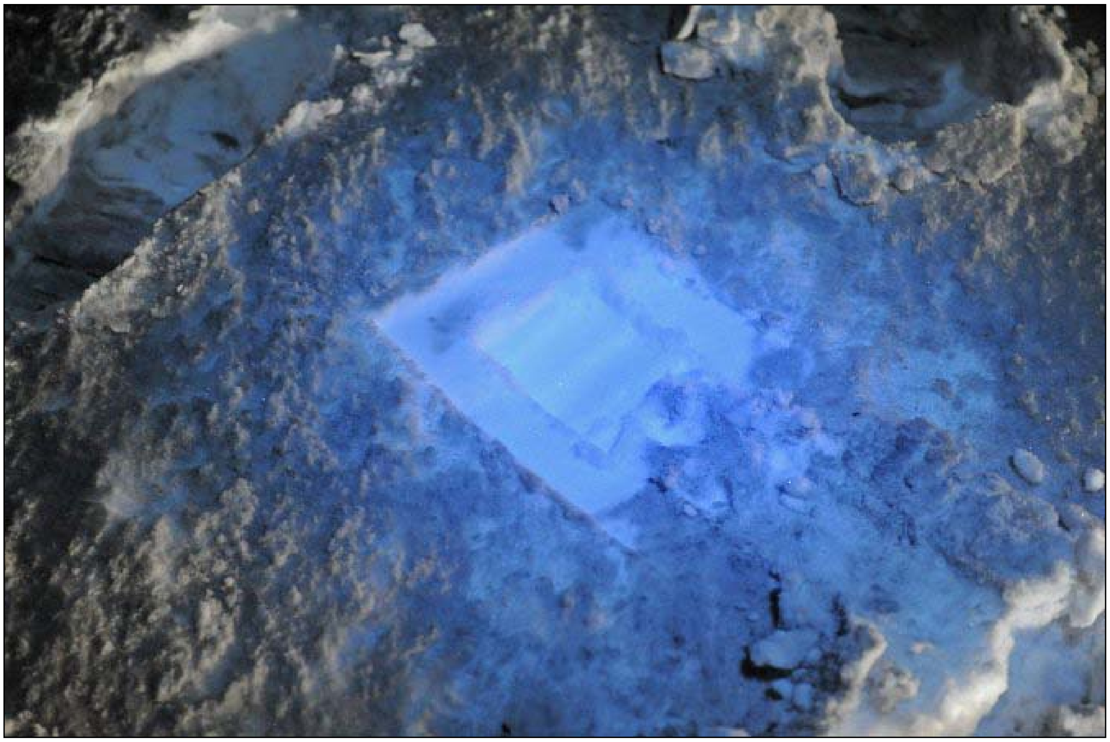

Figure 4-8. Sampling snow using lights.

Figure 4-9. Collecting particles in traps.

4.3.2 Equipment and munitions

The 105-mm tank gun is the main armament of the Canadian Forces Leopard C2 Main Battle Tank (as shown in Figure 4-1). This tank provides close and direct fire support and antitank defense for the mechanized battle group. The turret of the Leopard tank is the spaced-armor welded type and carries a crew of three: commander, gunner, and loader. The main armament consists of the 105-mm QF gun, either the British L7A3 or the American M68, with semi-automatic, horizontal sliding breechblock. The tube is 51 calibers in length and is equipped with a bore evacuator (fume extractor) and a thermal tube jacket. The barrel is rifled for 471 cm (185.5 in.) with a uniform twist of one turn in 18 calibers. The fire control equipment for this system is the Sabca Co.'s Tank Fire Control System (TFCS) with laser range finder.

All available ammunition types for the 105-mm gun were described in the Gagetown study [24]. Operational ammunition consisted of three types: armor piercing fin-stabilized discarding sabot (APFSDS), smoke white phosphorous (WP), and high explosive squash head (HESH); practice (training) ammunition consisted of short-range target practice discarding sabot (SRTPDS), target practice fin-stabilized discarding sabot (TPFSDS), squash head practice (SH Practice), and blank. The Leopard C2 tank can carry 59 rounds of ammunition. Most of theses rounds contain a tracer composition to help aim at the target. These rounds have a "T" at the end of their designation. As an example, APFSDS-T would be the operational weapon containing the tracer composition.

For the February 2009 trial, 90 SH Practice rounds with a tracer (SH/P-T, C109 A1) were fired. This training round is designed as a ballistic match for the current HESH L35 cartridges. The C109A1 differs from the C109 only in the simplified projectile design to reduce production costs (Figure 4-10 and Figure 4-11). Our rounds were stock number 1315 21 914 3294-0654, lot CA-06H11-01. The nominal propellant load consists of 3.0 kg of M1 (NH .034) propellant divided into three equal pockets within a viscose rayon cloth bag. A tin/lead foil strip is sewn into the upper section of the bag to act as a de-coppering agent. The projectile is similar in external configuration to the HESH projectile and contains an inert load of castor oil filler with a density of 1.6 g/mL in a plastic container.

Table 4-1 contains all the propelling charges and types of propellants for all available 105-mm tank ammunition.

Figure 4-10. Practice squash head.

Figure 4-11. Squash head being brought to the tank.

Table 4-1. 105-mm tank gun ammunition propelling charges.

Ammunition	Weight of propellants (g)	Type of propellants
APFSDS-T, M111	5800	M30 triple base
APFSDS-T, DM23A1	5800	M30 triple base
APFSDS-T, DM63C	6000	M26 double base
APFSDS-T, C76	5350	NQ/M triple base
APFSDS-T, M428	5800	M26 double base
HESH-T, L35	2857	M1 single base
WP-T M416*	2780	M1 single base
SR/TPDS-T, C148*	5120	M6 single base
TP/FSDS-T, C71*	5075	M6 single base
SH/PRACT, C109*	3000	M1 single base
* Ammunition studied in this report		

Table 4-2 shows the composition of propellant types normally found in practice 105-mm tank ammunition squash head and fin-stabilized discarding sabot. M1 is the propellant found in our practice rounds.

Table 4-2. Composition of single base propellants M1 and M6.

Chemical	Weight percentage in the propellant	
	M1	M6
Nitrocellulose	85% ± 2%	86% ± 2%
2,4-DNT	10% ± 2%	10% ± 2%
Dibutylphthalate	5% ± 1%	3% ± 1%
Potassium sulphate	1% ± 0.3%	0%
Diphenylamine	0.9% ± 1.2%	1% ± 1%

4.4 Experimental procedures

4.4.1 Sampling strategy and nomenclature

4.4.1.1 Propellant residues in particle traps

In November 2008, particle traps were placed in half circles 1, 5, 10, 15, 20, 30, and 40 m in front of a Leopard tank firing 105-mm ammunition at CFB Valcartier, Termoli range (Figure 4-12 and Figure 4-13). A total of 70 traps were installed in front of the tank in holders with weights to stabilize them (Figure 4-14). Ethanol was poured in the traps to improve the adhesion and capture of the propellant residues emitted. As mentioned, following the first series of firings, some plates were destroyed, and some caught fire (Figure 4-2 and Figure 4-3). Further experimentation was postponed until February 2009. These particle traps were acquired at a grocery store and were made of very thin aluminum; their purpose was primarily for re-heating rather than cooking food. They were definitely not robust enough to withstand a tank blast pressure. Although the traps were destroyed during the test firings, the trap holders made of stainless steel that DRDC built were not destroyed during the November 2008 trial (Figure 4-3).

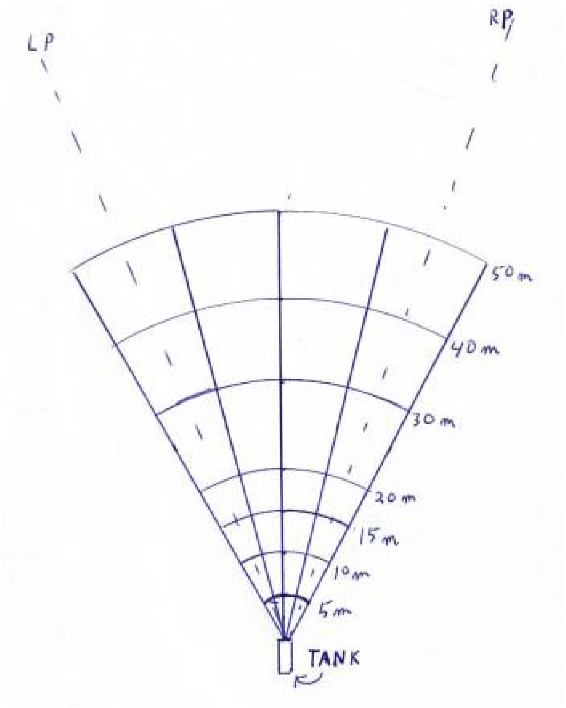

Figure 4-12. Half circles pattern of trays in front of Leopard tank.

Figure 4-13. Trays placed in front of tank (November 2008).

Figure 4-14. Particle traps in holders with weights.

In February 2009, traps that were stronger and heavier gauge were acquired from a commercial dealer. Their main usage was for large-scale cooking in industries or restaurants. They measured 53 x 48 cm, were 2.5-mm thick, with a height of 8 cm (Figure 4-15). Two types of holders were used: some were the type first deployed in the November 2008 trial; others were a new V-shaped design (Figure 4-16). Figure 4-16 also shows that a plume was formed after a few firings. The holders and traps can also be seen in this figure. For this trial, a total of 57 traps were set out in a series of transects at fixed distances in front of the tank. A rectangular shape was obtained using three traps positioned 3 m from the muzzle, five traps at 5 m, and then seven traps per row 10, 15, 20, 25, 30, 40, and 45 m in front of the gun muzzle. This resulted in a rectangular pattern with its longest axis in the firing direction. At the end of the firing, it was found that our setup resisted the firings of the 80 rounds. Some of the traps, especially those close to the gun's muzzle, were displaced but not flipped over. At the end of the trial, our traps were collected for analyses. At the end of the exercise, each row was combined to represent what was expelled at a specific distance. These samples were labeled row 1–9. Most of the traps contained snow that was recovered and put in plastic containers (Figure 4-17) for further analyses in the laboratory. Any traps that were displaced by the blast were combined with the closest row for analysis.

Figure 4-15. Stronger particle traps being installed on fresh snow cover.

Figure 4-16. Traps in holders with weights after a few firings.

Figure 4-17. Particles collection for analyses.

To avoid degradation of the energetic material residues, particle traps were sampled immediately after the firing was completed around 2100 hrs. All traps on a specific row were combined as row 1 to row 9. Nevertheless, no traps were turned over; all 57 traps were collected and analyzed. The snow and particles in the traps were transferred into plastic pails, and each trap was then thoroughly rinsed with ethanol and combined in the pail. All the pails were sealed for transport and named according to the nomenclature previously explained. Since the weather was very cold, no specific precautions were needed to protect the samples during transport to DRDC Valcartier. Upon arrival at the laboratory, the pails were kept at -20 °C until extraction.

4.5 Snow collection method

In addition to the collection of propellant residues on trays, researchers from CRREL collected samples from the snow surface. Multi-increment sampling with replicates and quality assurance procedures were carried out. The protocol used follows Walsh et al. [38]. The primary purpose of this redundant sampling was to directly compare the results of the two different sampling and analysis protocols.

4.5.1 Baseline sampling

Prior to the initiation of the trial, a snow sample was taken downrange of the tank position. A 20 x 20-cm flat polytetrafluoroethylene (PTFE) coated aluminum scoop was used to take 10 increments to a depth of 2.5 cm. The increments were collected in a single bag and kept separate from the post-firing samples prior to processing and analysis. The increments were taken downrange from the tank firing position along a centerline out to the sixth line of trays, 25 m from the firing position. Snow depths along this line varied from 11 cm up to 19.5 cm at the base of the snow berm. The average depth was 14 cm.

4.5.2 Post-firing decision unit delineations

The tank-firing exercise concluded late on a dark, foggy night. Light stanchions and the headlights of several vehicles were used to delineate the main plume area between the firing position and the snow berm. Even so, it was difficult to determine the extent of the plume (Figure 4-18). Sampling snow was accomplished using frontal light (Figure 4-19).

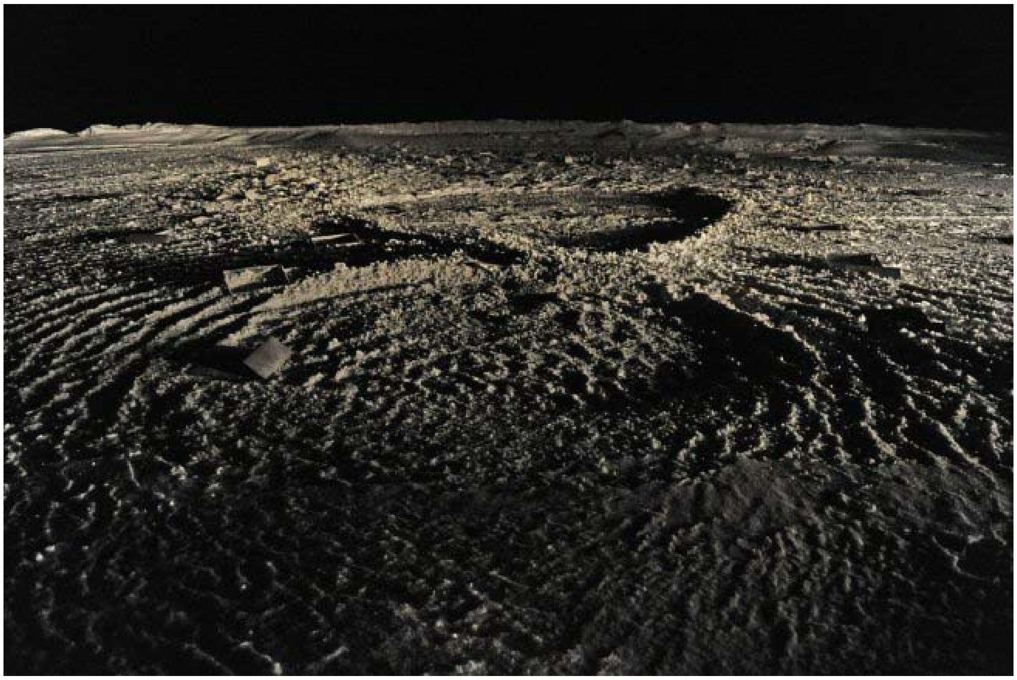

Figure 4-18. Main plume area immediately following cessation of firing.

Figure 4-19. Sampling snow using 20- x 20-cm scoop.

A wedge-shaped area 6-m across at the firing position, 26-m across at the berm 27-m away, with uneven sides of 28- and 30-m, was outlined as the main plume area (Figure 4-20). The area was outlined by packing the snow along the boundary edges and placing flags at the corners. Beyond this area, we outlined an additional downrange area that we designated as over the bank, since it was on a down slope. The sides of these areas were measured following the completion of sampling. The OTP (outside-the-plume) decision units encompass the areas up to 3 m from the edges of the main decision units. This strategy was used previously at Alaskan training areas [39].

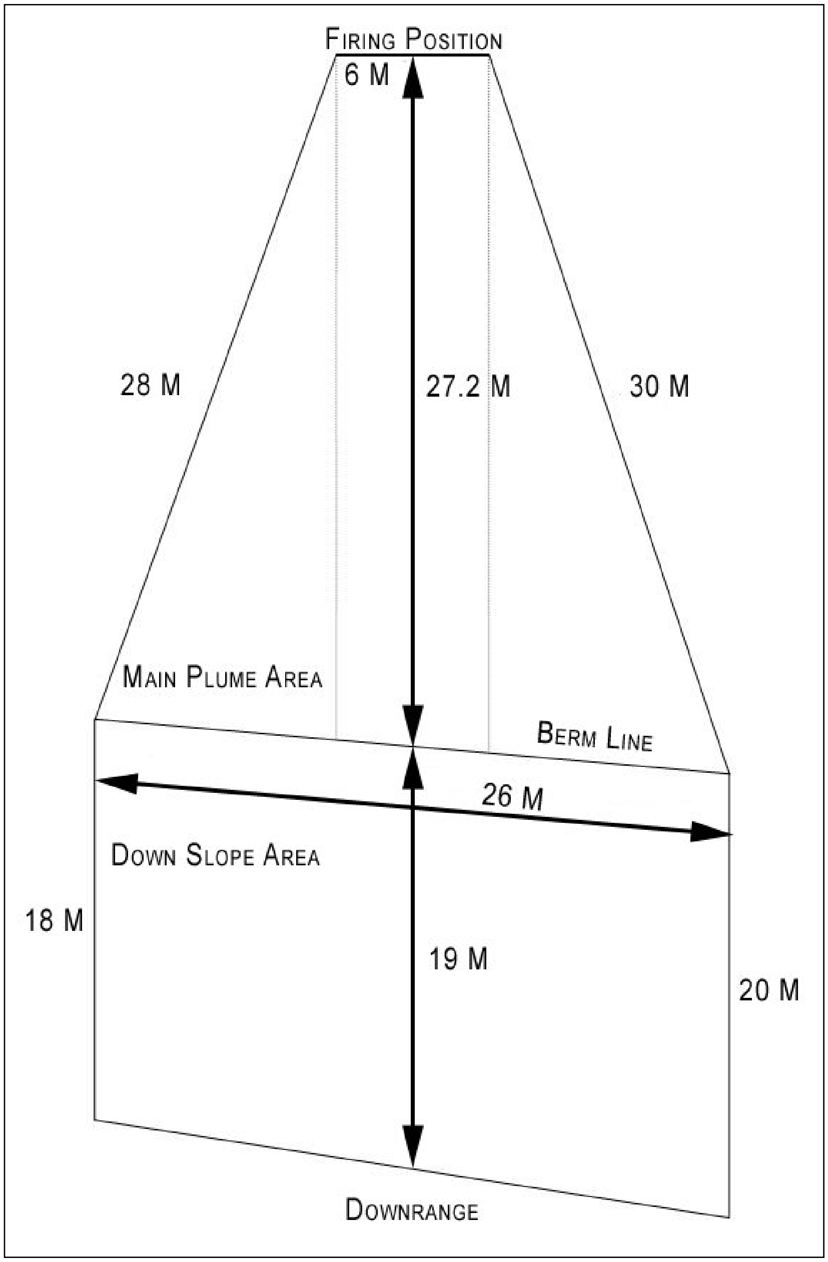

Figure 4-20. Layout of main decision units.

4.5.3 Snow sampling

Sampling started shortly after designation of the decision units was complete. The main plume area was sampled first. Then two OTP samples were taken along the long edges of the main plume area. Three replicate samples were then taken in the downslope area, followed by a single OTP along the edges and far end of the downslope area.

A systematic random approach was used for sampling the main plume area. The initial sampling locations were randomly determined and systematically carried through over the whole of the decision unit. The decision unit shape was not rectangular, so we sampled parallel to the 28-m side, working our way from the firing position to the top of the berm, then shifting towards the 30-m edge about 5 m to sample along a line parallel to the previous line. Four samples were built by collecting snow samples every 5 m: three surface samples and one subsurface sample beneath the same surface sample location at each stop (refer to Figure 4-7 and Figure 4-8). Surface samples were taken with a 20 x 20 x 2.5 cm PTFE-covered aluminum scoop. The subsurface sample was taken with a similar scoop 10 cm on a side. Samples were taken simultaneously at each sampling location. The increments for each sample were placed in a clean polyethylene bag that was labeled, tagged, and cinched with a tie-wrap following sampling. All samples from the same decision unit were stored and transported together.

The OTP samples for the main plume area were taken with a 10-cm scoop in a random-walk fashion along the outside edges of the decision unit. Two samples were separately taken. All increments were taken at the surface to a depth of 2.5 cm (Table 4-3). Bagging, labeling, storage, and transportation followed the procedure outlined above.

The downslope area decision unit proved a bit of a challenge for sampling. Previous drifting of snow resulted in snow depths in some areas in excess of a meter. However, we persevered and collected three plume samples and an OTP sample as outlined above (Figure 4-21). Table 4-3 describes the samples taken. Sampling started at 2100 hrs and was completed by 2300 hrs. The flags located at all the snow depth measurement points were blown away, so post-firing snow depth measurements could not be taken.

Table 4-3. Sampling data coming from snow collection.

Sample Description	Scoop Size (cm X cm)	Number of Increments	Sampled Area (m²)
Snow Background in front of tank before firing	20 x 20 x 2.5	10	0.4
Main Plume - Surface - Tank to berm - Rep 1	20 x 20 x 2.5	29	1.2
Main Plume - Surface - Tank to berm - Rep 2	20 x 20 x 2.5	29	1.2
Main Plume - Surface - Tank to berm - Rep 3	20 x 20 x 2.5	29	1.2
Main Plume - Subsurface of sample 09 DRDC-04	10 x 10 x 2.5	29	0.3
OTP* - 0-3 m - Tank side of berm - Rep 1	10 x 10 x 2.5	39	0.4
OTP* - 0-3 m - Tank side of berm - Rep 2	10 x 10 x 2.5	39	0.4
Plume - Surface – Down slope area - Rep 1	20 x 20 x 2.5	25	1.0
Plume - Surface - Down slope area - Rep 2	20 x 20 x 2.5	25	1.0
Plume - Surface - Down slope area - Rep 3	20 x 20 x 2.5	25	1.0
OTP* - 0-3 m- Down slope area	15 x 15 x 2.5	30	1.2
*OTP Outside the delineated plume			

Figure 4-21. Sampling in downslope area beyond berm.

4.6 Parameter, sample treatment, and analytical methods

4.6.1 Processing of samples in particle traps

To prepare the samples for Reverse Phase-High Performance Liquid Chromatography (RP-HPLC) analysis, the snow was melted and evaporated to dryness under a fume hood in the dark. Acetone was used to rinse the pail to completely extract the particles and transferred to a small beaker where it was evaporated to dryness again. The residues were recovered by adding acetonitrile (100 mL) (Figure 4-22). Usually, acetonitrile (15 mL) from this solution was recuperated, evaporated to dryness, re-extracted with acetonitrile (2.5 mL), diluted with water (2.5 mL), and injected into the HPLC for analysis. However, in all the samples, a green solid was observed to form during the evaporation of the acetonitrile solution (Figure 4-23) and this solid introduced interferences during the analyses. It was decided to get rid of this solid by evaporating the acetonitrile solution (15 mL) to dryness, recuperating the energetic residues with ethyl acetate (50 mL), and crushing the crystals using a glass spatula to break them into smaller pieces. The solid was then filtered and the organic solution was washed three times with water (40 mL). The organic phase was dried over magnesium sulfate and evaporated to dryness. The energetic residues were recuperated with acetonitrile (2.5 mL). After this extract was combined with water (2.5 mL) and the solution was filtered on a 0.45-micron filter, it was ready to be analyzed by HPLC.

Figure 4-22. Acetonitrile extraction of the pails.

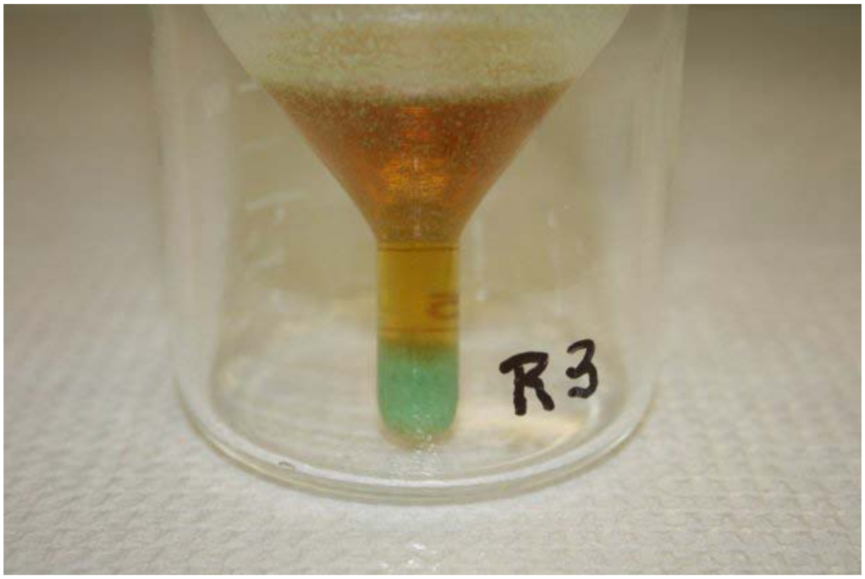

Figure 4-23. Unknown solid crystallization.

Prior to the HPLC analyses, extracts were maintained at 4 °C according to Method EPA 8330 update SW 846 (1994) [40]. Analyses were performed with an HPLC Agilent HP 1100 equipped with a degasser G1322A, a quaternary pump model G1311A, an autosampler G1313A, and an ultraviolet (UV) diode array detector model G1315A monitoring at 210, 220, and 254 nm. The injection volume was 20 µL and the column was a Supelcosil LC-8 (25 cm x 3 mm x 5 µm) eluted with 15:85 isopropanol/water (v/v) at a flow rate of 0.75 mL/min. The column temperature was maintained at 25 °C during the analysis. Standards and solvents were diluted 1:1, acetonitrile to water (0.5 mL AcN /0.5 mL water).

The green residue was recuperated, dried (Figure 4-24), and analyzed by Fourier transform infrared (FT-IR) and Raman spectroscopy. The analyses revealed the presence of cyanide and thiocyanate as the anion of this insoluble ionic compound. Combustion of gun propellants generates hydrogen cyanide [34, 35, 41] that may easily react with metals leading to metal cyanides that typically form green compounds. Metals analyses were performed by EXOVA Laboratories using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) and revealed that copper, boron, and potassium were the three main constituents of the metallic green compound. Copper was at the highest concentration at 180,000 ppm while potassium and boron were respectively at 250,000 and 3,100 ppm. Boron and potassium are often chemical components of the igniters, while the copper is coming from the rotating band. Consequently, it can be assumed that the green compound is a mixture of these chemicals (most probably a mixture of copper cyanide or cuprous thiocyanate).

Figure 4-24. Green solid isolated by evaporation.

4.6.2 Snow sample processing and analysis

Samples were stored in a cold area away from sunlight prior to transportation to the analytical chemistry laboratory at CRREL in Hanover, NH. At CRREL, the samples were processed following the procedure described in Walsh et al. [38]. The samples were melted, taking care not to allow the sample temperature to exceed 10°C or to refreeze. Using a vacuum filtration unit, the aqueous phase was separated from the soot or particulate fraction. The number of filters used and amount of filtrate generated were tracked. The filters were placed in a labeled jar and set out to dry. After drying, the jars were sealed and refrigerated. The filtrate fractions were mixed by vigorously shaking and two or four 500-mL aliquots were taken and placed in labeled bottles in a refrigerator after logging in the sample. All the glassware and reusable containers were carefully washed.

Filtration blanks were obtained by running 1000 mL of de-ionized water periodically through a freshly cleaned filtration apparatus and collecting filter and filtrate fractions. The aliquots in labeled bottles were pre-concentrated by passing through a Porapak RDX cartridge. Spikes or blanks were run at this time. The cartridges were eluted with acetonitrile (5 mL) to give a 100:1 concentration solution, and they were split into 3.5-mL and 1.5-mL fractions.

The filters were processed by adding acetonitrile in 10-mL increments until the filters were covered. The closed jars were then shaken for 18 hours. The acetonitrile volumes were recorded. Prior to the HPLC analysis, the acetonitrile extracts (1 mL) were mixed with reagent grade water (3.0 mL).

Following processing, the sample extracts were analyzed on an HPLC system for nitroaromatics and nitroamines, specifically 2,4-DNT, 2,6-dinitrotoluene (2,6-DNT), and NG. The HPLC was a modular system from Thermo Electron Corporation composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VS (visible spectrum) absorbance detector set at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15-cm × 3.9-mm (4-µm) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28 °C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

4.7 Results and discussion

4.7.1 Propellant residues in particle traps

During the tank trial in February 2009, 90 Squash Head practice rounds were fired between 1600 and 2100 hrs. Table 4-4 gives the distribution of the particle traps before and after the exercise. Some traps were moved by the blast from the original setup; nevertheless, none of the traps were flipped over and still represent an area of capture for the particles. By looking at Table 4-4, which also includes the 2,4-DNT mass for each row, it can be seen that most of the particles are deposited 20–25 m in front of the gun muzzle . It was also observed that more traps than originally installed at these distances were found in these lines (presumably coming from other rows). The particle trap’s dimensions of 53 cm x 48 cm produce a surface area of 0.2544 m^2. Taking into account that 57 traps were collected, this represents a surface of 14.5 m^2. By examining Figure 4-20 and doing the mathematics, the entire area was calculated to be 929 m^2. A total of 11.06 mg of 2,4-DNT was deposited in our 57 traps; so, by extrapolation, a total of 709 mg was deposited on the entire area following the firing of the 90

Squash Head practice rounds. It follows that each round deposited 7.89 mg of 2,4-DNT. Considering that one round contains 3 kg of M1 propellant and 10% of 2,4-DNT (meaning 300 g of 2,4-DNT), the rate of deposition of 7.89 mg /round represents 0.00263 % w/w of the original concentration of 2,4-DNT for this weapon platform.

Table 4-4. DNT concentrations obtained with particle trap method.

Sample	Distance (m)	# of Traps (pre-fire)	# of Traps (post-fire)	2,4-DNT (mg)
Row 1	3	3	2	1.11
Row 2	5	5	4	0.14
Row 3	10	7	5	0.05
Row 4 pail 1*	15	7	7	0.94
Row 4 pail 2	15			0.37
Row 5	20	7	8	3.08
Row 6	25	7	9	3.13
Row 7	30	7	7	0.88
Row 8	40	7	8	1.01
Row 9	45	7	7	0.35
Total		57	57	11.06

*Two pails were used for Row 4 since there was too much snow for only one pail.

In previous studies, it was observed that firing of 105-mm rounds from an artillery platform deposited at a rate of 0.5% w/w of the original concentration of 2,4-DNT [25, 31]. It must be said that the propellant charges in the 105-mm artillery rounds are smaller than in the 105-mm tank munitions, especially when the artillery guns are fired with a low number of charges. Since the 105-mm tank munitions have more propellant, it is quite likely that their combustion is more complete than with the equivalent artillery gun ammunition. The artillery is built to attack in indirect fire and is intended to hit long distances away. The tank ammunition is built to propel projectiles at high velocity using high kinetic energy, causing lethal effect in a direct fire. To achieve their terminal effects, the artillery gun ammunition propelling charges contain approximately 1.28 kg of propellant (seven bags) while the 105-mm tank ammunition contains from 3.0 to 6.0 kg of propellant from practice squash head to operational APFSDS rounds (Table 4-1). During the Nicolet trial, C-60 squash head artillery rounds were fired at charge 6 and charge 4, meaning that only 840 and

467 g of propellant were respectively burned, ejecting 0.23 and 0.39% of 2,4-DNT [25]. The tank squash head practice ammunition uses more than three times the amount of propellant compared to the artillery rounds of the Nicolet study [25]. This means that higher temperature and pressure in the tank gun barrel are leading to a cleaner combustion with smaller amounts of residues. This could be explained by the fact that the barrel is longer for a tank than for a howitzer, leading to more time at elevated pressure and temperature, which leads to cleaner combustion.

4.7.2 Propellant residues in snow samples

The baseline sample taken from the main plume area prior to the start of firing had very high levels of NG. No 2,4- or 2,6-DNT was detectable in the sample. Therefore, all DNT detected at the site can be attributed to the February 2009 tank trial. It was important to test for the presence of 2,4-DNT before our trial since Leopard tanks often fire 7.72 machine guns, which are small arms that contain 2,4-DNT in their firing formulation. The NG detected may have come from previous firing of a light armored vehicle 20-mm cannon that is often used in the same training area. The 20-mm ammunition contains NG at 10% and the Ball 20-mm contains 2,4-DNT at 8%. Usually, light armored vehicle exercises are done by firing the 20-mm rifle with both types of ammunition. It was therefore very important to assess the presence of NG and 2,4-DNT onsite before beginning our trial.

The main plume area contained most of the DNT residues from the propellant (Table 4-5). The plume surface sample averaged an estimated 390 mg of 2,4-DNT and 4.1 mg of 2,6-DNT when extrapolated over the complete decision unit. The one subsurface sample had 160 mg of 2,4-DNT and 1.8 mg of 2,6-DNT when extrapolated over the plume area. The down slope decision unit averaged 36 mg of 2,4-DNT and 0.28 mg of 2,6-DNT over the whole area, while the OTPs contained 9.1 mg and 1.0 mg of 2,4-DNT respectively. Most residues (92% of the combined mass of DNT) resided in the main plume area. Only 1.5% of the total estimated DNT mass was in the OTP sample adjacent to the main plume area. Beyond the berm, 6.1% of the total estimated mass of deposited DNT residues was found in the downslope area and 0.16% in that area’s OTP. Table 4-5 summarizes results, with a more complete data set provided in Appendix 4-A.

Table 4-5. DNT mass quantities obtained with the snow collection method.

Sample	2,4-DNT (mg)	2,6-DNT (mg)	DNT[1] (%)
Snow background in front of tank before firing	—	—	
Inside Plume - Surface – Main plume area - Rep 1	300	3.2	
Rep 2	290	3.0	
Rep 3	580	6.1	
Average:	390	4.1	65%
Inside Plume - Subsurface sample of 09 DRDC-04	160	1.8	27%
Main Plume Area total:	550	5.9	92%
OTP - 0-3 m - Tank side of snowbank - Rep 1	5.4	0.00	
Rep 2	13	0.00	
Average:	9.1	0.00	1.5%
Main Plume and OTP Areas total:	560	5.9	93.5%
Plume - Surface – Downslope area - Rep 1	29	0.27	
Rep 2	39	0.18	
Rep 3	41	0.41	
Average:	36	0.28	6.1%
OTP - 0-3 m- Downslope area	1.0	0.00	0.16%
Downslope Plume and OTP Areas total:	37	0.3	6.3%
Total estimated mass of analytes:	600	6.2	100%

[1] The percentages are % of the total mass.

As mentioned in the previous section, 90 rounds were fired; in each of these rounds, there was a total of about 300 g of 2,4-DNT. Using the snow results and dividing the total DNT estimated for the area by the number of rounds gives us a deposition rate of 6.7 mg DNT/round. This is 0.0022% of the original DNT load of the rounds, giving a combustion efficiency of 1-0.0022% or 99.9978% efficiency.

It is interesting to note that many of the residues in the main plume area were found below the surface. Fully 27% of all residues were estimated to reside in a 2.5-cm thick sample layer 2.5-cm below the surface. The muzzle blast from the Leopard tank's 105-mm rifled gun was ferocious, churning up and moving the snow in the first 20 m in front of the tank. In some areas, almost 10 cm of snow were removed from the surface. The muzzle blast from any direct-fire weapon will cause difficulties in sampling, not only in snow but also over soil. The subsurface sample concentration was 40% of the surface sample concentration. If the trend with depth is linear, the next lift would have contained about 66 mg, the next 27 mg, and so on. Adding these to the original 610 mg of DNT gives us approximately 720 mg of DNT. If this line of reasoning is valid, the mass of DNT residues per round becomes 8.0 mg/round, or 0.0027% of the original DNT load per round. This agrees very well with the 0.0026% deposition rate found with the particle traps method.

During the planning stages of this trial, we hypothesized that the deposition rate for the tank rounds would fall somewhere between those obtained for the 105-mm howitzer and the 155-mm howitzer. All three weapon systems use the same propellant formulation, all have long-rifled barrels, and all utilize large amounts of propellants. Previous tests have shown that higher propellant loads and longer barrels are a good indicator of high efficiency rates for the propellants. This test proved our hypothesis true. As seen in Table 4-6, the tank residue rates fall between the two howitzers.

Table 4-6. Deposition rates obtained with different weapon platforms.

Weapon Platform	Propellant	Load/Round (g)	Residues/Round (mg)	Residues/Load(%)
105-mm artillery[1]	M1 - I & II	42	34	0.08
105-mm artillery[2]	M1 - I & II	Varied	Varied	0.3 -0.05
155-mm artillery	M1	275	1.2	0.0005
105-mm tank[1]	M1	300	6.7	0.0022
105-mm tank[2]	M1	300	7.8	0.0026

[1]Performed by CRREL; [2]Performed by DRDC-Valcartier

4.8 Conclusion

In the context of assessing the contamination of firing positions of different weapon platforms, 105-mm tank gun practice rounds were fired during an exercise using a Leopard tank in CFB Valcartier in February 2009. This trial was performed to validate the results obtained in a previous trial conducted at CFB Gagetown. At CFB Valcartier, the first attempt to perform the trial was done in November 2008, but after firing the first set of munitions, the setup was destroyed and some traps caught on fire and the experiment had to be stopped. It was decided to re-conduct the test in February 2009 with a more robust system capable of withstanding the blast of the tank firings. In February 2009, a total of 90 squash head practice rounds were fired. That number represents 270 kg of M1 propellant, corresponding to 27 kg of 2,4-DNT burned during that exercise.

During the February 2009 event, two methods of particle collection were compared; the snow collection developed by CRREL and the particle traps method developed by DRDC Valcartier. For this trial, the new traps were positioned in front of the tank using a square pattern at 3, 5, 10, 15, 20, 25, 30, 40, and 45 m. This time our particle traps setup was efficient and robust enough to collect the particles. Results from both collection methods were compared. It was found that firing 105-mm tank gun ammunition leads to the accumulation of solid propellant residues in the vicinity of the gun at 0.00263 % of 2,4-DNT using the particle trap method. Using the snow collection method gave almost the same result, and a value of 0.0022% w/w of unburned 2,4-DNT was obtained, confirming the validity of these results. It was also found that most of the particles are deposited 20–25 m in front of the tank.

According to the latest results obtained from artillery exercises, it was found that 0.4–0.6% of 2,4-DNT is ejected during the firing of 105-mm artillery guns. In our February 2009 study, it was found that 0.0026% of unburned 2,4-DNT was ejected during the firing of the 90 tank gun ammunition rounds. At CFB Gagetown, no residues were identified; however, our setup was partly destroyed and it was concluded that our sampling strategy was not adequate. For that reason, we repeated this trial. Considering that residues were identified with the 155-mm artillery gun, it was hypothesized that 105-mm tank gun firings should give values between 155-mm and 105-mm artillery gun firings. This was proven by measuring the residues ejected using two different sampling collection methods.

Combustion of propellants in artillery or tank guns follows the laws of physics: the higher the pressure and temperature, the better the combustion, and the lesser the residues expelled at the gun muzzle. All three weapon systems use the same propellant formulation, have long rifled barrels, and utilize large amounts of propellants. Previous tests have shown that higher propellant loads and longer barrels are a good indicator of high efficiency rates for the propellants. The artillery is built to attack in an indirect fire mode and is intended to hit at long distances. The tank ammunition is built to propel projectiles at high velocity using high kinetic energy to cause lethal effect in a direct fire mode. The artillery 105-mm ammunition propelling charges contain approximately 1.28 kg of propellant while the 105-mm tank ammunition contains from 3.0 to 6.0 kg of propellant from practice to operational rounds.

The squash head practice round used in our study contains almost three times the amount of propellant as the artillery squash head C-60 practice rounds that were fired at charge 6 in Nicolet, Lac St-Pierre, Canada. This suggests that the higher temperature and pressure experienced in the tank gun barrel leads to a more complete or “cleaner” combustion without projection of solid unreacted residues. This is also observed in the 155-mm artillery gun, where the propellant loads are even bigger than the 105-mm artillery and tank ammunition, probably leading to very high pressure and temperature in the barrel. This is why very low percentages of 2,4-DNT (0.0005%) are ejected by 155-mm artillery firings. This was observed for all M1 single-base propellants, but this will also be true for the more powerful propellant charges such as the triple-base propellant charge used in the 155-mm artillery gun or in the 120-mm Challenger tank where higher pressure and temperature are expected. In these cases, it is foreseen that it will be difficult to measure any residues ejected by the platform because the combustion will be more efficient.

Finally, comparing the two sample collection methods was a fruitful exercise since it confirms and validates the results obtained during this trial. Both methods have their strengths and weaknesses. The snow collection method is by far the simplest and quickest method to perform. There is no need to deploy anything, you just use the scoop to collect the snow before and after live-firing, you measure the plume, and you analyze the results. The weakness is that you cannot perform this method all year long. On the other hand, the particle trap collection method can be done any time of the year, but measurements have to be done to install the traps according to the desired sampling pattern and the setup can suffer cross-contamination from the site if the soils surrounding the setup are very contaminated, especially in high-blast conditions. This cross-contamination can be evaluated and removed from the results, but more analyses are necessary. If we consider the sample treatment and analysis, both methods look similar.

In conclusion, it can be said that this trial was a success, and that we accomplished the study objective of analyzing residues expelled by the most difficult weapon platform. The next step in studying the firing positions will be to evaluate the propellant residues ejected by the firing of the tank rifle. As was seen, NG can be found at tank range firing positions, and this finding will have to be evaluated with these medium-caliber weapons.

4.9 Acknowledgements

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4.10 Nomenclature

ACN	acetonitrile
APFSDS	armour-piercing fin-stabilized discarding sabot
°C	degrees Celsius
CFB	Canadian Forces Base
CRREL	Cold Regions Research Engineering Laboratory
2,4-DNT	2,4-dinitrotoluene
DRDC	Defence Research and Development Canada
EL	Environmental Laboratory
FT-IR	Fourier transform infrared
HESH	high energy squash head

HPLC	high pressure liquid chromatography
ICP/MS	inductively coupled plasma/ mass spectrometry
Kg	kilogram
mL	milliliter
mm	millimeter
M/S	meter per second
NG	nitroglycerin
OTP	outside the plume
ppm	parts per million
PTFE	polytretrafluoroethylene
12th RBC	12th Régiment Blindé du Canada
RDDC	Recherche et Développement pour la Défense Canada
R&D	research and development
RDX	research development explosive, heaxahydro-1,3,5-trinitro-1,3,5-triazine
RP-HPLC	reverse-phase high pressure liquid chromatography
SERDP	Strategic Environmental Research and Development Program
SH	squash head
SRTPDS	short range target practice discarding sabot
TPFSDS	target practice fin stabilized discarding sabot
UXO	unexploded ordnance
v/v	volume/volume
VS	visible spectrum
w/w	weight/weight

4.11 References

1. Jenkins, T.F., J.C. Pennington, G. Ampleman, S. Thiboutot, M.R. Walsh, E. Diaz, K.M. Dontsova, A.D. Hewitt, M.E. Walsh, S.R. Bigl, S. Taylor, D.K. MacMillan, J.L. Clausen, D. Lambert, N. Perron, M.C. Lapointe, S. Brochu, M. Brassard, M. Stowe, R. Farinaccio, A. Gagnon, A. Marois, T. Gamache, B. Quémerais, L. Melanson, R. Tremblay, Y. Cuillerier, G. Gilbert, D. Faucher, S. Yost, C. Hayes, C.A. Ramsey, R.J.Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, and S.P. Saari. 2007. C*haracterization and fate of gun and rocket propellant residues on testing and training ranges: Interim report 1*. ERDC TR-07-1. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

2. Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, A.D. Hewitt, S. Brochu, J. Robb, E. Diaz, J. Lewis, H. Colby, R. Martel, K. Poe, K. Groff, K.L. Bjella, C.A. Ramsey, C.A. Hayes, S. Yost, A. Marois, A. Gagnon, B. Silverblatt, T. Crutcher, K. Harriz, K. Heisen, S.R. Bigl, T.E. Berry, Jr., J. Muzzin, D.J. Lambert, M.J. Bishop, B. Rice, M. Wojtas, M.E. Walsh, M.R. Walsh, and S. Taylor. 2006. *Distribution and fate of energetics on DoD test and training ranges: Interim report 6*. ERDC TR-06-12. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

3. Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, A.D. Hewitt, J. Lewis, S. Brochu, E. Diaz, M.R. Walsh, M.E. Walsh, S. Taylor, J.C. Lynch, J. Clausen, , Ranney, T.A., Ramsey, C.A., Hayes, C.A., Grant, C.L., Collins, C.M., Bigl, S.R., Yost, S., and Dontsova, K. 2006. *Distribution and fate of energetics on DoD test and training ranges: Final report*. ERDC TR-06-13. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

4. Jenkins, T.F., S. Thiboutot, G. Ampleman, A.D. Hewitt, M.E. Walsh, , Taylor, , Clausen, J., Ranney, T.A., Ramsey, C.A., Grant, C.L., Collins, C.M., Brochu, S., Diaz, E., Bigl, S.R., and Pennington, J.C. 2006. “Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges”; Chapter 2, SERDP, Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report; ERDC TR-06-13. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

5. Pennington, J. C., Jenkins, T.F., Thiboutot, S., Ampleman, G., and Hewitt, A.D. 2006. “Conclusions”, Chapter 6, Distribution and Fate of Energetics on DoD Test and Training Ranges; Final Report. ERDC TR-06-13. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

6. Pennington, J.C., Jenkins, T.F., Thiboutot, S., Ampleman, G., Clausen, J., Hewitt, A.D., Lewis, J., Walsh, M.R., Ranney, T.A., Silverblatt, B., Marois, A., Gagnon, A., Brousseau, P., Zufelt, J.E., Poe, K., Bouchard, M., Martel, R., Lewis, J., Walker, D.D., Ramsey, C.A., Hayes, C.A., Yost, S., Bjella, K.L., Trepanier, L., Berry, T.E., Lambert, D.J., Dubé, P., and Perron, N.M. 2005. “Distribution and Fate of Energetics on DoD Test and Training Ranges: Report 5,” ERDC TR-05-02. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

7. Ampleman, G., Thiboutot, S., Marois, A., and Gagnon, A. 2009. “Surface Soil Characterization of Explosives and Metals at the Land Force Central Area Training Centre (LFCA TC) Meaford, Ontario (Phase II) Final report; DRDC Valcartier TR 2009-218. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

8. Brochu, S., Diaz, E., Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Hewitt, A.D., Bigl, S.R., Walsh, M.E., Walsh, M.R., Bjella, K., Ramsey, C., Taylor, S, Wingfors, H., Qvarfort, U., Karlsson, R.-M., Ahlberg, M. Creemers, A., and van Ham, N. 2008. “Environmental Assessment of 100 Years of Military Training in Canadian Force Base Petawawa: Phase 1 – Preliminary Evaluation of the Presence of Munitions-Related Residues in Soils and Biomass of Main Ranges And Training Areas.” DRDC Valcartier TR 2008-118. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

9. Diaz, E., S. Brochu, S. Thiboutot, G. Ampleman, A. Marois, and A. Gagnon. 2007. *Energetic materials and metals contamination at CFB/ASU Wainwright, Alberta: Phase I*.DRDC Valcartier TR 2007-385. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

10. Thiboutot, S., A. Marois, A. Gagnon, T. Gamache, N. Roy, C. Tremblay, and G. Ampleman. 2007. *Caractérisation de la dispersion de résidus de munitions dans les sols de surface d'un secteur d'essai*. DRDC Valcartier TR 2007-110. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

11. Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, A. Gagnon, M. Bouchard, T.F. Jenkins, T.A. Ranney, and J.C. Pennington. 2004. "Evaluation of the *contamination by explosives and metals in soils, vegetation, surface water and sediment at Cold Lake Air Weapons Range (CLAWR), Alberta: Phase II, final report*. DRDC Valcartier TR 2004-204. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

12. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T.F. Jenkins, M. Walsh, K. Bjella, C.Ramsey, , and T.A.Ranney. 2004. *Environmental conditions of surface soils, CFB Gagetown Training Area: Delineation of the presence of munitions related residues (Phase III, final report)*. DRDC Valcartier TR 2004-205. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

13. Marois, A., A. Gagnon, S.Thiboutot, G. Ampleman, and M. Bouchard. 2004. *Caractérisation des sols de surface et de la biomasse dans les secteurs d'entraînement, Base des Forces Canadiennes, Valcartier*. DRDC Valcartier TR 2004-206. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

14. Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J. Brannon, J. Clausen, A.D. Hewitt, S. Brochu, P. Dubé, J. Lewis, T.A. Ranney, D. Faucher, A. Gagnon, J.A. Stark, P. Brousseau, C.B. Price, D. Lambert, A. Marois, M. Bouchard, M.E. Walsh, S.L. Yost, N.M. Perron, R. Martel, S. Jean, S. Taylor, C.A. Hayes, J.M. Ballard, M.R. Walsh, J.E. Mirecki, S. Downe, N.H. Collins, B. Porter, and R. Karn. 2004. *Distribution and fate of energetics on DoD test and training ranges: Interim report 4*. ERDC TR-04-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

15. Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, A. Gagnon, M. Bouchard, R. Martel, R. Lefebvre, C. Gauthier, J.M. Ballard, T. Jenkins, T. Ranney, and J. Pennington. 2003. *Evaluation of the impacts of live-fire training at CFB Shilo*: *Final report*. DRDC Valcartier TR 2003-066. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

16. Thiboutot, S., G. Ampleman, A. Gagnon, , and A. Marois. 2000. *Characterization of an unexploded ordnance contaminated range (Tracadie Range) for potential contamination by energetic materials*. Defence Research Establishment-Valcartier (DREV) Report TR-2000-102.

17. Ampleman, G., S. Thiboutot, S. Désilets, A. Gagnon, and A. Marois. 2000. *Evaluation of the soils contamination by explosives at CFB Chilliwack and CFAD Rocky Point*. DREV Report TR-2000-103.

18. Jenkins, T.F., S. Thiboutot, G. Ampleman, A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, C.M. Collins, S. Brochu, S.R. Bigl, and J.C.Pennington. 2005. *Identity and distribution of residues of energetic compounds at military live-fire training ranges*. ERDC TR-05-10. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

19. Pennington, J., T. Jenkins, G. Ampleman, S. Thiboutot, J. Brannon, J. Lewis, J. DeLaney, J. Clausen, A. Hewitt, M. Hollander, C. Hayes, J. Stark, A. Marois, S. Brochu, H. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brousseau, N. Perron, R. Lefebvre, W. Davis, T.A. Ranney, C. Gauthier, S. Taylor, and J.M. Ballard. 2003. Distribution and fate of energetics on DoD test and training ranges: Interim report 3. SERDP Interim Report 3, ERDC TR-03-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

20. Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D., Hewitt, N. Perron, D. Lambert, J. Clausen, , and J. J. Delfino. 2002. *Distribution and fate of energetics on DoD test and training ranges: Interim report 2*. ERDC TR-02-8. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

21. Pennington, J., T. Jenkins, G. Ampleman, S. Thiboutot, J. Brannon, J. Lynch, T. Ranney, J. Stark, M. Walsh, J. Lewis, C. Hayes, J. Mirecki, A. Hewitt, N. Perron, D. Lambert, J. Clausen, and J. Delfino. 2002. *Distribution and fate of energtic on DoD Test and training ranges: Interim report 1*. ERDC TR-01-13. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

22. Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A. B. Gelvin, and T.A. Ranney. 2001. *Sampling for explosives residues at Fort Greely, Alaska: Reconnaissance visit July 2000*. ERDC/CRREL Technical Report, ERDC/CRREL TR-01-15. Hanover, NH: U.S. Army Engineer Research and Development Center.

23. Jenkins, T.F., Pennington, J.C., Ranney, T.A., Berry, Jr., T.E., Miyares, P.H., Walsh, M.E., Hewitt, A.D., Perron, N., Parker, L.V., Hayes, C.A., and Maj. Wahlgren, E. 2001. *Characterization of explosives contamination at military firing ranges*. ERDC TR-01-05. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

24. Ampleman, G., S. Thiboutot, A. Marois, A. Gagnon, and D. Gilbert. 2008. *Evaluation of the propellant residues emitted during 105-mm Leopard tank live firing and sampling of demolition ranges at CFB Gagetown, Canada*. DRDC Report, TR 2007-515. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

25. Ampleman, G., S. Thiboutot, A. Marois, T. Gamache, I. Poulin, B. Quémerais, and L. Melanson. 2008. *Analysis of propellant residues emitted during 105-mm howitzer live firing at the Muffler Installation in Nicolet, Lac St-Pierre, Canada*. DRDC Valcartier TR 2007-514. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

26. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of gun propellant residues from 84-mm Carl Gustav rocket firing*. DRDC Valcartier TR 2007-408. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

27. Jenkins, T.F., A.D. Hewitt, C.L. Grant, S. Thiboutot, G. Ampleman, M.E. Walsh, T.A. Ranney, C.A. Ramsey, A.J. Palazzo, and J.C. Pennington. 2006. "Identity and distribution of residues of energetic compounds at Army live-fire training ranges." *Chemosphere* 63:1280.

28. Dubé, P., S. Thiboutot, G. Ampleman, A. Marois, and M. Bouchard. 2006. *Preliminary assessment of the dispersion of propellant residues from the static live firing of 105-mm howitzer*. DRDC Valcartier TM 2005-284. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

29. Walsh, M.R., S. Taylor, M.E. Walsh, S. Bigl, K. Bjella, T. Douglas, A.B. Gelvin, D. Lambert, N.M. Perron, and S.P. Saari. 2005. *Residues from Live-fire Detonation of 155-mm howitzer rounds*. ERDC/CRREL TR-05-14. Hanover, NH: U.S. Army Engineer Research and Development Center.

30. Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, , and S.P. Saari. 2006. *Energetic residues deposition from 60-mm and 81-mm mortars*. ERDC/CRREL TR 06-10. Hanover, NH: U.S. Army Engineer Research and Development Center.

31. Diaz, E., S. Thiboutot, G. Ampleman, D. Gilbert, D. Faucher, A. Marois, and A. Gagnon. 2007. Assessment of the Gun Powder Residues Dispersed by LG1 Mark II 105-mm and C3 105-mm Howitzers from Static Artillery Firings." Chapter 5 of the SERDP annual report: *Characterization and fate of gun and rocket propellant residues on testing and training range*s. ERDC Report TR 07-01. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

32. Poulin, I., E. Diaz, and B. Quémerais. 2008. *Particulate matter emitted from the M777 howitzer during live firing*. DRDC Valcartier TR 2008-215. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

33. Poulin, I., E. Diaz, , and B. Quémerais. 2008. "Characterization of air emissions from artillery live firing of LG1 Mark II 105-mm and M777 155-mm howitzers." Chapter 11 in *Characterization and fate of gun and rocket propellant residues on testing and training ranges: Final report*. ERDC TR-08-1. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

34. Quémerais, B., E. Diaz, I. Poulin, , and A. Marois. 2007. *Characterization of atmospheric emission produced by live gun firing: Test on the M777 155-mm howitzer*. DRDC Toronto TR 2007-102. Toronto, Quebec: Defence Research and Development Canada – Toronto.

35. Quémerais, B., L. Melanson, G. Ampleman, S. Thiboutot, I. Poulin, and E. Diaz. 2007. *Characterization of atmospheric emissions during live gun firing at the muffler installation in Nicolet, Lac St. Pierre, Canada: Test on howitzer 105 mm*. DRDC Toronto, TR 2007-060. Toronto, Quebec: Defence Research and Development Canada – Toronto.

36. Poulin, I., and E. Diaz. 2009. *Air quality measurements from live-firing of the 105-mm Leopard tank: Study of the gaseous and particulate matter emissions inside and outside a leopard tank*. DRDC Valcartier TR 2009-225. Val Belair, Quebec: Defence Research and Development Canada – Valcartier.

37. Savard, S. 2009. *Émission gazeuse à la bouche d'un canon"; Centre de Recherche Industrielle du Québec*. Contract W7701-7-1924/A, Dossier CRIQ numéro 640-PE35480, Rapport d'étape phase II, essai 2.

38. Walsh, M.R., M.E. Walsh, and C.A. Ramsey. 2007. *Measuring energetic residues on snow*. ERDC/CRREL TR-07-19. Hanover, NH: U.S. Army Engineer Research and Development Center.

39. Walsh, M.E., C.M. Collins, C.A. Ramsey, T.A. Douglas, R.N. Bailey, M.R. Walsh, A.D. Hewitt, and J.L. Clausen, 2007. *Energetic residues on Alaskan training ranges*. ERDC/CRREL TR 07-9. Hanover, NH: U.S. Army Engineer Research and Development Center.

40. U.S. Environmental Protection Agency. 2006. SW846 Method 8330B Nitroaromatics and nitramaines by HPLC. Available at: http://www.epa.gov/epaoswer/hazwaste/test/8330.pdf.

41. Quémerais, B., E. Diaz, I. Poulin, and A. Marois. 2008. *Characterization of atmospheric emissions produced by live gun firing: Test on the Carl Gustav anti-tank, 84 mm weapon*. DRDC Toronto, TR 2007-103. Toronto, Quebec: Defence Research and Development Canada – Toronto.

Appendix 4-A: Snow Results from CRREL

		2,4-DNT			2,6-DNT		Reporting Limits		
Sample Description	Snow Melt Volume (L)	Mass in Snowmelt (mg)	Mass in Soot (mg)	Total Mass in Sample (mg)	Mass in Soot (mg)	Total Mass in Sample (mg)	Mass in Snowmelt (mg)	Mass in Soot (mg)	Mass/m^2
Snow Background in front of tank before firing	1.26	0.000	0.000	0.000	0.0000	0.0000	0.0006	0.0005	0.003
Inside Plume - Surface - Main Area - Rep 1	5.30	0.015	0.815	0.830	0.0090	0.0090	0.0027	0.0015	0.004
Inside Plume - Surface - Main Area - Rep 2	5.98	0.021	0.782	0.804	0.0085	0.0085	0.0030	0.0015	0.004
Inside Plume - Surface - Main Area - Rep 3	5.80	0.025	1.586	1.611	0.0171	0.0171	0.0029	0.0015	0.004
Solid phase extraction (SPE 1)	5.80	0.024		1.610					
Solid phase extraction (SPE 2)	5.80	0.025		1.612					
Solid phase extraction (SPE 3)	5.80	0.025		1.612					
Inside Plume - Subsurface of 09 DRDC-04	1.42	0.001	0.113	0.114	0.0012	0.0012	0.0007	0.0005	0.004
OTP - 0-3 m - Tank side of berm - Rep 1	1.66	0.000	0.012	0.013	0.0000	0.0000	0.0008	0.0005	0.003
OTP - 0-3 m - Tank side of berm - Rep 2	1.54	0.001	0.030	0.030	0.0000	0.0000	0.0008	0.0005	0.003
Plume - Surface - Down slope area - Rep 1	3.22	0.002	0.057	0.059	0.0005	0.0005	0.0016	0.0005	0.002
Plume - Surface - Down slope area - Rep 2	3.16	0.002	0.077	0.079	0.0004	0.0004	0.0016	0.001	0.003
Plume - Surface - Down slope area - Rep 3	3.20	0.002	0.082	0.084	0.0008	0.0008	0.0016	0.0005	0.002
OTP - 0-3 m- Down slope area	2.28	0.000	0.006	0.006	0.0000	0.0000	0.0011	0.0005	0.001
SPE Blank	0.50								

Reporting Limits (mg/L): Aqueous Concentration (mg/L): 0.0005; Mass in Snow Melt (mg): Snow Melt Vol (L) x 0.0005; Solvent Extract Conc (mg/L): 0.05; Mass in Soot (mg): Extract Volume (L) x 0.05

5 Nitroglycerin Fate at a Former Antitank Range Firing Position

*Sonia Thiboutot, Guy Ampleman, Andre Marois, Annie Gagnon, Richard Martel, and Geneviève Bordeleau**

5.1 Abstract

Antitank rockets are propelled by double-base propellants composed of nitroglycerin (NG) embedded in a nitrocellulose (NC) matrix. Very few studies have been conducted on the long-term fate of propellant residues in the environment; this study was undertaken under SERDP project ER-1481 to fill this data gap. The site selected for study was the Carpiquet range, a former antitank range that was closed in 1975. This range is located southeast of the Valcartier training area in Quebec, Canada, along the shores of the Jacques-Cartier River. The rocket range spanned the river with the firing point on the south bank and the target impact area on the north bank. At the firing positions, a fence is located 5 m away, parallel to the former concrete firing wall. The old firing wall is 16 m long with one firing position at each end.

Using multi-increment sampling, five replicate soil samples were collected over a 16-m by 5-m rectangular region located behind the firing wall and samples were also collected in parallel decision units up to 30 m from the fence. Subsurface soils were collected from pits dug with a shovel up to 1 m deep in order to measure the vertical migration of NG with time. Sieving of the soil samples was conducted to determine which fractions held the highest concentrations of NG. The surface concentrations of NG are still at 4,000 mg/kg after more than 25 years of inactivity. Vadose zone monitoring equipment was installed by *Institut National de la Recherche Scientifique – Eau, Terre, et Environnement* (INRS-ETE). Four lysimeters were used for the sampling of interstitial water (depths: 10, 30, 60 cm, and background); their installation provided further information on the subsoil stratigraphy. A trench was also dug for the installation of other water monitoring equipment. High concentrations of NG were detected at the surface and colloidal penetration in the soil profile was also observed,

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while neither NG nor NG degradation products were detected in the interstitial water or underlying groundwater. Data from this study help to understand the long-term effect of NC-based propellant residues in soils. This work demonstrated that the surface soils of legacy sites should be monitored for propellant residues even after years of inactivity, but the risk for the groundwater is low.

5.2 Introduction

Many antitank ranges across Canada and the United States have been characterized up to now, representing the most heavily contaminated ranges in our training areas. Both the impact area and the firing position presented high levels of munitions constituents, namely octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX), trinitrotoluene (TNT) and heavy metals near the targets, with NG at the firing positions [1-9]. NG levels as high as 10,000 mg/kg were detected on the surface soil of the firing position at the Wellington antitank range in Gagetown, New-Brunswick [6; 8]. Trials also have been conducted to evaluate how much NG is deposited by the live firing of antitank munitions. Trials have been conducted using both Carl Gustav 84-mm rockets and M-72 66-mm rockets [10, 11]. Firing of each Carl Gustav 84-mm round generates 20 g of NG deposited mostly behind the rocket firing position, in the direction of the backblast; firing of the M-72 rocket led to approximately 50 mg of NG, again behind the firing position. Both trials demonstrated that 95% of the NG residues are deposited between 5 m and 15 m behind the firing positions, which corresponds to what has been observed in the surface soils behind the firing positions. The aim of the present study conducted by Defence Research and Development Canada – Valcartier (DRDC Valcartier) was to better delineate the contamination by NG and to better understand its long-term fate by collecting subsurface samples at various locations in the contaminated area. INRS-ETE also conducted a study on the fate of NG in groundwater by installing lysimeters in the unsaturated zone of the soil profile and monitoring wells at shallow depth in the water table.

The site selected for this study was the former Carpiquet antitank range, which has been closed since 1975 (Figure 5-1). It is located southeast of the Valcartier training area, along the shore of the Jacques-Cartier River and near the Bouchard Bridge. Firing used to take place over the river with the firing position on the south bank and the target impact area on the north bank. It is now heavily vegetated, and access to the former firing wall and target impact area is forbidden due to the high danger of the piezoelectric fuses in the unexploded ordnances (UXOs) still on this range. A fence is located 5 m behind the former concrete firing wall, thus blocking access to the wall. The old firing wall is 16 m long and has one firing position at each end. In 1998, the vegetation cover was not as thick, and a DRDC Valcartier team sampled the impact area in collaboration with an explosive ordnances disposal (EOD) expert. Sampling was conducted near two former target tanks on the north bank of the river. The GPS location of the targets and the samples were not recorded at that time. Levels of HMX between 5 and 2,000 mg/kg were detected in the surface soils near the targets [3].

Figure 5-1. Carpiquet former firing position.

5.3 Sampling strategy

5.3.1 Sampling team

The sampling was conducted on 12 June 2008 by Sonia Thiboutot, Guy Ampleman, Annie Gagnon, and André Marois from DRDC Valcartier, and by Geneviève Bordeleau and Richard Martel from INRS-ETE. Chief Warrant Officer Savard, EOD expert, joined the sampling team to ensure its safety by conducting UXO clearance/avoidance with a metal detector.

5.3.2 Sampling strategy

In August 2007, soil behind the firing wall was sampled to verify whether NG could still be detected after a closure of more than 30 years. Two field duplicates were collected within a 5-m wide by 16-m long rectangle parallel to and directly behind the firing wall. The sampling area is shown in Figure 5-2. The two samples were collected according to the systematic multi-increment sampling approach (Figure 5-3), using 75 increments per sample. Concentrations of NG in the two samples were 1,280 and 1,113 mg/kg.

The area sampled in 2007 was re-sampled in 2008 using a larger decision unit (DU) that encompassed the total length of the concrete firing wall. The judgmental sampling was conducted in a rectangular DU of 16 m by 5 m along the fence, using 100 increments and collecting five replicates (rep). This decision unit was labeled as DU-A, and samples were labeled S-Car-Rep-1 to 5 (referring to: Soil-Carpiquet-Replicate #). The GPS coordinates of the DU-A limits are presented in Table 5-1, and sample descriptions are presented in Table 5-2.

Figure 5-2. Area sampled in 2007.

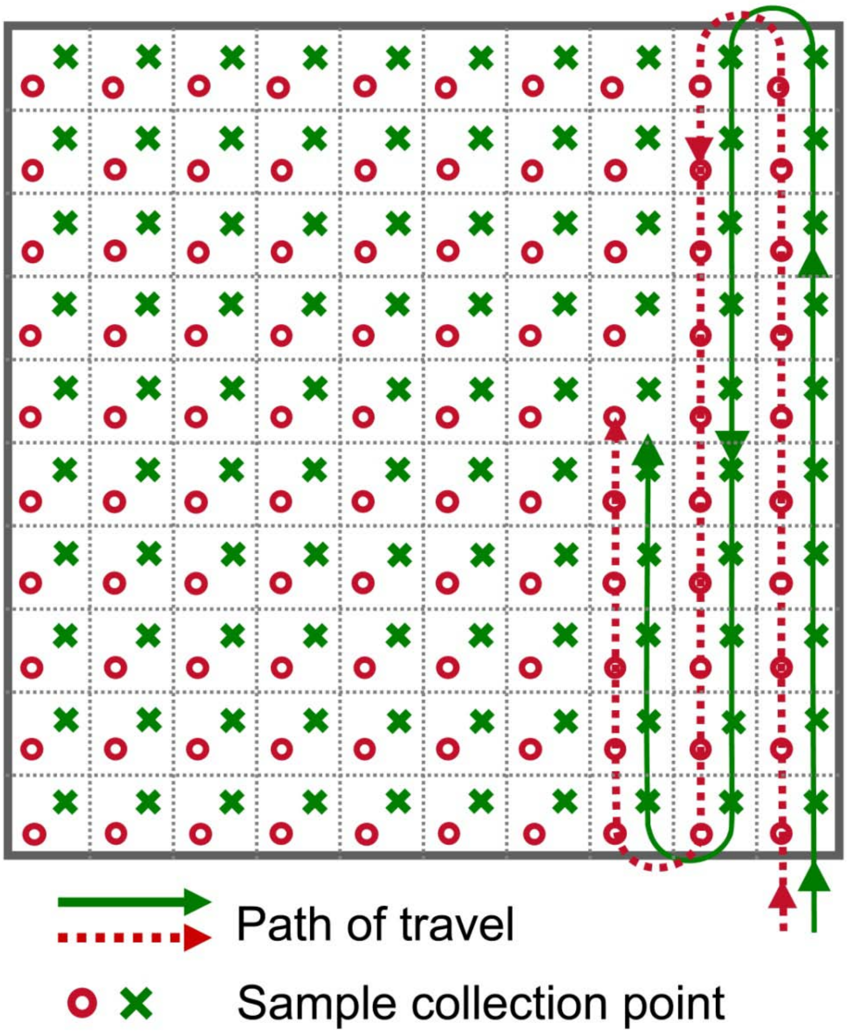

Figure 5-3. Systemtatic multi-increment sampling approach.

Table 5-1. Soil sample GPS locations.

Sample	Characteristic	GPS coordinates
S-Car-P1	Profile sample, location P1	5201628 0309801
S-Car-P2	Profile sample, location P2	5201616 0309793
S-Car-P3	Profile sample, location P3	5201602 0309809
S-Car-P4	Profile sample, location P4	5201615 0309816
S-Car-Limit 1	Limit 1 of decision unit, 16m by 5m	5201628 0309801
S-Car-Limit 2	Limit 2 of decision unit, 16m by 5m	5201616 0309793
S-Car-Limit 3	Limit 3 of decision unit, 16m by 5m	5201602 0309809
S-Car-Limit 4	Limit 4 of decision unit, 16m by 5m	5201615 0309816

Table 5-2. DRDC samples, nomenclature, and description.

Sample	Description	Details
S-Car-Rep- 1	DU-A 16x5m within limits-1234	First replicate/100 sub-samples
S-Car-Rep-2	DU-A 16x5m within limits-1234	Second replicate/100 sub-samples
S-Car-Rep-3	DU-A 16x5m within limits-1234	Third replicate/100 sub-samples
S-Car-Rep-4	DU-A 16x5m within limits-1234	Fourth replicate/100 sub-samples
S-Car-Rep-5	DU-A 16x5m within limits-1234	Fifth replicate/100 sub-samples
S-Car-Rep-6	DU-A 16x5m within limits-1234	Sixth replicate for grain size fractions
S-Car-0-2m	DU-B 16x2m	0-2 m from the fence
S-Car-2-4m	DU-C 16x2m	2-4m from the fence
S-Car-4-6m	DU-D 16x2m	4-6m from the fence
S-Car-6-8m	DU-E 16x2m	6-8 m from the fence
S-Car-6-8m dup	DU-E 16x2m	6-8m from the fence, field duplicate
S-Car-8-10m	DU-F 16x2m	8-10 m from the fence
S-Car-10-12m	DU-G 16x2m	10-12m from the fence
S-Car-10-12m dup	DU-G 16x2m	10-12m from the fence, field duplicate
S-Car-12-14m	DU-H 16x2m	12-14 m from the fence
S-Car-14-16m	DU-I 16x2m	14-16m from the fence
S-Car-16-18m	DU-J 16x2m	16-18m from the fence
S-Car-18-20m	DU-K 16x2m	18-20m from the fence
S-Car-Road ext.	DU-L 16x2m	25-27 m from the fence, across access road
S-Car-P1-0-5cm	Profile sample, location P1	from surface to 5 cm deep
S-Car-P1-5-10cm	Profile sample, location P1	from 5 to 10 cm deep
S-Car-P1-10-15cm	Profile sample, location P1	from 10 to 15 cm deep
S-Car-P1-15-20cm	Profile sample, location P1	from 15 to 20 cm deep
S-Car-P1-20-25cm	Profile sample, location P1	from 20 to 25 cm deep
S-Car-P1-25-30cm	Profile sample, location P1	from 25 to 30 cm deep
S-Car-P1-30-35cm	Profile sample, location P1	from 30 to 35 cm deep
S-Car-P1-35-40cm	Profile sample, location P1	from 35 to 40 cm deep
S-Car-P1-40-45cm	Profile sample, location P1	from 40 to 45 cm deep
S-Car-P1-40-45cm dup	Profile sample, location P1	from 40 to 45 cm deep, field duplicate
S-Car-P1-45-50cm	Profile sample, location P1	from 45 to 50 cm deep
S-Car-P1-45-50cm dup	Profile sample, location P1	from 45 to 50 cm deep field duplicate
S-Car-P1-50-60cm	Profile sample, location P1	from 50 to 60 cm deep
S-Car-P2-0-5cm	Profile sample, location P2	from surface to 5 cm deep
S-Car-P2-5-10cm	Profile sample, location P2	from 5 to 10 cm deep
S-Car-P2-5-10cm dup	Profile sample, location P2	from 5 to 10 cm deep, field duplicate
S-Car-P2-10-15cm	Profile sample, location P2	from 10 to 15 cm deep
S-Car-P2-15-20cm	Profile sample, location P2	from 15 to 20 cm deep
S-Car-P2-20-25cm	Profile sample, location P2	from 20 to 25 cm deep
S-Car-P2-25-30cm	Profile sample, location P2	from 25 to 30 cm deep

Table 5-2 (cont.). DRDC samples, nomenclature and description.

Sample	Description	Details
S-Car-P2-30-35cm	Profile sample, location P2	from 30 to 35 cm deep
S-Car-P2-35-40cm	Profile sample, location P2	from 35 to 40 cm deep
S-Car-P2-40-45cm	Profile sample, location P2	from 40 to 45 cm deep
S-Car-P2-45-50cm	Profile sample, location P2	from 45 to 50 cm deep
S-Car-P2-50-60cm	Profile sample, location P2	from 50 to 60 cm deep
S-Car-P3-0-5cm	Profile sample, location P3	from surface to 5 cm deep
S-Car-P3-5-10cm	Profile sample, location P3	from 5 to 10 cm deep
S-Car-P3-5-10cm dup	Profile sample, location P3	from 5 to 10 cm deep field duplicate
S-Car-P3-10-15cm	Profile sample, location P3	from 10 to 15 cm deep
S-Car-P3-15-20cm	Profile sample, location P3	from 15 to 20 cm deep
S-Car-P3-20-25cm	Profile sample, location P3	from 20 to 25 cm deep
S-Car-P3-25-30cm	Profile sample, location P3	from 25 to 30 cm deep
S-Car-P3-30-35cm	Profile sample, location P3	from 30 to 35 cm deep
S-Car-P3-35-40cm	Profile sample, location P3	from 35 to 40 cm deep
S-Car-P3-40-45cm	Profile sample, location P3	from 40 to 45 cm deep
S-Car-P3-45-50cm	Profile sample, location P3	from 45 to 50 cm deep
S-Car-P3-45-50cm dup	Profile sample, location P3	from 45 to 50 cm deep field duplicate
S-Car-P3-50-60cm	Profile sample, location P3	from 50 to 60 cm deep
S-Car-P4-A	Profile sample, location P4	from 95 to 100 cm deep
S-Car-P4-B	Profile sample, location P4	from 70 to 80 cm deep
S-Car-P4-C	Profile sample, location P4	from 50 to 60 cm deep
S-Car-P4-D	Profile sample, location P4	from 40 to 50 cm deep
S-Car-P4-E	Profile sample, location P4	from 30 to 40 cm dep
S-Car-P4-F	Profile sample, location P4	from 20 to 30 cm deep
S-Car-P4-G	Profile sample, location P4	from 10 to 20 cm deep
S-Car-P4-H	Profile sample, location P4	from 2 to 10 cm deep

Parallel rectangular DUs of 2 m wide by 16 m long were also sampled directly along the fence up to 20 m away from it, at 2-m intervals, to verify the concentration gradient of NG with respect to the distance from the firing position (Figure 5-4 and Figure 5-5). These DUs were labeled DU-B to DU-K, and samples were labeled S-Car-x to y meters and built from 100 multi-increments within each DU. NG deposition studies indicated that most of the contamination was deposited behind the firing position, from 5 to 20 m from the firing position [10, 11], which corresponds to the area sampled in this study. In the middle-left portion of this general area, a dense vegetative cover (circled on Figure 5-5) prevented the soil sampling; therefore, only half the distance (8 m) was sampled on the right-hand portion for DUs E and F.

At the border of these parallel DUs was an access road, and another rectangular DU of 2 m by 16 m was sampled across the access road between 30 and 32 m away from the firing wall. This later DU was labeled DU-L. Figure 5-4 presents a drawing of the Carpiquet site, with the position of the old firing wall, the fence, the DUs sampled, the vegetation cover, and the locations of the four profile samples.

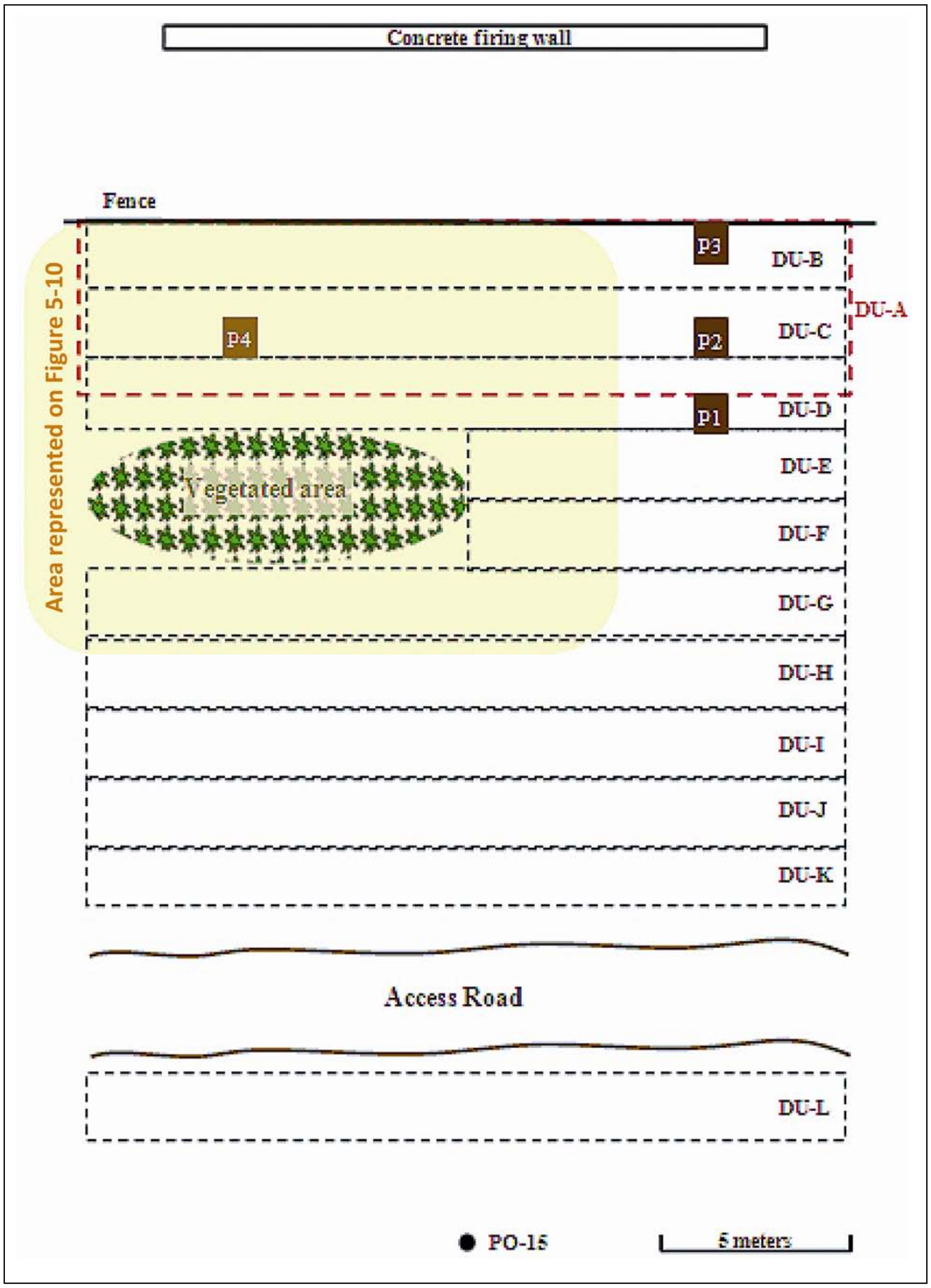

Figure 5-4. Location of soil samples (surface samples DU-A to L) and profile sampling locations (P1 to P4) at Carpiquet, including groundwater monitoring well (PO-15).

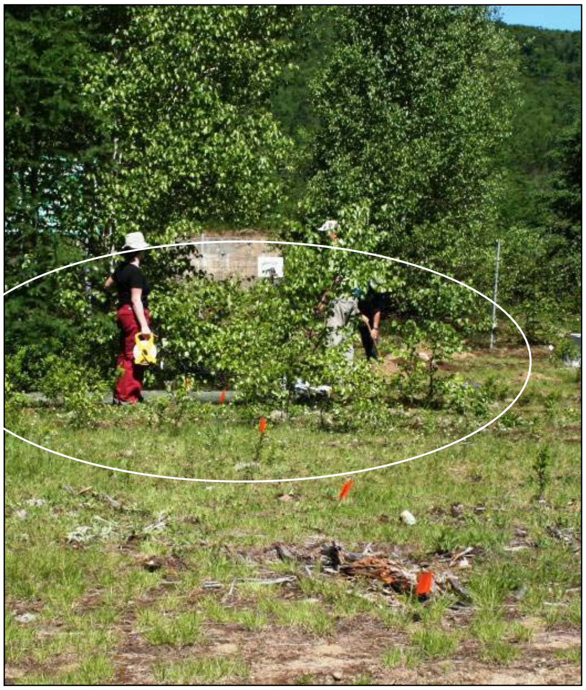

Figure 5-5. Sampling DU-C to DU-H.
The flags delinate the limits of each DU.

Subsurface soils were collected in order to measure the vertical migration of NG with time. Pits were dug using a shovel (Figure 5-6) up to 60 cm deep for three pits (P1–P3) and up to 1 m deep for one pit (P4). Prior to digging, the site was proofed to ensure the absence of metallic UXO using a Forester metal detector Ferex 4.021 (Figure 5-7 and Figure 5-8). To ensure the safety of personnel, the site was proofed prior to digging and then at regular intervals of 15-cm soil layers.

Figure 5-6. Digging for subsurface sampling.

Figure 5-7. Proofing profile sampling location.

Figure 5-8. Forester metal detector used for proofing.

Three profile pits (P1 to P3) were dug at approximately 12, 9, and 6 m from the firing wall, directly behind the right firing position, while P4 was located behind the left firing position approximately 9 m from the wall (Figure 5-4). Table 5-1 – Table 5-3 present information relative to samples collected.

Table 5-3. INRS samples, nomenclature, description, and stratigraphy,

Sample	Description	Details	Soil Stratigraphy
S-Carp-BG-1	Background sample	Surface sample	
S-Carp-BG-2	Background sample	Surface sample	
S-Carp-P1-A	Profile sample, location P1	50-60 cm deep	Fine to medium sand
S-Carp-P1-B	Profile sample, location P1	35-42 cm deep	Black coarse sand, some rust
S-Carp-P1-C	Profile sample, location P1	25-35 cm deep	Coarse sand, gravel, pebbles
S-Carp-P1-D	Profile sample, location P1	15-25 cm deep	Coarse sand, gravel, pebbles, tr. o.m.
S-Carp-P1-E	Profile sample, location P1	5-15 cm deep	Coarse sand, gravel, pebbles, o.m.
S-Carp-P1-F	Profile sample, location P1	0-5 cm deep	Medium to coarse sand, gravel, o.m.
S-Carp-P3-A	Profile sample, location P2	50-60 cm deep	Coarse sand
S-Carp-P3-B	Profile sample, location P2	40-50 cm deep	Coarse sand
S-Carp-P3-C	Profile sample, location P2	30-40 cm deep	Coarse sand, tr. gravel
S-Carp-P3-D	Profile sample, location P2	20-30 cm deep	Med. to coarse sand, tr. gravel, tr. o.m.
S-Carp-P3-E	Profile sample, location P2	10-20 cm deep	Med. to coarse sand, tr. gravel, tr. o.m.
S-Carp-P3-F	Profile sample, location P2	0-10 cm deep	o.m., fine to very coarse sand
S-Carp-P4-A	Profile sample, location P4	95-100 cm deep	Fine sand and silt
S-Carp-P4-B	Profile sample, location P4	70-80 cm deep	Fine sand and silt
S-Carp-P4-C	Profile sample, location P4	50-60 cm deep	Fine sand and silt
S-Carp-P4-D	Profile sample, location P4	40-50 cm deep	Gravel and sand
S-Carp-P4-E	Profile sample, location P4	30-40 cm dep	Gravel and sand
S-Carp-P4-F	Profile sample, location P4	20-30 cm deep	Gravel and sand, tr. o.m.
S-Carp-P4-G	Profile sample, location P4	10-20 cm deep	Gravel and sand, tr. o.m.
S-Carp-P4-H	Profile sample, location P4	2-10 cm deep	Gravel and sand, tr. o.m.
S-Carp-P4-I	Profile sample, location P4	0-2 cm deep	Fine to coarse sand, o.m.
S-North-A*	North wall of trench	70-115 cm deep	Fine to coarse sand, o.m.
S-North-B*	North wall of trench	65-70 cm deep	Med. to coarse sand, some pebbles
S-North-C*	North wall of trench	0-65 cm deep	Med. to coarse sand, gravel, pebbles, stones
S-South-A*	South wall of trench	80-180 cm	Clayey silt

*: Samples marked with an asterisk have undergone NG analyses on the different grain size fractions.

tr. – trace; o.m. – organic matter

Once the pits were dug, the sub-surface sampling was conducted (Figure 5-9). A stainless steel sampling spoon was used to dig perpendicularly into the pit wall in the first three pits (P1 to P3), from the surface to the bottom of the pit. Intervals of soil were collected using a measuring tape as a reference. Samples were collected perpendicular to the edge of the pit, always at the same vertical location. Soil samples were collected at each 5-cm interval down to 50 cm and then at 10-cm intervals from 50 to 60 cm deep. Care was taken to avoid cross-contamination from the wall of the pit. Samples were labeled S-Car-PX, x to y cm, for Soil-Carpiquet-Profile sample from P1, 2, or 3 from x to y cm deep.

Figure 5-9. P1 to P3 (left); collection of the profile samples in P1 (right).

The P4 pit was sampled by the INRS-ETE team from the bottom to the top, and samples were taken mainly at 10-cm intervals down to 100 cm. Samples were labeled S-Car-P4-A to I. INRS-ETE also collected samples from P1, P2, and P3 for analysis of NG degradation products. Following the soil sampling, some equipment for monitoring the vadose zone was installed by INRS-ETE as depicted in Figure 5-10.

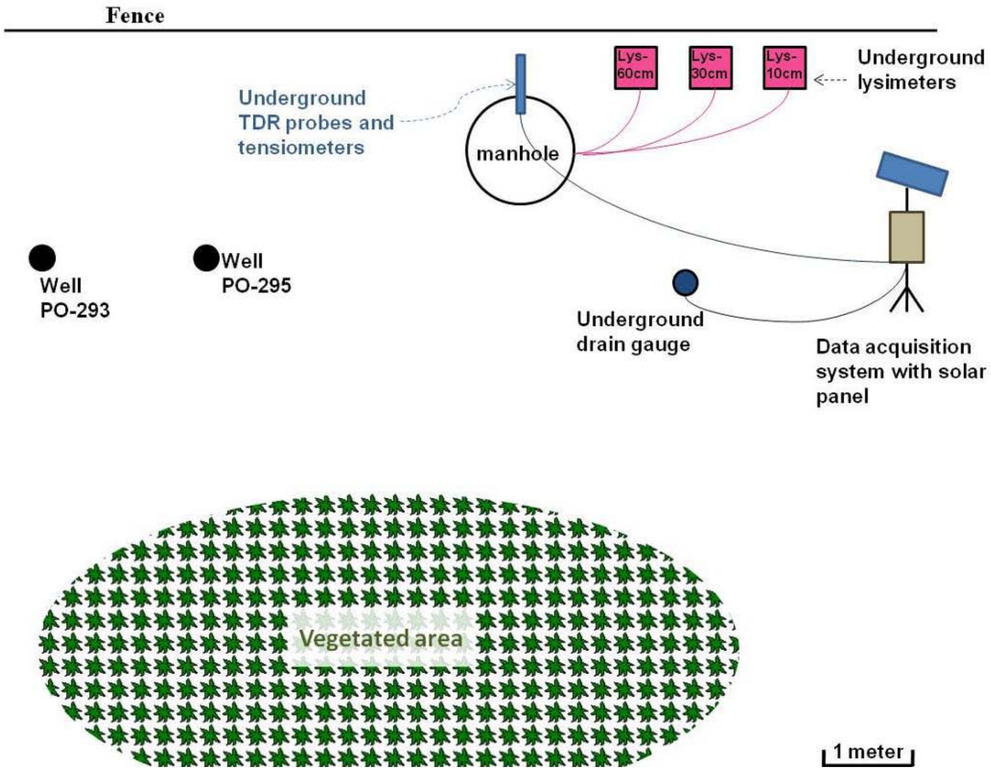

Figure 5-10. Location of groundwater monitoring equipment at Carpiquet (orange-lettered area referred also in Figure 5-4).

Four lysimeters were used for sampling the interstitial water; their installation also provided further information on the subsoil stratigraphy and movement of NG and its degradation products in groundwater from the unsaturated zone. Three lysimeters were installed 6.1 m from the firing wall at depths of 10, 30, and 60 cm below ground surface (Lys-10, Lys-30, Lys-60). The fourth lysimeter was installed as a background (BG) at a location 45 m southeast of the firing wall and at a depth of 40 cm. The lysimeters consisted of boxes made of polyvinylidene fluoride (PVDF), measuring 30 cm in width and length. The height of the box depended on the installation depth. For the 10-cm, 30-cm, and 40-cm (BG) lysimeters, the height was equal to the installation depth which means that the lysimeters extended all the way to the soil surface. For the 60-cm lysimeter, the box extended from 20-cm to 60-cm deep. At the bottom of the boxes, a hole was fitted with a connector, and Teflon tubing was attached to it, running downward through the soil profile and into a permanent access manhole, where it ended in a 10-L glass bottle used for sampling. The boxes were open at the top to allow water to percolate through the lysimeter and reach the Teflon tubing. A small piece of stainless steel screen was put above the tube opening in the box to prevent the tube from getting clogged with sediment (Figure 5-11). During the installation, layers of soil (10-cm deep) were removed successively at the location where the lysimeters were to be installed and placed over plastic tarp. When the lysimeters were put in place at the desired depth, they were backfilled with the local soil layers, in the same order, so as to induce minimal disturbance of the soil profile (Figure 5-12). For the 10-cm lysimeter, the soil was directly backfilled by a slice of soil having the same dimension and thickness as the lysimeter. Figure 5-13–Figure 5-16 present the various stratigraphies encountered. Many sampling campaigns were carried out during the months following installation.

Tensiometers and time domain reflectometry (TDR) probes were also installed to allow monitoring of the soil matrix tension and moisture content, respectively (Figure 5-14). This data can be used to calculate the aquifer recharge rate. When used in conjunction with the concentrations of NG and degradation products from the water samples, the rate of contaminant transfer from the soil to the aquifer can be calculated.

Figure 5-11. Installation of lysimeters at Carpiquet.

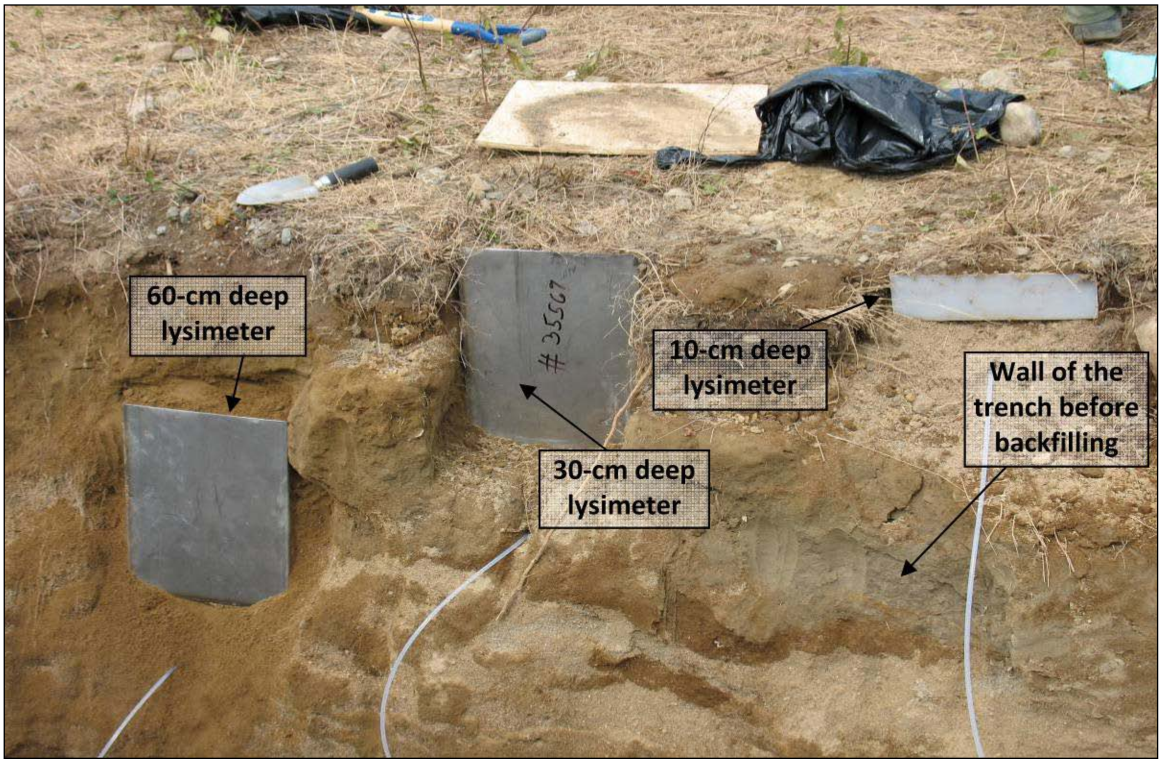

Figure 5-12. Example of lysimeters installed at the same depths as those on Carpiquet.

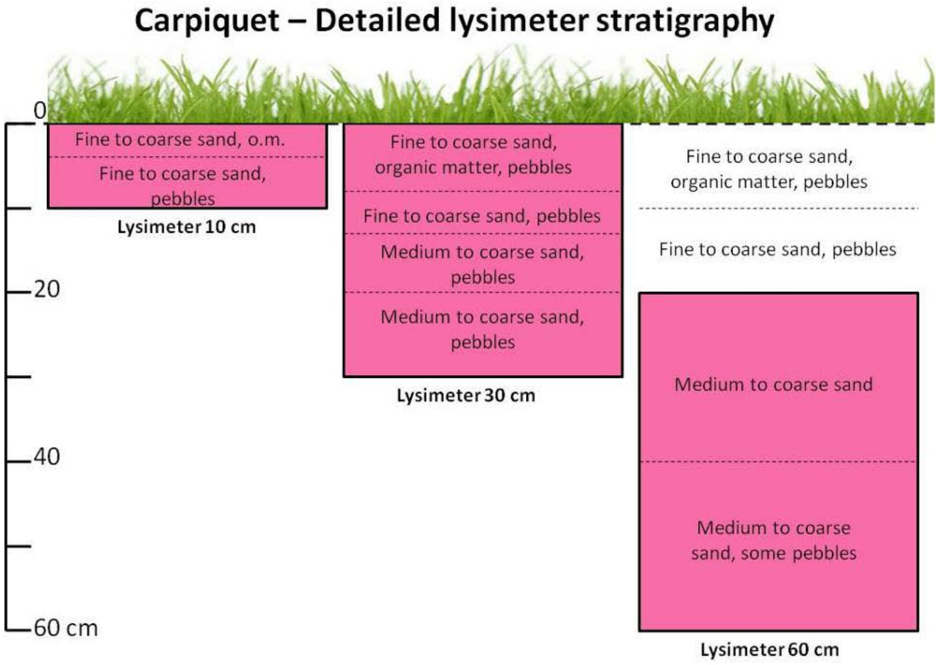

Figure 5-13. Stratigraphy at the three water sampling lysimeters.

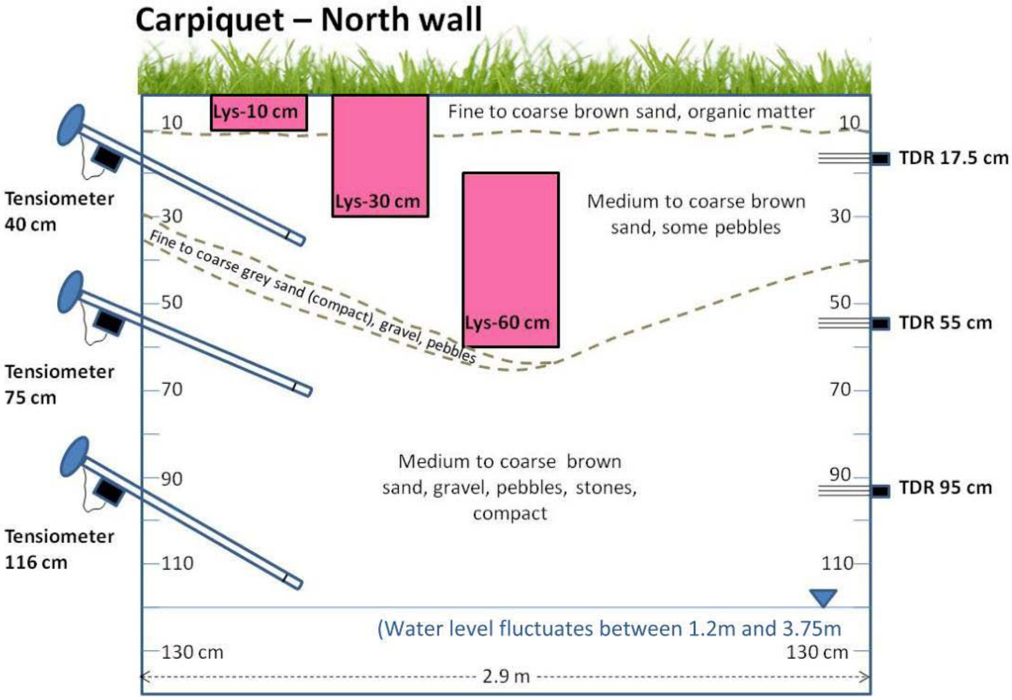

Figure 5-14. North wall stratigraphy of the trench used for the installation of tensiometers and TDR probes.

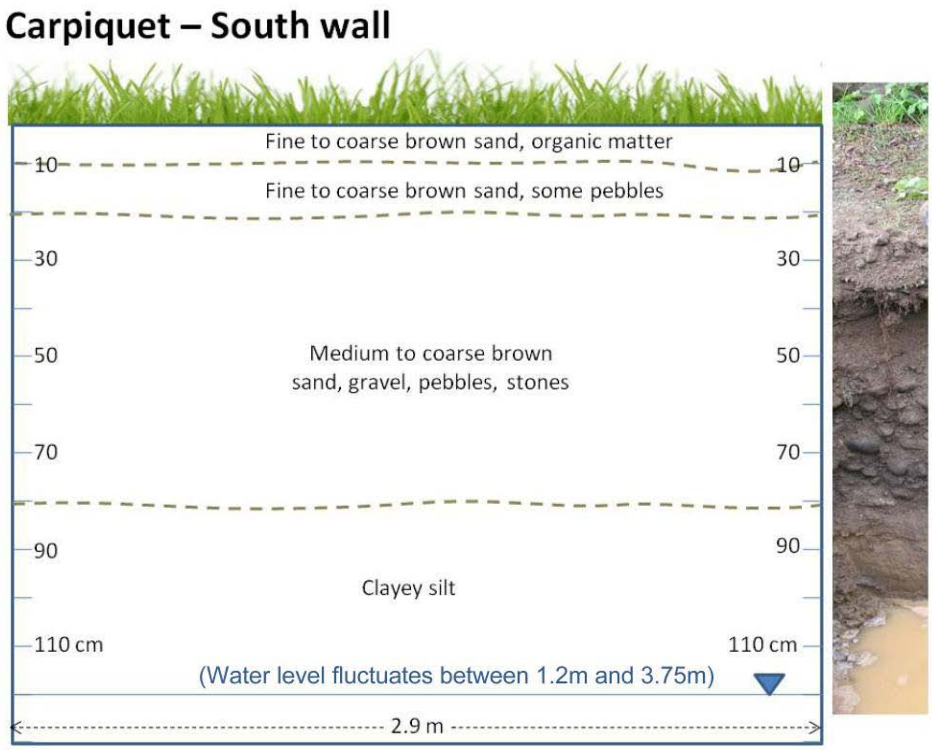

Figure 5-15. Trench south wall stratigraphy.

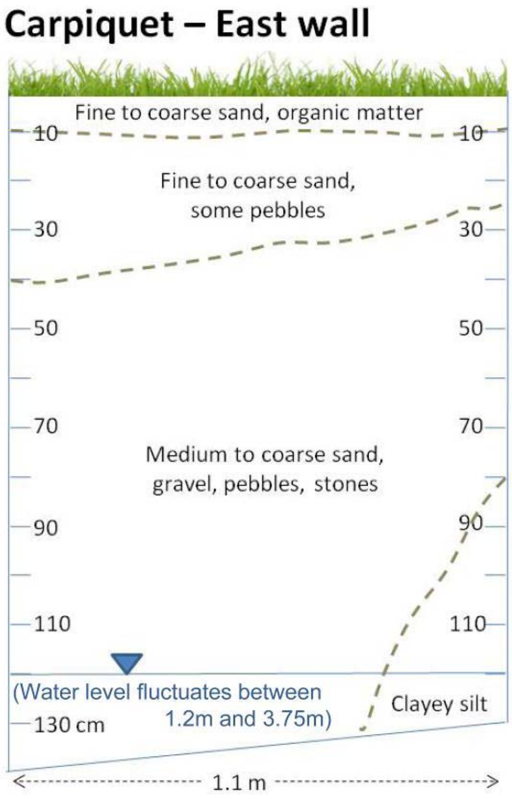

Figure 5-16. Trench east wall stratigraphy.

Finally, three groundwater monitoring wells were installed at the site to allow sampling of water from the saturated zone. Two are located 8.5 m behind the right-hand firing position (PO-293 and PO-295); the other is 35.4 m behind the center of the firing wall (PO-15). All three have a screen length of 1 meter. The depth of the bottom of the screen for each well is the following: 4 m for PO-293, 5 m for PO-295, and 5 m for PO-15. The well depths were chosen to sample the upper part of the saturated zone. Because the water at this site fluctuates significantly, between 1.20 m and 3.75 m, according to measurements made between July 2008 and April 2009, the wells were installed at the minimum depth that would prevent them from drying during the summer. Table 5-4 summarizes the water samples collected from the wells and the lysimeters. The double "x" indicates that a duplicate sample was collected.

Table 5-4. Groundwater samples collected from monitoring wells and lysimeters (INRS).

Sampling Date	Lys-10	Lys-30	Lys-60	Lys-BG	PO-15	PO-293	PO-295
07/11/2008		x		x			
17/12/2008		x					
13/03/2009		x	x	x			x
26/03/2009					x		x
03/04/2009	xx	xx	xx	xx		x	
09/04/2009	xx	x				x	
16/04/2009	xx		x	x			
22/04/2009	x	x		x	x		x
23/04/2009	x		xx				x
27/04/2009	x	xx		x			
28/04/2009	x	x	x			x	
x – single sample collected; xx – duplicate sample collected.							

5.4 Sample processing and analytical method

5.4.1 Sample handling and treatment

A total of 91 soil samples were collected, including 7 field duplicates. The surface soil samples collected in this study were multi-increment composite samples of the top 2 cm of the surface, and were composed mostly of soil including a small proportion of mosses. The soil profile samples were collected at multiple discrete intervals. Samples were stored in polyethylene bags (DRDC Valcartier samples) or glass jars covered with aluminum foil (INRS-ETE samples). Immediately after collection, all samples were placed in coolers, brought back to DRDC Valcartier or INRS-ETE the same day, and either frozen for later analysis (INRS-ETE) or kept in the dark at 4 ^{o}C until their treatment a few days later (DRDC Valcartier).

The soil samples were dried in a hood for 24 hours in the dark and were homogenized by adding acetone to form a slurry, which was then evaporated. Most surface soil samples presented a hard crust layer after the homogenization step, due to the high concentration of NC in the soil matrix (Figure 5-17). This layer was carefully broken with a pestle and the soil was carefully mixed prior to sieving. Soils were sieved through 10-mesh sieves (2 mm) and extracted according to the following procedure.

The dried, homogenized, and sieved samples collected by the DRDC team were analyzed at the DRDC Valcartier laboratory. They were spread out on a flat surface, and small increments from different locations were composed to build a 10-g soil sample for extraction. Ten grams of soil were put into an amber glass vial and mixed with acetonitrile (10 mL). A vortex was applied for one minute, followed by a sonication period of 18 hours in a cooling ultrasonic bath, in the dark. The samples were left to settle for 30 minutes. Acetonitrile (2 mL) was decanted from the vial and diluted with water (2 mL) containing calcium chloride (1%). The solution was filtered on a 0.45 micron filter and a volume of 20 µL was injected into the high-pressure liquid chromatography (HPLC) system.

Figure 5-17. Carpiquet surface soil sample S-Car-Rep-1 after acetone homogenization.

The soil samples collected by the INRS team were analyzed at the hydrogeology laboratory of INRS-ETE. After being dried and homogenized, they were spread out on a flat surface, and small increments were combined to build an 8-g soil sample for extraction. The 8-g soil aliquot was put into an amber glass vial and mixed with 10 mL of dichloromethane. A vortex was applied for 1 minute, followed by a sonication period of 18 hours in a cooling ultrasonic bath, in the dark. The samples were left to settle for 30 minutes. Two mL of the dichloromethane were collected from the vial and filtered on a 0.45 micron filter. The dichloromethane was dry evaporated, and 2 mL of methanol was added. The solution was vortexed and put in an ultrasonic bath for 15 minutes. A volume of 20 µL was collected to inject into the HPLC.

For the water samples collected by the INRS team, a volume of 1 mL of sample was mixed with 1 mL of methanol. The solution was vortexed, filtered on a 0.45 micron filter, and a volume of 20 µL was collected to inject into the HPLC.

5.4.2 Analysis

The soil extracts were maintained at 4°C until analyzed by HPLC according to Method EPA 8330b. At DRDC, analyses were performed with an HPLC Agilent HP 1100 equipped with a degasser G1322A, a quaternary pump model G1311A, an autosampler G1313A, and an ultraviolet (UV) diode array detector model G1315A monitoring at 210, 220, and 254 nm. At INRS, the analyses were performed with an HPLC Agilent HP 1200 equipped with a degasser G1322A, a quaternary pump model G1311A, an autosampler G1329A and a UV diode array detector model G1315D monitoring at 210, 220, and 254 nm. At both labs, the injection volume was 20 µL and the column was a Supelcosil LC-8 (25 cm x 3 mm x 5 µm) eluted with 15:85 isopropanol/water (v/v) at a flow rate of 0.75 ml/min. The column temperature was maintained at 25^{o}C during the analysis. Standards and solvents were diluted 1:1, acetonitrile to water (0.5 mL ACN/0.5 mL water). The quantification limit for this method was 0.1 mg/kg for DRDC and 0.3 mg/kg for INRS. At INRS, the compounds that were analyzed were NG, 1-mononitroglycerin (1-MN), 2-mononitroglycerin (2-MN), 1,2-dinitroglycerin (1,2-DN), and 1,3-dinitroglycerin (1,3-DN).

5.4.3 Sieving

A sixth replicate collected within DU-A by the DRDC team was sieved at INRS to measure the NG content in the various soil fraction sizes. This was undertaken to better characterize the contaminant size partitioning after many years in the environment. A soil mass of 2.4 kg was collected and sieved using the following mesh sizes: 5, 2, 1, 0.5, 0.250, 0.125, 0.053, and 0.02 mm. The sieving process was conducted using a vibrating sieving table, and cold water (4 °C) was used to ease the process. A sample of the water used for sieving was brought back to DRDC and analyzed for its NG concentration. No NG was detected, so the use of water does not appear to interfere with the results. The low temperature of the water, the protective layer of NC, and the short residence time prevented the dissolution of NG. Figure 5-18 shows the sieving apparatus used. Samples were brought back to DRDC, dried, and weighed. Each fraction was then processed for analysis as described in above in the section on sample handling and treatment. A portion of each fraction was kept intact in a cold, dark area and reacted with Expray test kit spray to allow the formation of a reddish color on propellant particles. Pictures of the soil fractions after the Expray spray treatment were taken by using an Olympus stereomicroscope SZ61-Tr. This microscope includes a Greenough optical system and allows high-definition low-distortion three-dimensional color pictures. The pictures were taken using a 20x magnification.

Figure 5-18. Sample sieving at INRS-ETE laboratory for the DRDC sample.

The INRS team also collected four samples (S-Carp-North-A, S-Carp-North-B, S-Carp-North-C, S-Carp-South-A) for analysis of NG and its degradation products on the different grain size fractions. Those samples represent the four different stratigraphic units found within the main trench that was dug to install the probes and access manhole. The mesh sizes of the sieves were 8, 4, 2, 1, 0.5, 0.25, 0.125, and 0.063 mm. As for the DRDC analyses, sieving was conducted using a vibrating sieving table, but no water was used except for cleaning the sieves between samples.

5.5 Results

5.5.1 Surface and sub-surface soils

The NG concentrations in soil samples measured at the DRDC Valcartier laboratory are presented in Table 5-5, while Table 5-6 shows the results obtained for the samples collected and analyzed by the INRS team.

Results obtained for field duplicates from DRDC show a good reproducibility for the large DU using 100 increments with relative standard deviations (RSDs) between field replicates lower than 10%. This demonstrates that the sampling strategy, sample treatment, and homogenization succeeded in overcoming the high spatial heterogeneity of the NG dispersion. The RSD was higher for the replicate from sub-surface sampling or for smaller DUs. The sub-surface samples were discrete samples and the high spatial heterogeneity explains the higher variation encountered.

The mean surface concentration of NG in DU-A was 4,000 ± 400 mg/kg, in an 80-m^2 area located behind the FPs. The environmentally stable NC matrix of the double-base propellant protected NG from degradation for more than 25 years in the soil surface at this location. Figure 5-19 presents the variation in surface concentrations of NG in the decision units DU-B through DU-K. The NG concentrations gradually decrease from 0 m to 8 m then increase between 8 and 12 m, and gradually decrease again after 12 m. If we take into account that the fence (limit of DU-B) is 5 m away from the firing position, the maximum NG concentration is located 15 m behind the firing position; this corresponds to the deposition pattern measured for the 84-mm and 66-mm antitank rocket firing trials [10, 11]. NG was still detected 27 m behind the fence, and levels were increasing slightly from DU-K to DU-L. Historical review of munition usage in this range includes the use of mortar in the area behind the firing position, which could explain the presence of NG at such a distance from the antitank firing position. This would also explain the presence of low concentrations of NG (3 mg/kg) in one of the two background samples collected by INRS at a location 45 m southeast of the firing wall. DU-B and DU-C were encompassed in DU-A, and the concentrations of NG measured in DU-B and DU-C corresponded to the mean concentration measured in DU-A.

Table 5-5. NG concentrations in soil samples (DRDC results).

Sample	NG Concentration (mg/kg)	Sample	NG Concentration (mg/kg)
S-Car-Rep-1 (DU-A)	4683	S-Car-P2-5-10cm	1920
S-Car-Rep-2 (DU-A)	3824	S-Car-P2-5-10cm dup	952
S-Car-Rep-3 (DU-A)	4290	S-Car-P2-10-15cm	1024
S-Car-Rep-4 (DU-A)	4060	S-Car-P2-15-20cm	5
S-Car-Rep-5 (DU-A)	3682	S-Car-P2-20-25cm	0.1
S-Car-0-2m (DU-B)	4534	S-Car-P2-25-30cm	n.d.
S-Car-2-4m (DU-C)	3474	S-Car-P2-30-35cm	n.d.
S-Car-4-6m (DU-D)	2132	S-Car-P2-35-40cm	0.2
S-Car-6-8m (DU-E)	1258	S-Car-P2-40-45cm	0.1
S-Car-6-8m dup (DU-E)	3372	S-Car-P2-45-50cm	0.2
S-Car-8-10m (DU-F)	4418	S-Car-P2-50-60cm	0.1
S-Car-10-12m (DU-G)	4128	S-Car-P3-0-5cm	2732
S-Car-10-12m dup (DU-G)	4456	S-Car-P3-5-10cm	244
S-Car-12-14m (DU-H)	844	S-Car-P3-5-10cm dup	51
S-Car-14-16m (DU-I)	366	S-Car-P3-10-15cm	3
S-Car-16-18m (DU-J)	57	S-Car-P3-15-20cm	382
S-Car-18-20m (DU-K)	22	S-Car-P3-20-25cm	13
S-Car-Road ext. (DU-L)	80	S-Car-P3-25-30cm	13
S-Car-P1-0-5cm	4216	S-Car-P3-30-35cm	5
S-Car-P1-5-10cm	1792	S-Car-P3-35-40cm	51
S-Car-P1-10-15cm	52	S-Car-P3-40-45cm	1
S-Car-P1-15-20cm	6	S-Car-P3-45-50cm	n.d.
S-Car-P1-20-25cm	0.3	S-Car-P3-45-50cm dup	n.d.
S-Car-P1-25-30cm	0.6	S-Car-P3-50-60cm	5
S-Car-P1-30-35cm	10	S-Car-P4-A	7
S-Car-P1-35-40cm	6	S-Car-P4-B	0.2
S-Car-P1-40-45cm	3	S-Car-P4-C	2
S-Car-P1-40-45cm dup	4	S-Car-P4-D	2
S-Car-P1-45-50cm	4	S-Car-P4-E	0.1
S-Car-P1-45-50cm dup	1	S-Car-P4-F	n.d.
S-Car-P1-50-60cm	8	S-Car-P4-G	51
S-Car-P2-0-5cm	2823	S-Car-P4-H	975

Table 5-6. NG concentrations in soil profile samples (INRS results).

Sample	NG (mg/kg)
BG-1 (surface)	3.1
BG-2 (surface)	0
S-Carp-P-1 (A), 50-60 cm	2.4
S-Carp-P-1 (B), 35-42 cm	2.5
S-Carp-P-1 (C), 25-35 cm	3.6
S-Carp-P-1 (D), 15-25 cm	11.7
S-Carp-P-1 (E), 5-15 cm	459
S-Carp-P-1 (F), 0-5 cm	4464
S-Carp-P-3 (A), 50-60 cm	0
S-Carp-P-3 (B), 40-50 cm	0
S-Carp-P-3 (C), 30-40 cm	32.1
S-Carp-P-3 (D), 20-30 cm	3.0
S-Carp-P-3 (E), 10-20 cm	2.9
S-Carp-P-3 (F), 0-10 cm	1346
S-Carp-P-4 (A), 95-100 cm	15.4
S-Carp-P-4 (B), 70-80 cm	0
S-Carp-P-4 (C), 50-60 cm	2.6
S-Carp-P-4 (D), 40-50 cm	8.1
S-Carp-P-4 (E), 30-40 cm	10.9
S-Carp-P-4 (F), 20-30 cm	3.4
S-Carp-P-4 (G), 10-20 cm	15.4
S-Carp-P-4 (H), 2-10 cm	2180
S-Carp-P-4 (I), 0-2 cm	4780

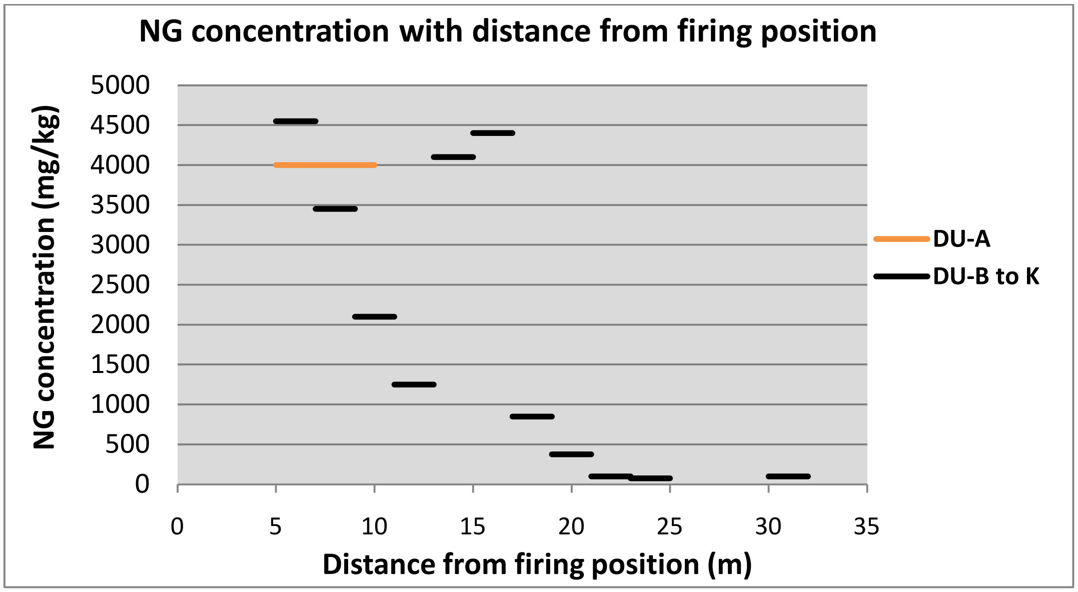

Figure 5-19. NG surface concentrations with distance from the firing position (FP).

The NG concentrations measured by DRDC and INRS in surface samples (depth 0-5 cm) from profiles P1 to P4 varied from 975 to 4,216 mg/kg; these values are within the range of concentrations measured in DU-B to G, where the profile samples were located. The only concentration exceeding those values was from a shallower surface sample in P4 (depth 0–2 cm) collected by INRS (4,780 mg/kg).

Looking at the variation in NG concentration with depth, we see that the concentrations rapidly decreased; in the four locations sampled, most of the NG was detected in the uppermost 15 cm of soil. After a sharp decrease in NG concentration, there was often a slight increase around 30–40 cm (DRDC P1, P3 and INRS P3, P4), and then another slow decrease, as illustrated on Figure 5-20 for location P1 and for three other sites sampled across Canada. For P4, a second increase in concentration was noticed by both INRS and DRDC at a depth of 95–100 cm, but no sample was collected below this depth. This phenomenon has also been observed in active live fire ranges [2; 4; 6] and was attributed to a change in the soil stratigraphy with depth. The slight increase in NG concentration was attributed to a layer of soil which would have presented a higher level of fine soil particles and would therefore stop the migration of fine NC/NG particles. The hypothesis was that the vertical migration of NG in the soil profile would have been driven by particle migration with rain/water infiltration or colloidal transport but not by dissolution/precipitation of NG. The stratigraphy of

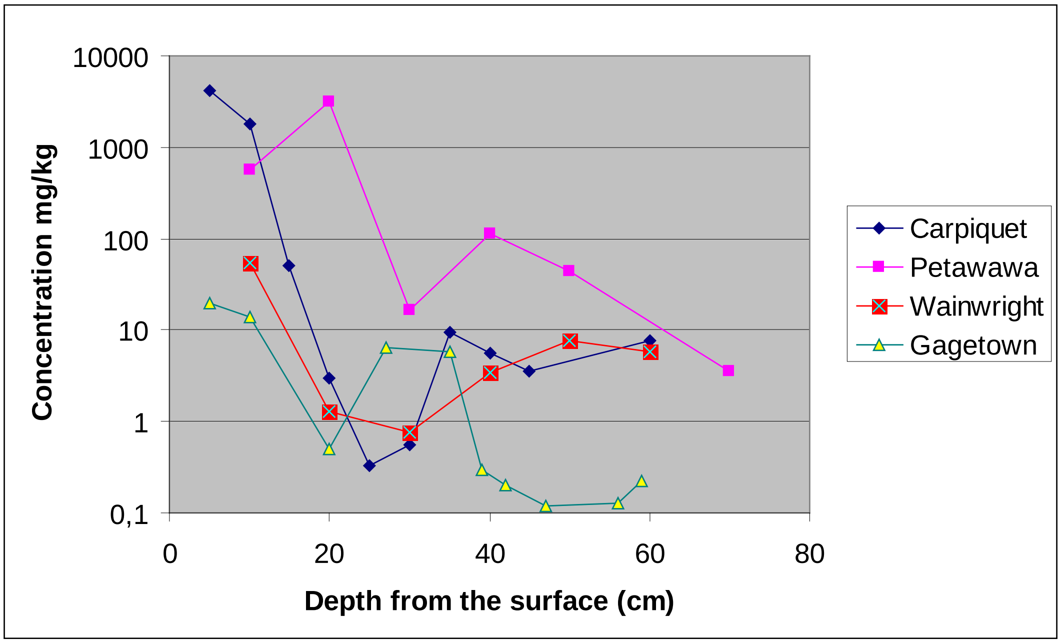

Figure 5-20. Concentrations of NG with depth at four Canadian antitank firing positions.

the Carpiquet soil with depth did not confirm our hypothesis; the soil layer at 30–40 cm did not present the proposed finer grain particles. Another potential explanation now under study is the relation between the hydric equilibrium and the root zone. The soil layer located at approximately 30 cm deep represents the limit of the root zone and this could explain the discrepancy almost always observed at this depth in NG concentrations.

Comparing results from samples collected by DRDC and INRS in pits P1 and P3 is difficult because they were not exactly at the same depths. DRDC collected samples at 5-cm intervals, while INRS collected samples mainly at 10-cm intervals. However, when results from similar depths are compared (taking the average NG concentration in two 5-cm intervals from DRDC and comparing to the corresponding 10-cm interval from INRS), the results are consistent in most cases (Table 5-7). The main differences may be attributed to the fact that samples were discrete rather than composite. Collection of composite samples in soil profiling is therefore recommended for future work. It is also obvious from the results in Table 5-7 that a fine discrimination of samples in the upper layers of soil is very important. In the uppermost 20 cm of soil, although the concentrations in the 10-cm INRS samples represent well the average concentration in the corresponding 5-cm DRDC samples, they fail to detect the high concentrations found in the shallowest DRDC samples. Furthermore, high concentration at location P4 at 0-2 cm (Table 5-6) suggests that a 2-cm interval at the soil surface is relevant, because NG concentration was higher in this sample than in the 0–5 cm samples collected in the other pits.

All soil samples collected by INRS were analyzed for NG and its degradation products. However, degradation products were never detected in any of the samples even though NG was present in high concentration in several samples. This suggests that no degradation is currently taking place, or that, if some limited degradation is taking place, it is happening so rapidly that no intermediate products are detected. The half-life of NG in the environment has been studied by Jenkins et al. [12] and was demonstrated to be very short. NG is rapidly transformed and mineralized in the environment and, therefore, its presence after 25 years in the environment can be explained only by the protection of the NC matrix. The lysimeter study was undertaken to verify if this upper layer of NC/NG particles was still a source of either NG or NG degradation products for groundwater (see the later section discussing groundwater results).

Table 5-7. Comparison of results for soil profile samples collected by INRS and DRDC.

INRS		DRDC		
Sample	NG (mg/kg)	Sample	NG (mg/kg)	Average NG (mg/kg)
S-Carp-P-1 (A), 50-60 cm	2.4	S-Car-P1-50-60cm	8	8
S-Carp-P-1 (B), 35-42 cm	2.5	S-Car-P1-35-40cm	6	6
S-Carp-P-1 (C), 25-35 cm	3.6	S-Car-P1-30-35cm	10	5.3
		S-Car-P1-25-30cm	0.6	
S-Carp-P-1 (D), 15-25 cm	11.7	S-Car-P1-20-25cm	0.3	3.2
		S-Car-P1-15-20cm	6	
S-Carp-P-1 (E), 5-15 cm	459	S-Car-P1-10-15cm	52	922
		S-Car-P1-5-10cm	1792	
S-Carp-P-1 (F), 0-5 cm	4464	S-Car-P1-0-5cm	4216	4216
S-Carp-P-3 (A), 50-60 cm	<d.l.	S-Car-P3-50-60cm	5	5
S-Carp-P-3 (B), 40-50 cm	<d.l.	S-Car-P3-45-50cm dup	<d.l.	
		S-Car-P3-45-50cm	<d.l.	
		S-Car-P3-40-45cm	1	
S-Carp-P-3 (C), 30-40 cm	32.1	S-Car-P3-35-40cm	51	28
		S-Car-P3-30-35cm	5	
S-Carp-P-3 (D), 20-30 cm	3.0	S-Car-P3-25-30cm	13	13
		S-Car-P3-20-25cm	13	
S-Carp-P-3 (E), 10-20 cm	2.9	S-Car-P3-15-20cm	382	192
		S-Car-P3-10-15cm	3	
S-Carp-P-3 (F), 0-10 cm	1346	S-Car-P3-5-10cm	244	1009
		S-Car-P3-5-10cm dup	51	
		S-Car-P3-0-5cm	2732	

<d.l.: below detection limit

5.6 Sample sieving: contaminant partitioning

The masses of each soil fraction, concentration of NG measured, and total NG content of the soil fractions are presented in Table 5-8 and Table 5-9. Figure 5-21–Figure 5-24 present the results as a function of NG concentrations and as a function of total NG masses both for DRDC and INRS.

As mentioned earlier, the sieved sample from DRDC was taken from the soil surface, while INRS sieved four samples, each encompassing the whole depth of the different stratigraphic units present at the site. In the DRDC sample, the highest concentrations and the highest mass of NG were found in the 0.125- to 2-mm fractions (Figure 5-21). In the INRS samples, NG was almost exclusively detected in the sample taken between 0 and 65 cm in depth (north wall of trench). In this case, the highest NG concentrations were found in the 0.063- to 0.5-mm fractions (Figure 5-22). When considering the mass of each grain size fraction within the samples, most of the NG was found in the 0.25- to 2-mm fractions for the DRDC sample (Figure 5-23), while in the INRS samples it was found mostly in the fraction size 0.25 to 0.5 mm (Figure 5-24). This means that over the whole profile between 0 and 65 cm, a greater proportion of NG was detected on finer particles, as opposed to the surface soil sample where NG was detected on a wider range of particle sizes, and mostly on the larger particles. This is supported by the results from the sample taken at 65–70 cm depth, where all of the NG was detected on the 0.25–0.5-mm fraction. This could mean that the vertical migration of NG is due to colloidal small particle movement with water infiltration.

Table 5-8. NG concentrations in soil fractions (DRDC results).

Soil fraction	Soil mass (g)	NG concentration (mg/kg)	NG mass (mg)
> 5 mm	800	0	0
2-5 mm	244	46	11
1-2 mm	727	1474	1071
0.5-1 mm	228	3538	805
0.250-0.5 mm	190	4281	814
0.125-0.250 mm	68	2183	148
0.053-0.125 mm	56	671	38
0.020-0.053 mm	4	538	2
< 0.020 mm	49	54,3	3

Table 5-9. NG concentrations in soil fractions (INRS results).

Identification			Soil mass (g)	NG concentration (mg/kg)	NG mass (mg)
North wall	0-65 cm	< 0.063 mm	3.9	n.a.	n.a.
		0.063 - 0.125 mm	10.6	6.9	0.073
		0.125 - 0.25 mm	28.2	19.2	0.540
		0.25 - 0.5 mm	120.2	28.6	3.443
		0.5 - 1 mm	748.0	1.2	0.925
		1 - 2 mm	826.2	0.2	0.130
		2 - 4 mm	92.8	0	0
		4 - 8 mm	33.6	0	0
	65-70 cm	< 0.063 mm	1.8	n.a.	n.a.
		0.063 - 0.125 mm	20.2	0	0
		0.125 - 0.25 mm	128.9	0	0
		0.25 - 0.5 mm	66.5	0.2	0.013
		0.5 - 1 mm	64.4	0	0
		1 - 2 mm	95.4	0	0
		2 - 4 mm	74.4	0	0
		4 - 8 mm	69.3	0	0
	70-115 cm	< 0.063 mm	40.2	0	0
		0.063 - 0.125 mm	61.2	0	0
		0.125 - 0.25 mm	56.0	0	0
		0.25 - 0.5 mm	25.3	0	0
		0.5 - 1 mm	94.2	0	0
		1 - 2 mm	289.4	0	0
		2 - 4 mm	250.5	0	0
		4 - 8 mm	441.6	0	0
South wall	80-180 cm	< 0.063 mm	253.8	0	0
		0.063 - 0.125 mm	218.9	0	0
		0.125 - 0.25 mm	89.0	0	0
		0.25 - 0.5 mm	0.0	n.a.	n.a.
		0.5 - 1 mm	0.0	n.a.	n.a.
		1 - 2 mm	0.0	n.a.	n.a.
		2 - 4 mm	0.0	n.a.	n.a.
		4 - 8 mm	0.0	n.a.	n.a.
n.a.: non available, because the mass of the soil fraction was too small to allow analysis					

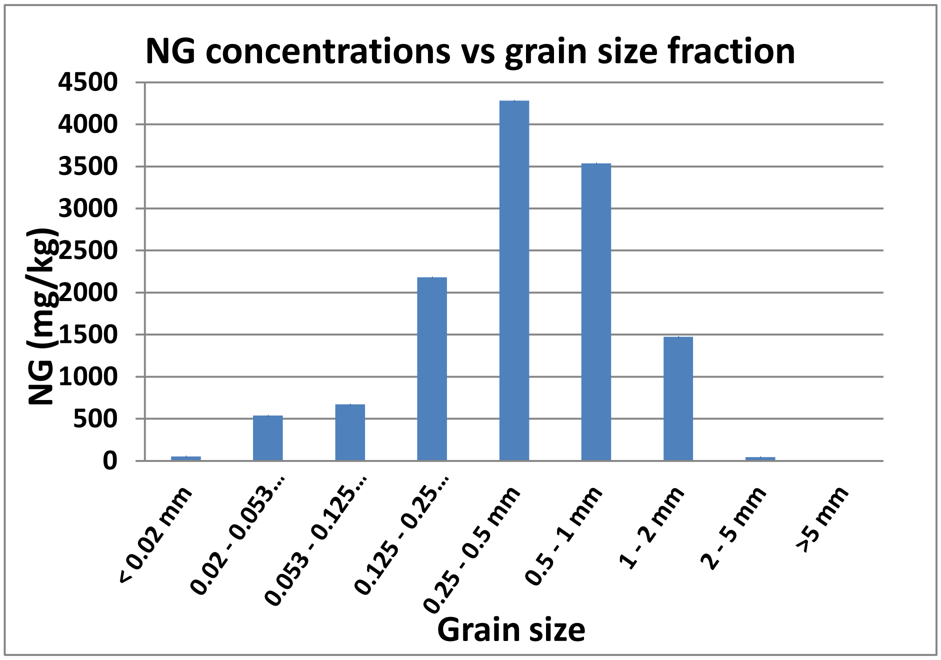

Figure 5-21. Concentrations of NG in soil fractions (DRDC).

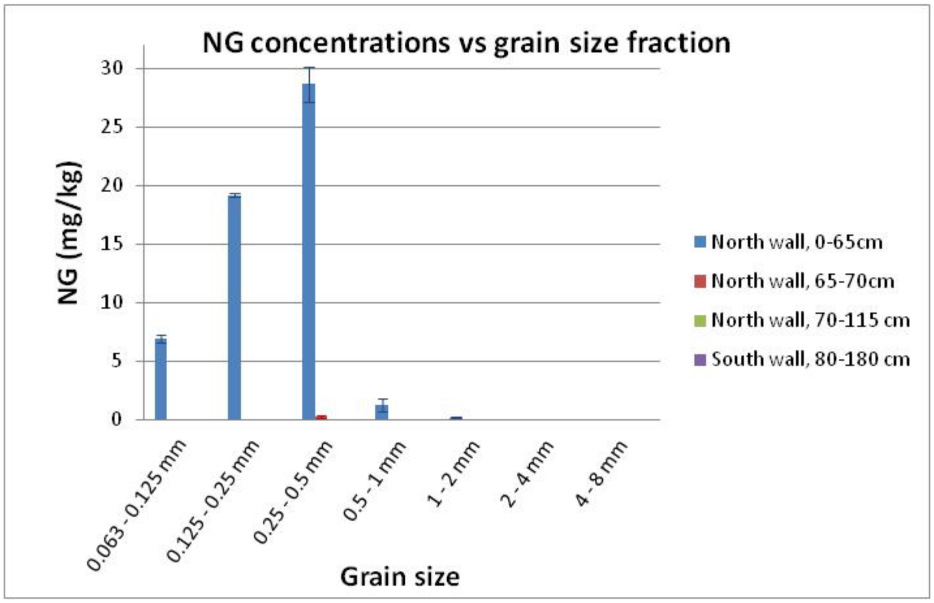

Figure 5-22. Concentrations of NG in soil fractions (INRS).

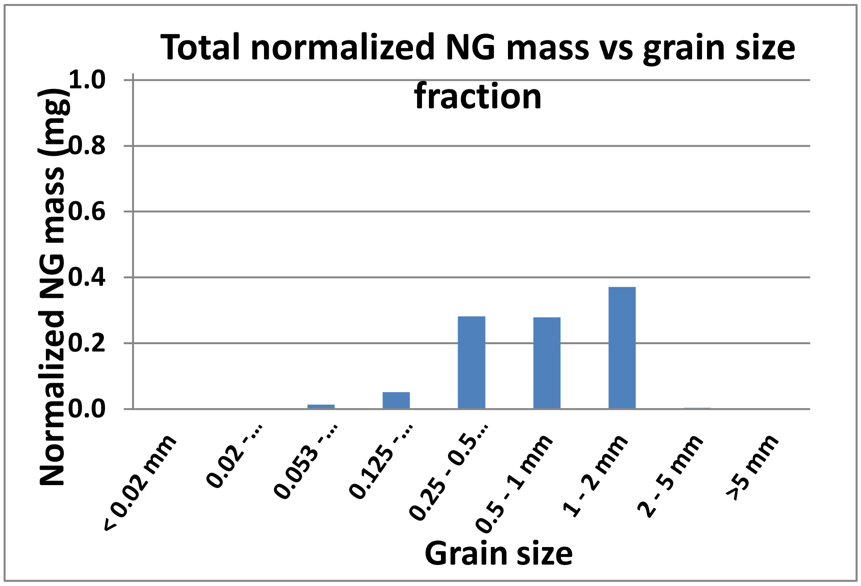

Figure 5-23. Total normalized NG mass in soil fractions (DRDC).

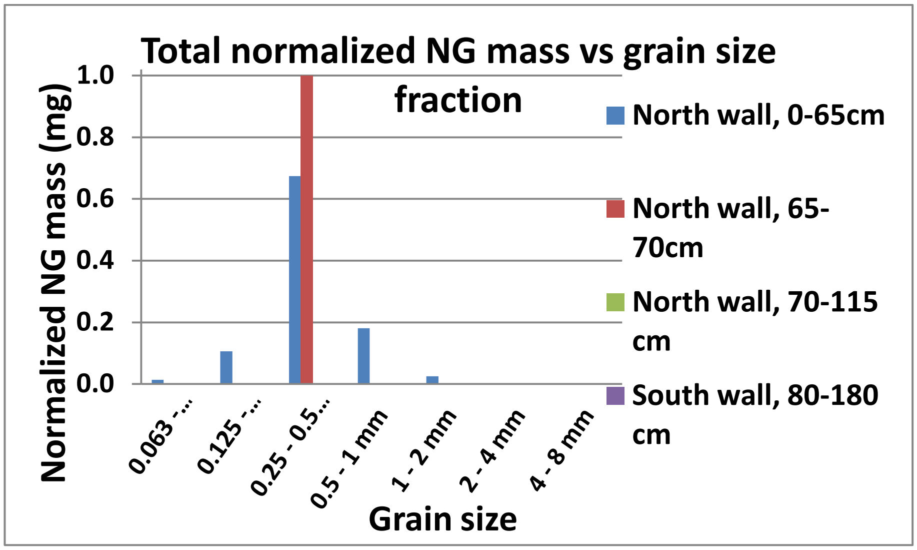

Figure 5-24. Total normalized NG mass in soil fractions (INRS).

Figure 5-25 and Figure 5-26 present representative pictures of propellant particles that were taken after the soil fractions reacted with an Expray kit spray for the reaction of NG content. The propellant particles are easily visible on the pictures and are similar to propellant particles found in active live-fire ranges. The pictures show that NG is embedded in the NC matrix (fibers) and has moved in the soil profile as colloidal solid particles.

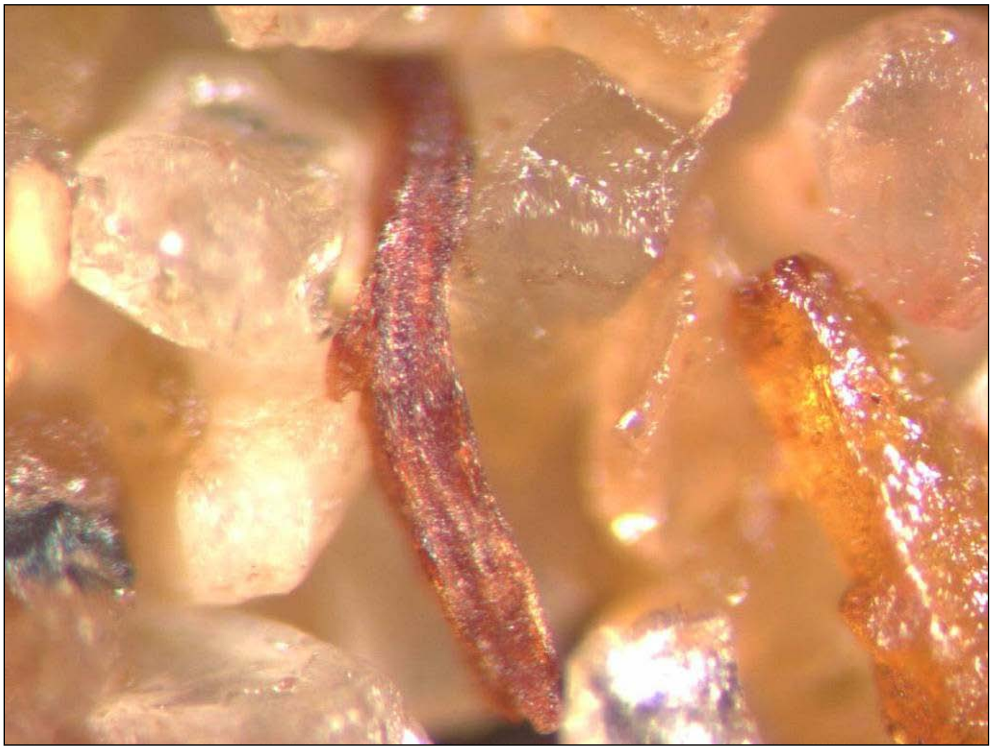

Figure 5-25. A sieved soil fraction between 0.25 and 0.5 mm.

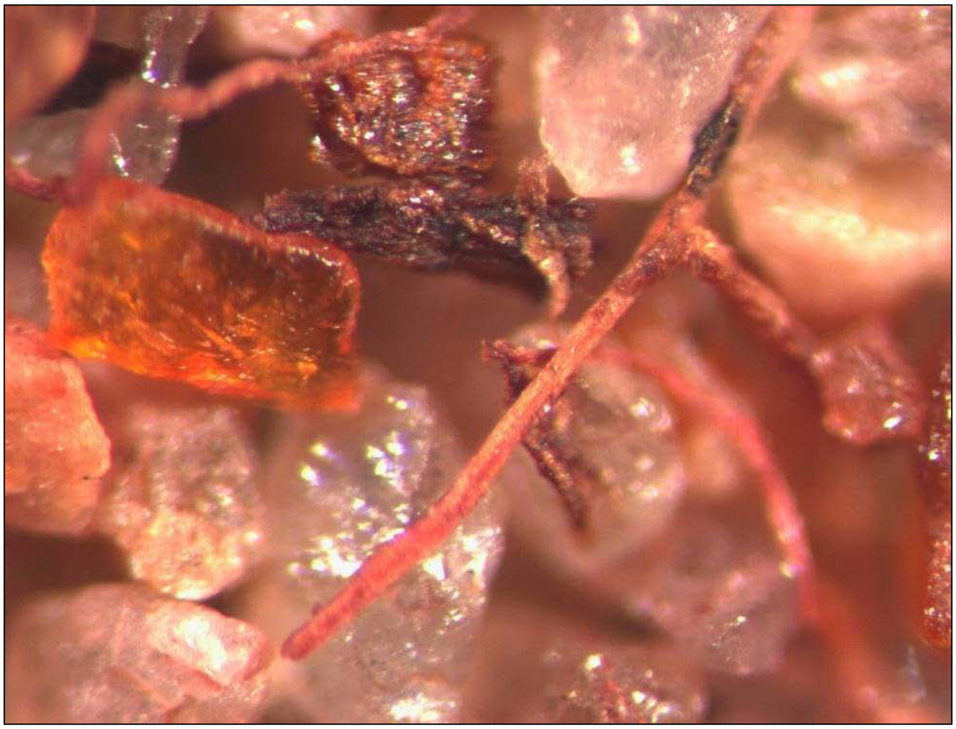

Figure 5-26. A sieved soil fraction between 1 and 2 mm.

5.7 Groundwater

Among all the samples that were collected from the lysimeters and groundwater monitoring wells (see Table 5-4), neither NG nor its degradation products were detected. In all cases, the detection limit was equal to or below 3 µg/L. The absence of NG in groundwater confirms that NG at this site is stable in soils due to the protection of the NC matrix. NG can only be detected in soils because it is being extracted from the soil grains and NC matrix using acetone or dichloromethane.

The background lysimeter (Lys-BG) was installed to monitor the natural nitrate load in groundwater and to compare it with samples from the other lysimeters (Lys-10, Lys-30, and Lys-60). If NG had been detected in groundwater, it is possible that nitrate concentrations would have been higher than the expected natural concentrations. Indeed, it was demonstrated that the degradation of NG releases nitrite (NO_2^-), which can be oxidized to nitrate (NO_3^-) in the presence of oxygen [13]. However, NG was not detected in any of the samples, and nitrate concentrations were both comparable in all lysimeter samples and within the range of expected natural concentrations.

5.8 Conclusion

The present study of the Carpiquet range was undertaken to better understand the long-term fate of propellant residues in the environment. It was found that, when deposited as propellant residue in a NC matrix, NG is highly persistent in the environment and is still detected at levels of 4,000 mg/kg behind the firing position of a former antitank range, after more than 25 years of inactivity. Most of the NG is still present at the soil surface, while soil penetration of NG is measured up to 1 m deep. The NG concentrations decrease with depth, with a small re-increase in concentrations around 30 cm deep, as observed in active antitank firing ranges. This was believed to be due to soil stratigraphy, but our results showed no correlation between the soil size fraction and this increase. The discrepancy always observed around this depth could be explained by the root zone limit and hydric equilibrium, which would result in a slight increase of contaminant concentration at the root zone limit.

At the soil surface, most of the NG is within solid particles of a size between 0.25 and 2 mm. At depth, most of the NG mass was found within the 0.25- to 0.5-mm fraction. This suggests that the vertical migration of

NG is mostly due to the migration of small particular propellant grains or colloidal migration, and has probably represented a slow NG desorption source in the past, when surface NG was still available for desorption from the NC matrix. Results from the lysimeters installed on the site demonstrated that neither NG nor NG degradation products are detected in the infiltrated water. This means that the site is at equilibrium, and all the NG that was bio-available had leached in the past, and the remaining NG is irreversibly entrapped in the NC matrix.

These conclusions are applicable to former antitank ranges that are included in legacy training ranges over North America. This means that the firing positions of these ranges might still present high concentrations of NG in the surface soils, and depending on the future uses of these sites, it might represent a threat to human health. However, with time, all the NG that was leachable from the NC-based propellant grains has been washed out, and the risk for groundwater is considered low.

5.9 Acknowledgements

The authors want to acknowledge CWO Savard from Munitions Experimental Test Center Valcartier for the proofing for UXO avoidance of the sub-surface sampling locations that ensured a safe sampling campaign. The Land Force Quebec Area Training Centre range control team is also acknowledged for the safe access to the former antitank range. Finally, the authors would like to thank Clarisse Deschênes-Rancourt and Richard Lévesque, from the INRS, for performing some of the laboratory analyses.

5.10 Nomenclature

BG	background
Car or Carp	Carpiquet range
DU	decision unit
DRDC	Defence Research and Development Canada
EOD	explosive ordnances disposal
ER	Environmental Restoration
FP	firing position
HPLC	high pressure liquid chromatography
INRS-ETE	Institut National de la Recherche Scientifique – Eau, Terre, et Environnement
Lys	lysimeter
NC	nitrocellulose
NG	nitroglycerine
HMX	octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine
o.m.	organic matter
PVDF	polyvinylidene fluoride
Rep	replicate
R&D	research and development
SERDP	Strategic Environmental Research and Development Program
TDR	time domain reflectometry
tr	trace amounts
TNT	trinitrotoluene
UV	ultraviolet
UXO	unexploded ordnance
v/v	volume/volume

5.11 References

1. Ampleman, G., S. Thiboutot, A. Marois, and A. Gagnon. 2008. *Evaluation of the contamination by explosives and metals in soils at the Land Forces Central Area Training Centre (LFCATC), Meaford, Ontario (Phase I)*. DRDC Valcartier TR 2008-390.

2. Brochu, S., E. Diaz, S. Thiboutot, G. Ampleman, A. Marois, A. Gagnon, A.D. Hewitt, S.R. Bigl, M.E. Walsh, M.R. Walsh, K. Bjella, C. Ramsey, S. Taylor, H. Wingfors, U. Qvarfort, R.M. Karlsson, M. Ahlberg, A. Creemers, and N. van Ham. 2008. *Environmental assessment of 100 years of military training in Canadian Force Base Petawawa: Phase 1 – preliminary evaluation of the presence of munitions-related residues in soils and biomass of main ranges and training areas*. DRDC Valcartier TR 2008-118.

3. Thiboutot, S., G. Ampleman, A. Marois, and A. Gagnon. 2008. *Caractérisation des sols de surface du champ de tir et secteurs d'entraînement de la garnison Valcartier*. DRDC Valcartier TR 2008-190.

4. Diaz, E., S. Brochu, S. Thiboutot, G. Ampleman, A. Marois, and A.Gagnon. 2007 *Energetic materials and metals contamination at CFB/ASU Wainwright, Alberta(Phase I)*.DRDC Valcartier TR 2007-385.

5. Ampleman, G., S. Thiboutot, R. Martel, C. Edlund, R.M. Karlsson, M. Alhberg, J. Sjöström, U. Qvarfort, K. Bladfält, N. Van Ham, and W.Duvalois. 2005 *Evaluation of the contamination by explosives and metals in soils at the Älvdalen Shooting Range: Part 1 investigation strategies and sampling*. FOI Report 1619-SE.

6. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, K. Bjella, C. Ramsey, and T.A.Ranney. 2004. *Environmental conditions of surface soils, CFB Gagetown Training Area: Delineation of the presence of munitions related residues (Phase III, final report)*. DRDC Valcartier TR 2004-205.

7. Marois, A., A. Gagnon, S. Thiboutot, G. Ampleman, , and M. Bouchard. 2004. *Caractérisation des sols de surface et de la biomasse dans les secteurs d'entraînement, Base des Forces Canadiennes, Valcartier*. DRDC Valcartier TR 2004-206.

8. Thiboutot, S., G. Ampleman, J. Lewis, D. Faucher, A. Marois, R. Martel, J.M. Ballard, S. Downe, T. Jenkins, and A.Hewitt. 2003. *Environmental conditions of surface soils and biomass prevailing in the training area at CFB Gagetown, New Brunswick*. DRDC Valcartier TR 2003-152.

9. Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, A. Gagnon, M. Bouchard, R. Martel, R. Lefebvre, C. Gauthier, J.M. Ballard, T. Jenkins, T. Ranney, and J.Pennington. 2003. *Evaluation of the impacts of live fire training at CFB Shilo (final report)*. DRDC Valcartier TR 2003-066.

10. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of gun propellant residues from 84-mm Carl Gustav rocket firing*. DRDC Valcartier TR 2007-408.

11. Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, and D. Gilbert. 2009. *Nitroglycerine deposition from M-72 antitank rocket firing*. DRDC Valcartier TR 2009-003, February 2009.

12. Jenkins, T. F., C. Bartolini, and T.A. Ranney. 2003. *Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in moist, unsaturated soil.* ERDC/CRREL TR-03-7, April 2003.

13. Martel, R., and G. Bordeleau. 2009. *Batch tests on RDX and NG degradation processes, and isotopic characterization of the resulting nitr*ate. INRS Research Report R-967 for the Ministry of National Defence.

6 Environmental Fate and Transport of Nitroglycerin from Propellant Residues at Firing Positions in the Unsaturated Zone

Aurélie Bellavance-Godin, Richard Martel, Guy Ampleman,
and Sonia Thiboutot

6.1 Abstract

The fate and transport of propellants at military firing positions was examined in this study. The study focused on characterizing the impact on soil and groundwater at antitank firing points. The munitions utilize double-base propellants containing nitrocellulose (NC) and nitroglycerin (NG) with some munitions containing up to 7.8% potassium perchlorate ($KClO_4$). The compounds of interest were NG and its metabolites and perchlorate. A solid phase extraction method coupled with high-pressure liquid chromatrography-ultraviolet (HPLC-UV) analysis was developed to monitor both NG and its degradation products in the water samples. The soil from two firing positions was examined. Initial concentrations of NG and perchlorate were 3145 mg/kg, and 3.52 ug/kg for the Gagetown/Valcartier columns, and 5652 mg/kg and 53.5 ug/kg for the Petawawa columns. Nitrite and nitrate initial concentrations were 307 mg/kg and 296/mg/kg and 483 mg/kg and 634 mg/kg respectively. Water was applied to the columns following the recharge patterns of their respective locations. Effluent of the columns was sampled to evaluate the contaminants transport through the unsaturated zone. High concentrations of NG, dinitroglycerol (DNG), mononitroglycerol (MNG), nitrites, and nitrates were detected in the Gagetown column effluent. All the mobile fractions of these compounds were flushed out of the soil column within a 1-year period of infiltration. In the Petawawa columns, no nitrite, NG, DNG, nor MNG was detected in the effluent of the columns. Only perchlorate and nitrate, mainly from oxidation of nitrite through degradation of NC, NG, MNG, and DNG, were detected in the effluent. Groundwater in the unsaturated zone under antitank firing position may be contaminated by dissolved NG, NG metabolites, nitrite, nitrate, and

perchlorate. However, in the saturated zone, the concentrations of these pollutants are diluted by the flowing groundwater.

6.2 Introduction

The use of energetic materials is central to the training of military personnel for combat operations. During live-fire training, these materials are not fully consumed, leading to deposition and accumulation of energetics on training lands. In the last decade, increased environmental awareness has led the Canadian Forces to undertake studies to evaluate the environmental impact of military activities such as live firing on training ranges on soil and water.

The main goal of this project is to study the fate of propellant residues on large soil columns, as no data were available in the literature on this topic, with the exception of two studies conducted on a smaller scale (Mirecki 2006; Hewitt and Bigl 2005). Soils from firing positions sampled in various training ranges across North America have proven to be impacted with high levels of NG from shoulder-fired rocket and small arm propellants or 2,4-Dinitrotoluene (2,4-DNT) from artillery or tank live firings (Dubé et al. 2006; Faucher et al. 2008).

This study was aimed at characterizing the impacts of military activities on water quality at antitank firing positions. The sites selected for the study were at Garrison Valcartier, Québec, and at CFB Petawawa, Ontario. The type of ammunition used in antitank ranges includes the M-72 66-mm or 84-mm Karl Gustav shoulder-fired rockets, containing a double-base propellant with 54.6% NC, 35.5% NG, and 7.8% $KClO_4$, used as an oxidant (Hewitt and Bigl 2005) in the 66 mm whereas no $KClO_4$ is added in the 84 mm. NG is a highly toxic substance used as an energetic plasticizer for both gun and rocket propellants (Christodoulatos 1997). The combustion processes in the rockets is incomplete and results in the deposition and accumulation of propellant residues at the soil surface. Approximately 14% of NG in the Karl Gustav ammunition and 0.2% for the M-72 remains at the firing position in the form of residual propellant (Jenkins et al. 2007; Thiboutot et al. 2007, 2009). The difference could be related to the formulation, but could also be explained by the fact that the two weapons have differently designed combustion chambers. Furthermore, the polymeric NC matrix protects the NG, as its environmental half-life has been determined to be less than a day (Jenkins 2003). NC leads to slow desorption processes of the embedded energetic materials. The compounds of interest were NG, its metabolites (1,2-dinitroglycerine, 1,3-dinitroglycerine, 1-mononitroglycerine, 2-mononitroglycerine, nitrites, and nitrates), and perchlorate. NC is not included because it is considered non-toxic and not soluble. NG has no U.S. Environmental Protection Agency (EPA) or Environment Canada guidelines for drinking water or soil quality. However, the National Research Council of Canada has set preliminary human health guidelines on military bases of 2500 mg/kg for soil and 280 µg/L for water, and a guideline of 7.8 mg/kg in soil for groundwater protection (Robidoux et al. 2006).

For the purpose of the study, the soils from two firing positions containing propellant residues were spread on the surface of four columns containing uncontaminated sand from the Arnhem training range of CFB Valcartier and from CFB Petawawa. The soils were watered following the recharge patterns of their respective region, and interstitial water output of the columns was sampled in order to evaluate the contaminants fate and transport through the unsaturated zone.

6.3 Soil and propellant sampling methodology

Sampling was conducted in two steps. The first was collecting uncontaminated soil samples representative of the geological formations of the two contaminated sites (Valcartier and Petawawa); the second was collecting soils containing high levels of propellant residues behind antitank firing positions, which were later spread across the surface of the uncontaminated soil columns. The contaminated soils were collected at CFB Petawawa and CFB Gagetown.

6.4 Uncontaminated soil sampling

The uncontaminated soil samples used in the column tests were representative of the soil at the two antitank firing positions. The Petawawa uncontaminated soil sample was collected outside of the impact area, east of the Trans-Canadian highway, and put into six 200-L drums. Prior to sampling, the six drums were cleaned using acetone and distilled water to eliminate any trace of contamination that may have potentially occurred in past usage. To ensure collection of a homogeneous sample during filling, shovels of soil were alternately distributed in the six drums. These soils were used in the laboratory to fill two columns.

The Valcartier uncontaminated soil was collected in a sand pit next to the Arnhem antitank training range but outside of the danger template of the weapon. Three 200-L drums of soil collected by Lewis (Lewis 2007), as well as three other similar drums, were filled according to the above procedure and were used to fill three sand columns in the laboratory.

The clean soils from both locations were tested for NG, perchlorate, nitrite, and nitrate content by using the analytical methods described in the following section. The clean soils showed none of the products.

6.5 Propellant residues sampling

The soils containing high levels of propellant residues were collected on training range A of CFB Petawawa and at the Wellington training range of CFB Gagetown. The soil with residues from Wellington Range replaced those from the originally planned CFB Valcartier Arnhem Range, because a gravel pad had been laid over the firing position at CFB Valcartier, thus making the sampling of residues impossible. The residues from Gagetown (considered equivalent to those of Valcartier) were placed on clean soil from Valcartier.

The Gagetown propellant residues were collected from firing positions 1 and 2 of the Wellington Range. The residues were collected over a thickness of approximately 1 to 2 cm using a stainless steel spoon (Figure 6-1). Sampling was performed 1 m behind the firing positions. Sampling at firing position 1 was done within an area having a length of 3 m and a width of 2 m, for a triangular sampling pattern of approximately 3 m^2 (Figure 6-2), while sampling at position 2 was done over an area of approximately 7.5 m^2. Three 20-L pails, previously washed with acetone and distilled water, were filled. The soil was sieved at the *Institut National de la Recherche Scientifique* (INRS) in order to eliminate grain size fractions larger than 5 mm. The final volume of propellant residues mixed with soil was approximately 10 L.

Figure 6-1. Sampling propellant residues at firing position 2 of the Wellington antitank range, CFB Gagetown.

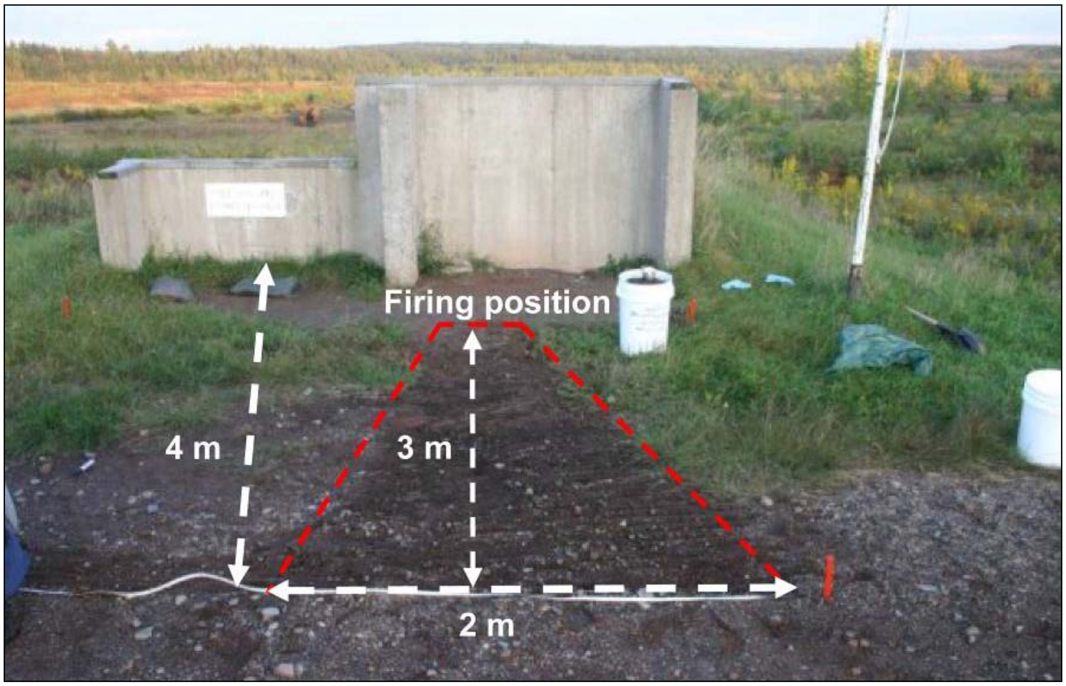

Figure 6-2. Firing position 1 of the Wellington antitank range, following propellant residue sampling at CFB Gagetown.

The Petawawa propellant residues were collected at firing positions 4 and 5 of antitank range A (Figure 6-3). The residues were collected across a thickness of 1 to 2 cm and over an area of 25 m^2, using a shovel, and were stored in five 20-L pails. Since the soil texture in this area is very coarse, a preliminary sieving to remove particles larger than 5 mm was attempted in the field, followed by further sieving in the laboratory at INRS to remove all particles larger than 5 mm in diameter. The final volume of propellant residues and soil was reduced to one 20-L pail. Samples from the Petawawa and Gagetown firing positions were stored in darkness at 4°C, to prevent degradation and/or transformation of the compounds prior to laboratory testing.

Figure 6-3. Sampling of propellant residues at the firing positions on antitank training range A, at CFB Petawawa.

6.6 Laboratory methodology

6.6.1 Soil columns

The columns were built from stainless steel, and the inside was layered with Teflon® in order to prevent any interaction with energetic material (EM). The base of the columns consisted of a Teflon plate held in place by a steel plate. The Teflon plates were machined with seven outflow holes. Each hole is located in the middle of a cone approximately 1 mm in depth and 20 cm in diameter, to avoid accumulating water lenses at the base of the column. Column dimensions (Figure 6-4) were chosen to avoid wall effects, by using a height-to-diameter ratio of less than two (Martel and Gélinas 1996).

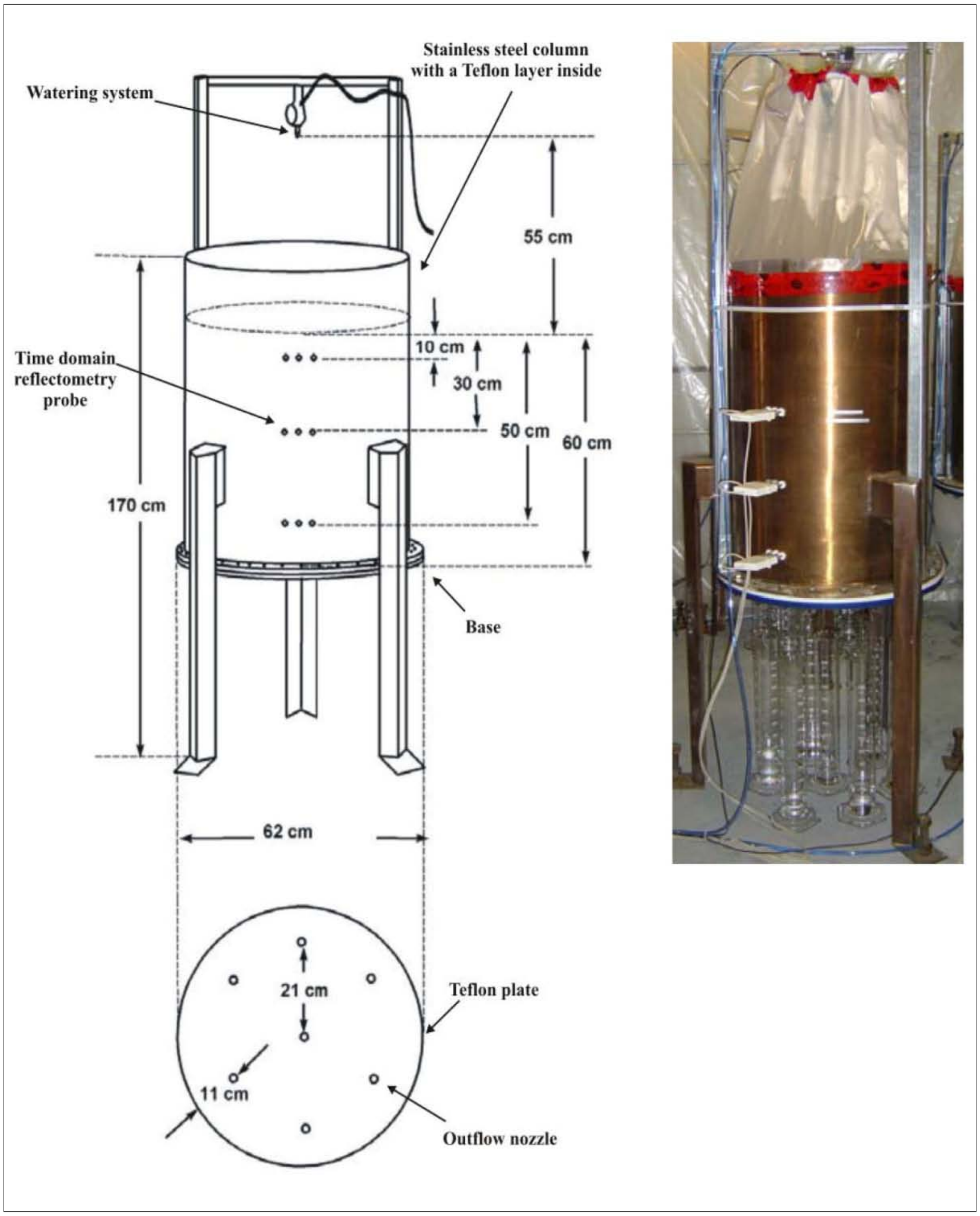

Figure 6-4. Dimensions of the sand columns.

Fiberglass rods were inserted in each of the seven holes to maintain a similar minimum tension in all holes of the soil columns. The rods had an average length of 15.2 cm ± 0.2 cm from the base of the column to the opposite extremity of the rod. The rods covered the bottom of each cone depression at the base of the column.

The six columns were filled by successive layers of soil 1.6 cm in thickness, with a mass of 8 kg. The clean soil was previously sieved to remove the grain size fraction larger than 8 mm. The column diameter (59.6 cm) was at least 100 times greater than the d_{50} of the sand (0.277 mm for the Petawawa sand; 0.375 mm for the Valcartier sand), and respected the criterion for avoiding preferential flow on the walls of columns (Martel and Gélinas 1996). The height of soil in each column was 60 cm. A group of three columns containing the same soil was simultaneously filled to ensure homogeneity. Water content was determined from the average of the water content values of the collected samples at each day of filling. Each soil layer was compacted using an electrical compactor with a 25-cm circular plate. Before adding the following layer, the soil was scarred with a comb to a depth of around 2 mm, so as to create hydraulic contact between the soil layers.

The propellant-contaminated soils from both sampling sites were added to the surface of the columns. A 5-kg mass of uncompacted soil contaminated with propellant residues resulted in a thickness of approximately 2 cm of residues on each column. The Gagetown residues were placed on the two columns containing the Valcartier soil (Columns B and C). Column A containing Valcartier soil was used for the application of sodium bromide (NaBr), a non-reactive solute that allows the determination of the transport pore volume, of the retardation factor, and thus of the adsorption coefficient. The NaBr was diluted in distilled water contained in the column watering containers at a concentration of around 400 mg/L of Br^-. The propellant residues from Petawawa were placed on the two columns containing the Petawawa soil (Columns E and F). Column D containing the Petawawa soil was used for the application of NaBr.

The automated watering system allowed exact measurement of the water volume applied to the columns. Each column was fed from individual 30-L distilled water container simulating rainwater at pH around 6 or 7. The containers were connected in parallel to a pressurized air system, which ensures a 30-psi pressure. Flow rates at the nozzles used for watering were similar for each column. The watering rates applied to the columns corresponded to the specific recharge observed at Valcartier or Petawawa (Table 6-1), i.e., for 30 days at 8 hr/day during spring and for 61 days at 24 hr/day in the fall. Also, the infiltration rate at Valcartier is 1.5 times more abundant than in Petawawa. For the experiment, 2 years (each spring and fall) were accelerated into 1 year. For both sites, the spring water infiltration rate was two times the fall infiltration. The opening of the valves, and thus the nozzles of the watering system, was controlled by a programmed CR-10X data logger (Campbell Scientific, Logan, UT); this unit also allowed us to measure and record basic parameters (battery voltage, program signature, temperature) and the water content in soil column profile.

Table 6-1. Water infiltration rates in sand columns.

Season	Recharge (mm)	Volume of water sprayed on columns (L)	Time laps of recharge (day)	Time laps of recharge (hr/day)	Flow rate (L/hr)
Petawawa					
Fall	75.2	21.0	61	24	0.014
Spring	162	45.2	30	8	0.188
Total	**237**	**66.2**			
Valcartier					
Fall	116	32.4	61	24	0.022
Spring	253	70.6	30	8	0.294
Total	**369**	**103**			

Time domain reflectometry (TDR) probes were placed at three levels in the columns in order to precisely measure the water content in the soil profile. The TDR probes were installed at 10 cm, 30 cm, and 50 cm from the top of the columns.

6.6.2 Soil sampling in columns

At the end of the experiment, soils were sampled to determine residual concentrations of energetic materials adsorbed to soil particles. The first two cm of soil containing residues of propellants had been sampled by collecting three sub-samples of 500 mL each. Sampling was also done deeper in the sand column in layers of 5, 10, and 15 cm. In each layer, five to seven sub-samples were taken with a stainless steel trowel washed with acetone, distilled water, and ethanol for bacterial antiseptic purposes between each layer.

6.7 Chemical analysis

The initial NG concentrations in the soils collected at both firing positions were analytically determined at DRDC-Valcartier and at INRS-ETE laboratories with EPA 8330B method using HPLC-UV (EPA 1996). The detection limit for NG was 500 µg/kg, and a representative soil sample was collected from the two source terms (Gagetown and Petawawa) after careful homogenization. Neither the acetone slurry nor the grinding was conducted prior to analysis on the whole sample to avoid changing the physicochemical properties of the source term. The source terms were homogenized through mixing and sub-sampled at various locations. The samples collected for analysis were then further homogenized with the use of the acetone slurry. Pierced aluminum paper foil was used to minimize the risk of analyte loss while evaporating the acetone.

The NG, DNG, and MNG concentrations in the effluent collected at the bottom of columns were analytically determined at the INRS-ETE Québec laboratory using solid phase extraction and HPLC and following a method developed at INRS (Appendix 6-A). In water samples, the practical quantification limits for such analyses were: 5 to 50 µg/L for 1-MNG, 2 to 20 µg/L for 2- MNG, 20 to 200 µg/L for 1,2-DNG, 10 to 100 µg/L for 1,3-DNG, and 4 to 400 µg/L for NG. Methods for analyses of DNG and MNG in soils are still in development. The perchlorate concentrations were analytically determined at the Environment Canada laboratory in Burlington, Ontario, and/or at the Maxxam laboratory in Ste. Foy, Quebec, following the liquid chromatography tandem mass spectrometry (LC/MS/MS) method, which has a detection limit of 0.5 µg/kg in soil and 0.02 µg/L in water. Analyses of anion concentrations (nitrite, nitrate, and bromides) in water samples were performed at INRS-ETE using a DIONEX ion chromatograph (ICS-2000 Ion Chromatography System). These detection limits were from 0.001 to 0.1 mg/L for nitrite, from 0.022 to 2.2 mg/L for nitrate and from 0.015 to 0.15 mg/L for bromide in water. TOC, CEC, iron content, and particle size distribution were determined for the soil in the columns and the surface source materials. The NO_2-NO_3 content was determined with method 33-3.2 (Keeney and Nelson 1982). The detection limit was 1.5 mg/kg for nitrite and 9.3 mg/kg for nitrate in soil. TOC was defined according to method 12 and a C, H, N analyzer coupled with an oxidizer oven (Environment Canada Centre Saint Laurent 1992). The total iron content in soil was analyzed with inductively coupled plasma – atomic emission spectroscopy (ICP-AES) following an aquaregia digestion. CEC in soil was determined with the method according to Gillman and

Sumpter (1986). The soil particle size distribution was defined with sieves for particles higher than 63 µm and with a laser particles size analyzer for particles smaller than 63 µm. The pH, electrical conductivity, and oxydo-reduction potential of the source term were also measured in 50 mL of distilled water solution containing 10g of soil (Thomas 1996) using an Accumet Excel 50 apparatus. Bacterial analyses were also performed in soil of the column at the end of the infiltration test at INRS-ETE using the Total Cell Count (TCC). A 0.5-g portion of soil was diluted in 4.5 mL of sterilized saline (0.85% NaCl) demineralized water. Aliquots of 0.1 mL were spread on petri plates and then incubated at 4 °C and 21 °C for 24–30 hours before cell count and identification.

6.8 Results and interpretation

6.8.1 Propellant residues

The NG, perchlorates (ClO_4^-), nitrites (NO_2^-), and nitrates (NO_3^-) concentrations in the soils collected at firing positions were analytically determined (Table 6-2). The high concentrations of NG, NO_2^-, and NO_3^- are explained by the NC matrix of the propellant residues that protects NG from biotic and abiotic processes. NG, NO_2^-, and NO_3^- are likely still embedded within the NC matrix and are not in contact with the soil for possible biodegradation or washing (Jenkins 2003).

Table 6-2. NG, ClO_{4-}, NO_{2-}, NO_{3-}, MNG, and DNG concentrations in the firing position surface soil and the calculated source term at the surface of the soil Columns B,C,E, and F.

	Gagetown (Column B and C)				Petawawa (Column E and F)			
	Propellant residues		Source term of 5 kg		Propellant residues		Source term of 5 kg	
NG	3145	mg/kg_{soil}	15.73	g	5652	mg/kg_{soil}	28.26	g
ClO_{4-}	3.52	µg/kg_{soil}	17.60	µg	53.46	µg/kg_{soil}	267.3	µg
NO_{2-}	307	mg/kg_{soil}	1.54	g	483	mg/kg_{soil}	2.42	g
NO_{3-}	296	mg/kg_{soil}	1.48	g	634	mg/kg_{soil}	3.17	g
1,2 DNG	97	mg/kg_{soil}	0.48	g	197	mg/kg_{soil}	0.98	g
1,3 DNG	24	mg/kg_{soil}	0.12	g	55	mg/kg_{soil}	0.27	g
1-MNG	trace		trace		trace		trace	
2-MNG	trace		trace		trace		trace	

Normally, NO_{2-} and NO_{3-} are compounds that quickly wash through the unsaturated zone. NG is also known to be soluble and not retarded. Higher concentration of perchlorate in Petawawa residues compared with Gagetown residues may indicate that they are more recent or that more M-72

66 mm was used instead of 84 mm. With these results and knowing the mass of residues applied on the columns (5 kg), the source term for NG, ClO_{4-}, NO_{2-}, and NO_{3-}, can be calculated for both Gagetown and Petawawa source terms. Results for MNG will be derived when the development of the analytical method for soils has been completed.

6.9 Hydrogeological characteristics of soils

Both uncontaminated soils from Valcartier and Petawawa consisted of sand with negligible silt and clay fractions (Table 6-3). The CEC is therefore low, as cation exchanges takes place on the fine grain size fraction. The carbon content is also negligible for both soils (<1%). The mean water content of each column, average values for pore volume, porosity, and bulk density were determined for each soil (Table 6-3).

Table 6-3. Physical parameters of uncontaminated soils in the columns.

Parameter	Valcartier	Petawawa
Physical parameters		
CEC (meq/100 g soil)	1.61	1.87
Total Organic Carbon (TOC) (%)	0.1	<0.1
Gravel (%)	2	0
Very coarse sand (%)	8	< 1
Coarse sand (%)	18	5
Medium sand (%)	40	49
Fine sand (%)	24	33
Very fine sand (%)	7	11
Silt (%)	< 1	< 1
Clay (%)	< 1	< 1
Classification (USDA)	sand	sand
d50 (mm)	0.375	0.277
Hydraulic Parameters		
Total soil volume (L)	168	168
Pore volume (L)	64	66
Water content (kg/kg)	0,07	0,04
Transport pore volume (L)	Col.A : 33 Col.B : 36 Col.C : 33	Col.D : 28 Col.E : 28 Col.F : 34
Effective porosity	0.259	0.328
Total porosity	0.383	0.390
Bulk density (kg/m^3)	1778	1757
Hydraulic Cond. (10^{-2} cm/s)	3.75	4.55

The Valcartier sand, which was coarser than the Petawawa sand, has a lower pore volume and porosity. The pore volume, which influences the transport of water, was determined with tracers. Bromides were used for Columns A and results were extended for Column C. The transport pore volume for Column B was determined by nitrites and nitrates, considered as non transformed or retarded tracers. Bromides were also used for Columns D and results were extended for Column E. The transport pore volume for Column F was determined by perchlorate, considered a tracer that is neither transformed nor retarded. Determination of transport pore volume is explained in more details in the solute results section.

The hydraulic conductivity of soils was measured using a Guelph infiltrometer. The average saturated hydraulic conductivity (K_{sat}) values obtained were 3.75 x 10^{-2} cm/s for the Valcartier sand, and 4.55 x 10^{-2} cm/s for the Petawawa sand. Unsaturated hydraulic conductivity of the soil, which depends on the soil saturation level and the tension applied to each column, was also measured with the Guelph tension infiltrometer. The relatively finer Petawawa sand presented higher unsaturated hydraulic conductivity versus applied tension values than the coarser Valcartier sand (Figure 6-5). Those results were in agreement with theoretical notions, as finer sand possesses a higher capillarity and has a lower risk of hydraulic breakdown.

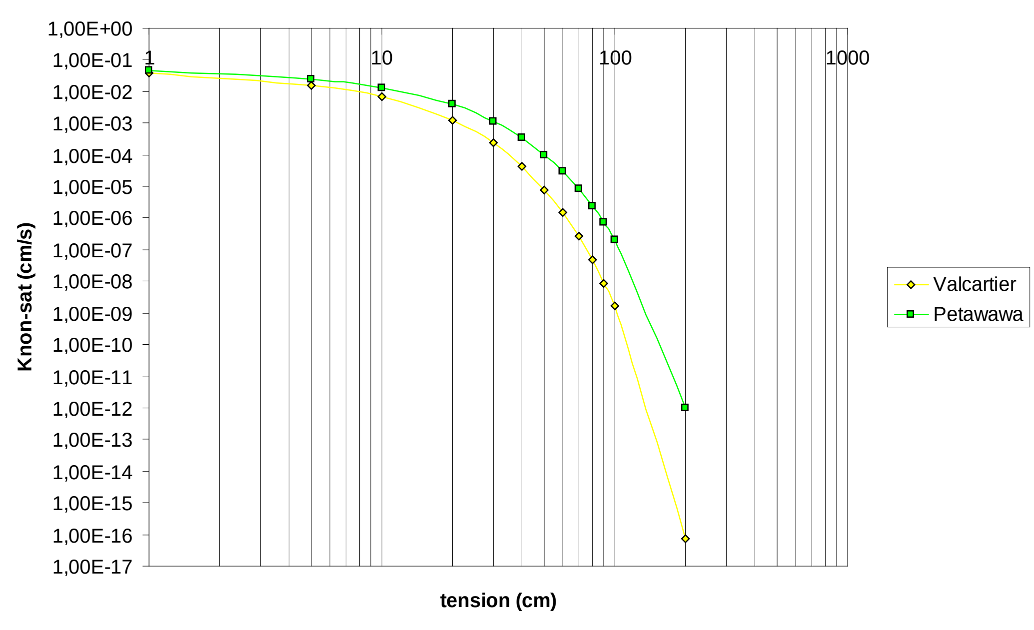

Figure 6-5. Mean unsaturated hydraulic conductivity vs. tension for both soils.

6.9.1 Observed infiltration flow and outflow

The columns were brought to a steady state of flow prior to the experiments. The springtime infiltration period had two significant deviations for the inflow rate. The electric valve on Column E simulating Petawawa jammed open on day 1 of the infiltration, and was stopped the day after. During this 24-hour period, Column E was completely flooded. The infiltration for Column E was stopped and restored on day 6. Then, the electric valve jammed again and flooded the column. Again, the infiltration for Column E was stopped the day after and restored on day 19. The valve was subsequently repaired and worked properly.

The measured infiltrated water quantities were similar to the expected values from each recharge regime for Columns A, C, D, and F. Visible leaks were present in Columns B and E. Column B had significant leaks at the base, which explains the high infiltrated water volume read on the container graduated scale during the first spring infiltration period. Because the leaks in Container B were too serious, that experiment was abandoned during the first autumn infiltration period. Column E also had leaks, but they were discontinuous. We attempted to seal these containers again during the first summer drying period, without noticeable improvements.

Figure 6-6, which plots the cumulative measured outflow for each column, shows that the outflow of the Valcartier columns is higher than Petawawa columns according to precipitation/recharge regime of these respective areas. Also, spring outflow is about two times the fall outflow. The slope also shows that the recharge intensity is more important in spring than in fall. The outflow water volumes for Columns A and C (Valcartier) were relatively similar. Column B is not shown because it was abandoned earlier during the first fall period. However, the outflow water volumes for Columns D, E, and F (Petawawa) varied. Column A and D, the columns with the bromide tracer, were stopped after the second spring period since the objective of having the transport pore volume was reached.

Column F was the closest to the intended infiltration flow. Outflow rate for Column D was too slow because of the nozzle performance. The opposite was true for Column E; its watering system nozzle was leaking slightly, increasing the amount of water applied on the column and the amount of water sampled at the bottom. Also, the outflow water volumes for Column E were quite significant following the two-step flood during the first spring.

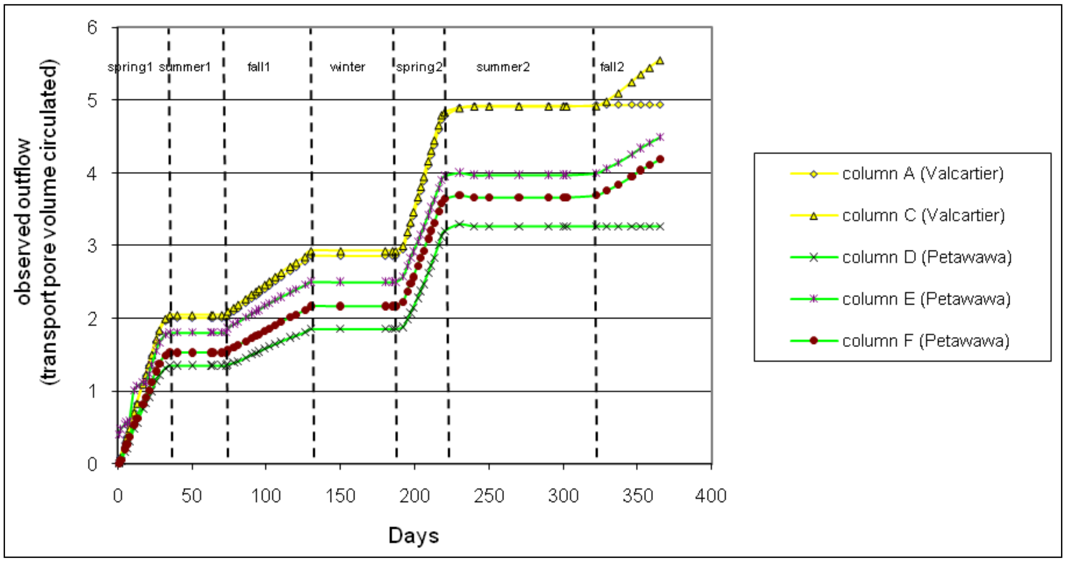

Figure 6-6. Cumulative measured outflow for each column.

6.10 Time domain reflectometry results

Moisture content in the columns was monitored using TDRs at 10-, 30-, and 50-cm depths. Moisture content in sand columns increases with depth and is consistent with tension profile within the column. Data from the TDRs in Columns A and F representing springtime infiltration at Valcartier and Petawawa, respectively, are shown in Figure 6-7 and Figure 6-8. Precipitation events were scheduled every 15 minutes for 8 hours a day during 31 days of springtime.

The transient daily fluctuations in moisture content were clearly visible during this period in the upper part of the soil profile and attenuate with depth. The flow, although transient, is at equilibrium. This means that from one day to the next, the overall moisture content did not increase or decrease during the springtime flow. In other words, the daily fluctuations did not show long-term upward or downward trends during the springtime infiltration period. However, the magnitude of changes in moisture content between Column A and F are quite different. Two reasons could explain this difference. First, the patterns of watering on the two sites were different. The recharge at Valcartier is higher than at Petawawa (369 mm/yr compared to 237 mm/yr). Also, the Petawawa soil texture is finer than Valcartier; therefore, the water is more closely related to soil particles and the residual moisture content is higher.

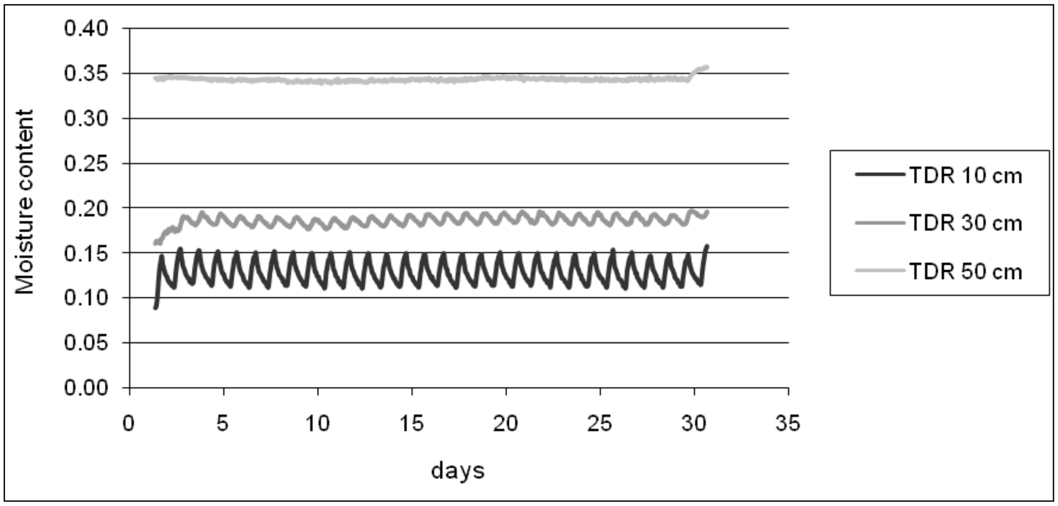

Figure 6-7. TDR data from springtime infiltration in Column A – Valcartier.

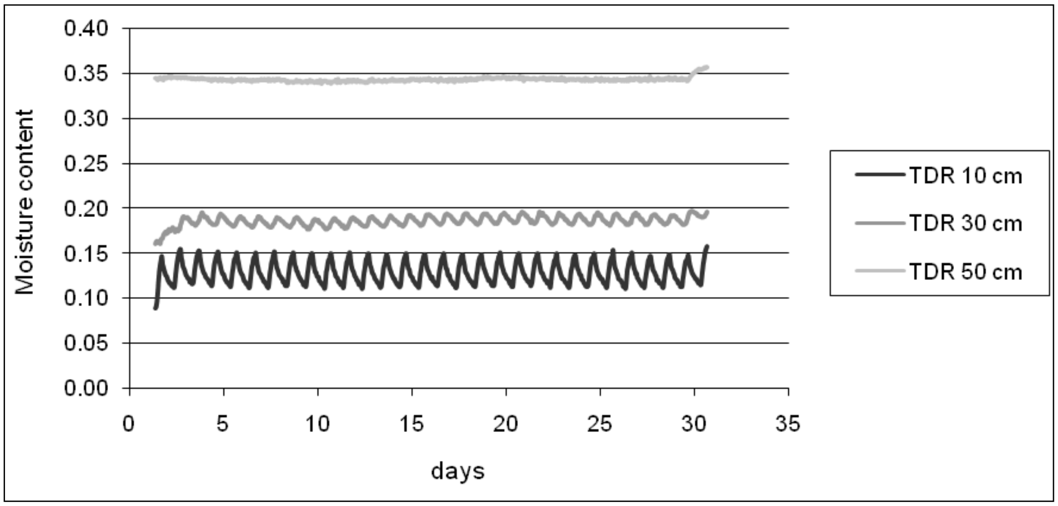

Figure 6-8. TDR data from springtime infiltration in Column F – Petawawa.

Moisture data from the TDRs in Column A during simulated fall infiltration in Valcartier are shown in Figure 6-9. Precipitation events were scheduled every 4 hours for 24 hours eachof 61 days. The transient daily fluctuations in moisture content were not visible during this period. However, from one day to the next, the overall moisture content did not increase or decrease during the fall time flow.

Figure 6-10 shows the average moisture contents measured in Column A at 10-, 30-, and 50-cm depths throughout the total duration of the test. Due to a programming error, moisture data for the first 10 days of simulated fall time are not available. The water content in the soil decreased significantly at 10 and 30 cm after the first springtime infiltration. This drop occurred rapidly at the beginning of the drying period, after which moisture levels reached equilibrium. Also, at the beginning of the second springtime infiltration, the moisture quickly returned to its maximum value. The phenomenon of moisture variation was less pronounced following the first autumn infiltration since precipitation events are less abundant than in the springtime. In contrast, at 50 cm, no variation of moisture was noted until the second summer period. The first significantly shortened summer (30 days) did not allow the column to desaturate at the base (50 cm). The second summer, which lasted around 90 days, had this effect. Given the little difference between the values of moisture at 50 cm and the value of porosity at the beginning of the experiment, it is possible that the soil at 50 cm had reached saturation.

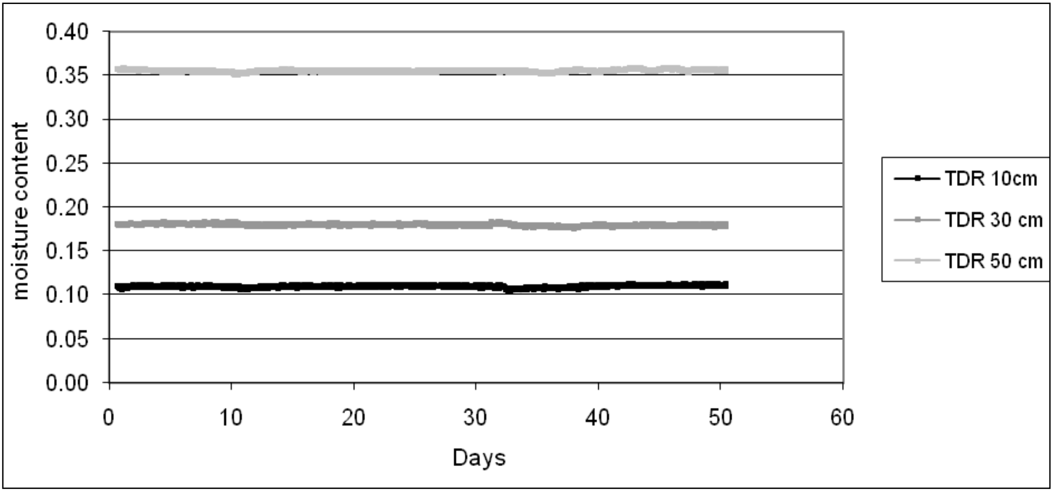

Figure 6-9. TDR data from fall infiltration in Column A – Valcartier.

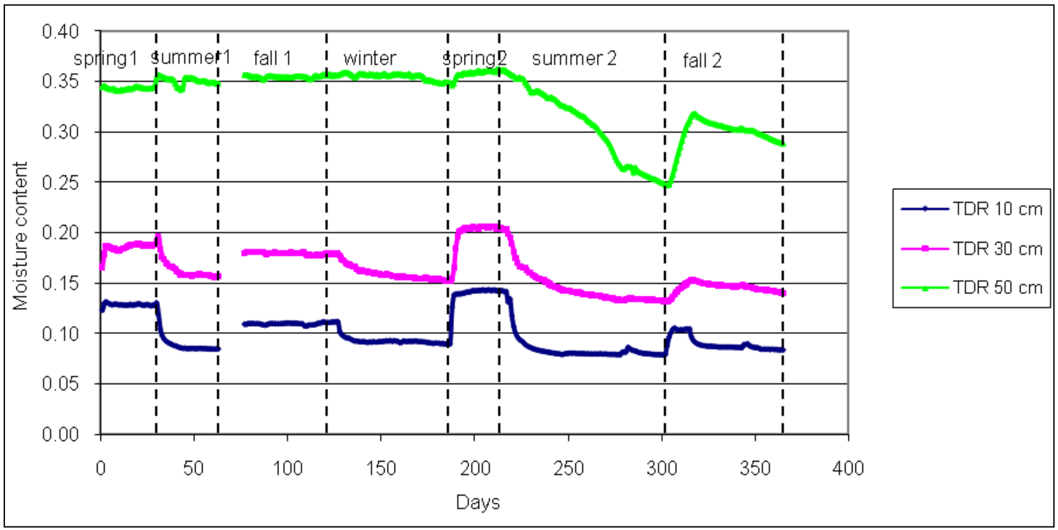

Figure 6-10. TDR data of Column A – Valcartier.

6.11 Laboratory temperature

The experiment was housed in a climate-controlled laboratory in order to reproduce subsurface conditions (Figure 6-11). Another reason to control temperature is because it has an impact on the solute dissolution. Seasonal fluctuations in temperature will impact the unsaturated zone to a depth of approximately 10 m. The experimental plan called for refrigerating the laboratory to 8 °C during the springtime and fall infiltrations and during the winter period. However, actual temperatures varied between 5 °C and 15 °C. Following the springtime infiltration period, the lab would be warmed to approximately 15 °C to reproduce sub-surface conditions during the summer dry period. During winter period, the laboratory obviously cannot be frozen.

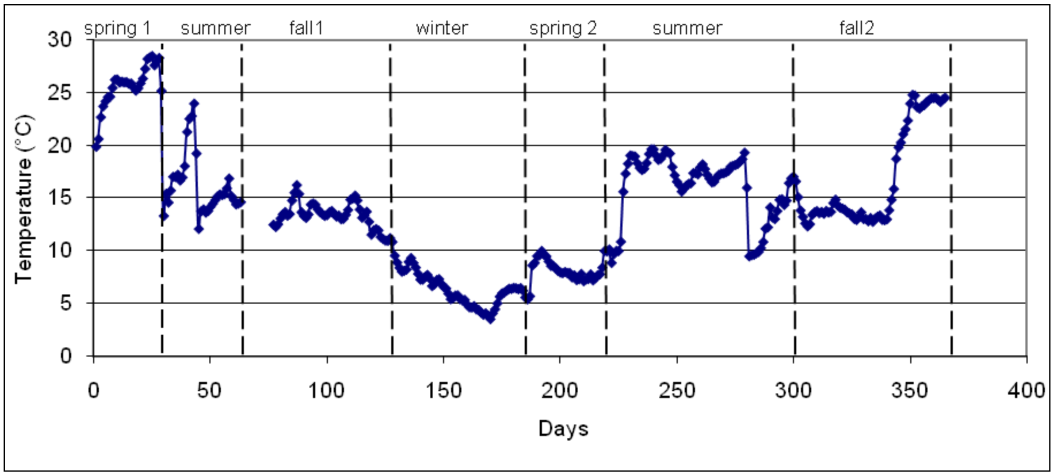

Figure 6-11. Laboratory temperature during experimentation.

Unfortunately, a major mechanical failure of the refrigeration unit that cooled the laboratory caused temperatures to rise at the beginning of the first springtime infiltration until they reached 31 °C. Another failure caused high temperatures at the end of the second fall infiltration. These periods of warm temperatures may have had an impact on the dissolution rates and solubility of residues in water. In fact, the average temperature of the first spring was on the order of 25 °C; whereas it was 13 °C for the first fall, 8 °C for the second spring, 12 °C for first half of the second fall, and 25 °C for the last third of the second fall.

6.12 Solute fate and transport

6.12.1.1 Bromides

Studies of fate and transport present data with respect to the pore volumes eluted. In the saturated regime, one pore volume is the quantity of water required to completely fill the pore spaces of a given quantity of soil. Most contaminant transport studies are performed in saturated conditions, and the concept of pore volume is commonly used in the literature to describe the quantity of fluid which has passed through a saturated soil column (Lewis 2007). Thus, the breakthrough of fluid traveling at the average linear velocity is achieved when one pore volume has passed through a column of soil. Of course, in the unsaturated regime, the pores are filled with both water and air, so one pore volume will not represent the point at which all the water in a column has been theoretically replaced. Pore volume that participates in transport within the unsaturated zone is found using a tracer.

Indeed, a transport pore volume, for a continuous source of solute, is attained when concentrations sampled at the bottom of the columns correspond to half of the initial concentration. According to this assumption, and because a continuous source of dissolved bromides (considered as tracer) was applied on columns, transport pore volume is 51.1% of the total pore volume for Column A (Valcartier) and 42.7 % for Petawawa sand (Column D) corresponding to 33 L (Column A) for Valcartier and 28 L (Column D) for Petawawa (Figure 6-12). The significantly higher concentrations in bromides correspond to the first sample following a period of drying (Figure 6-13). The water in the fiberglass wicks evaporates during the drying period, thus concentrating the Br-. This phenomenon is more pronounced for samples of the Petawawa soil since the volumes of water at each sampling period are less important due to the precipitation regime; therefore, the dilution is lower. Furthermore, the decreasing slope in bromide concentrations corresponds to a stop of supply in bromides (Figure 6-13). Indeed, when the equilibrium in bromide concentration was reached (around 400 mg/L), columns were watered with distilled water only. Recovery percentage for bromides (i.e., quantity sampled at the bottom of columns versus quantity diluted in distilled water contained in the column watering containers), was 91% for Column A (Valcartier) and 100% for Column D (Petawawa).

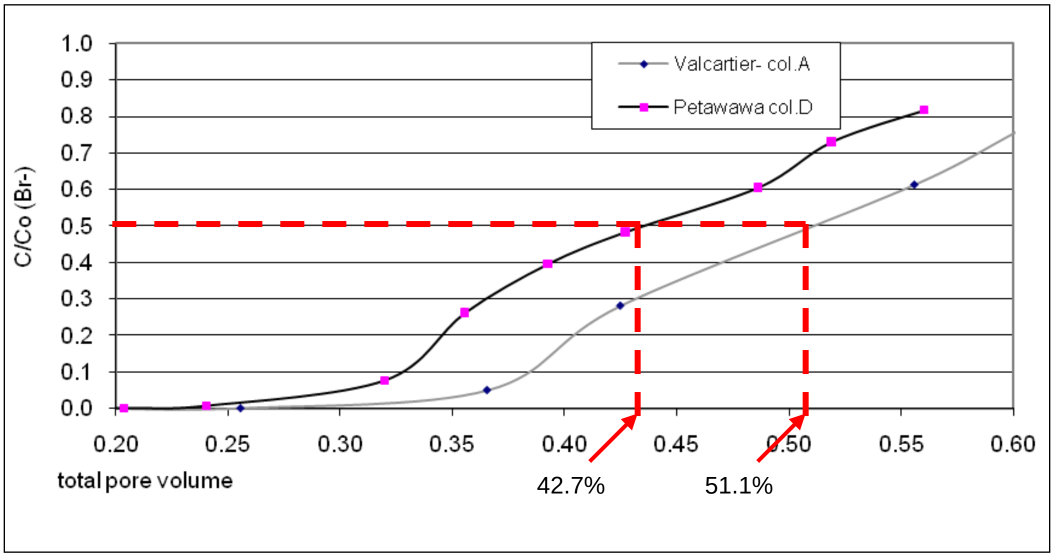

Figure 6-12. Bromides vs. total pore volume from Columns A (Valcartier) and D (Petawawa).

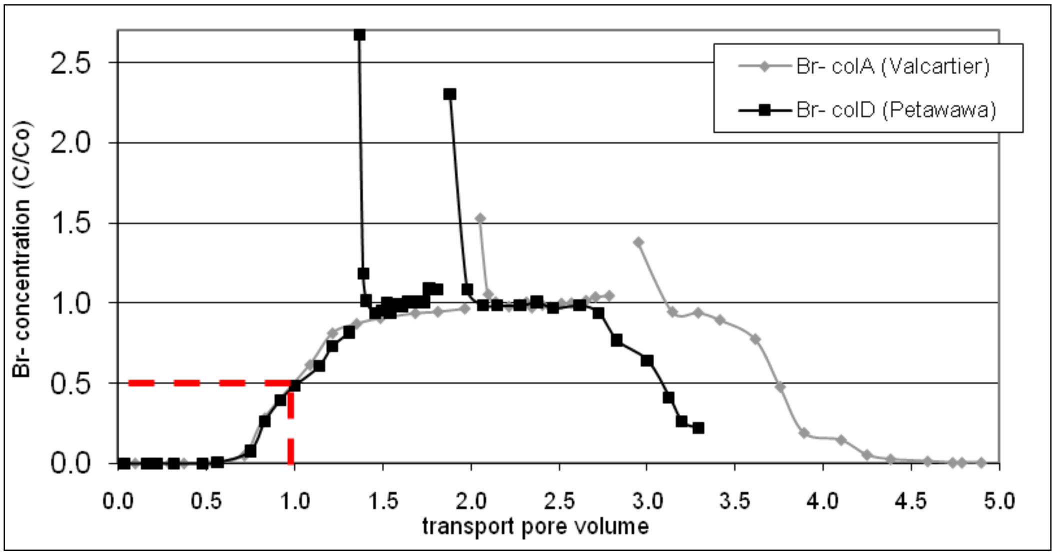

Figure 6-13. Bromides vs. transport pore volumes from Columns A (Valcartier) and D (Petawawa).

6.12.1.2 Perchlorates

The graph of perchlorate concentration as a function of total pore volume for Column F (Petawawa) shows that the transport pore volume for this column with Petawawa sand is 51.1% of the total pore volume or 34 L (Figure 6-14).

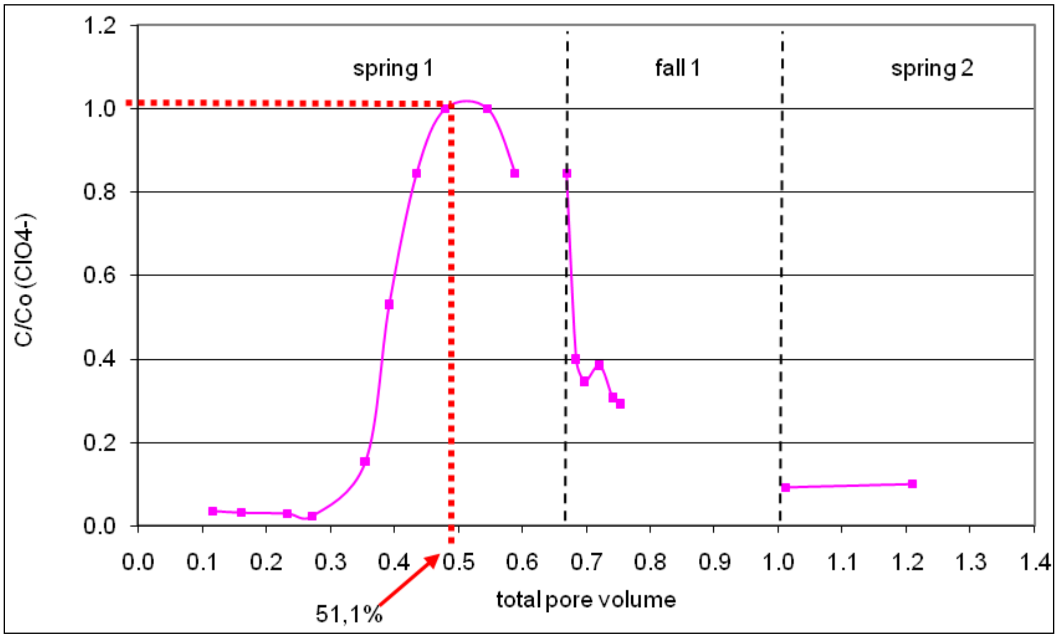

Figure 6-14. Ratio of transport pore volume to total pore volumes, Column F, Petawawa.

Perchlorate is known to flow through soil without adsorption, transformation, and biodegradation under aerobic conditions. Thus, perchlorate is released from nitrocellulose particles and can be seen as a pulse of tracer in this experiment. Perchlorate concentrations were followed only for Column F, since the Petawawa residues had a much higher initial concentration of perchlorates (53.46 µg/kg) compared to Gagetown (3.52 µg/kg). A sharp rise in concentration is observed even at 0.6 transport pore volumes for this element (Figure 6-15). A maximum of 13 µg/L was observed at one transport pore volume. The maximum concentration limit (MCL) in drinking water is 6 µg/L (Health Canada 2007). The breakthrough curves for perchlorate and bromide were compared and demonstrated that perchlorate is not retarded because the pulse of perchlorate fits with the bromide continuous delivery breakthrough curve (Figure 6-16). Perchlorate is also not affected by anionic exclusion. Both bromides and perchlorates have similar behaviors and are considered to be tracers (Tipton et al. 2003). The transport pore volume for a pulse of solute is attained when concentrations in the effluent correspond to the maximum concentration. Percentage recovery of perchlorates (quantity of perchlorate in the effluent versus quantity in propellant residues) is 95%. A quantity of 5% lost is within the experimental analytical error.

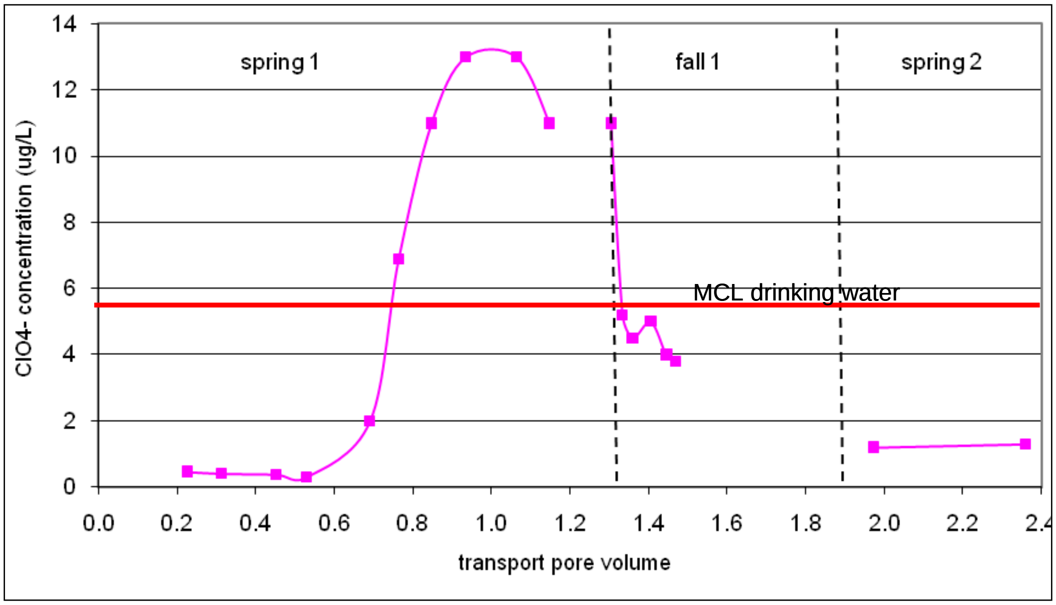

Figure 6-15. Perchlorate concentration vs. transport pore volumes, Column F, Petawawa.

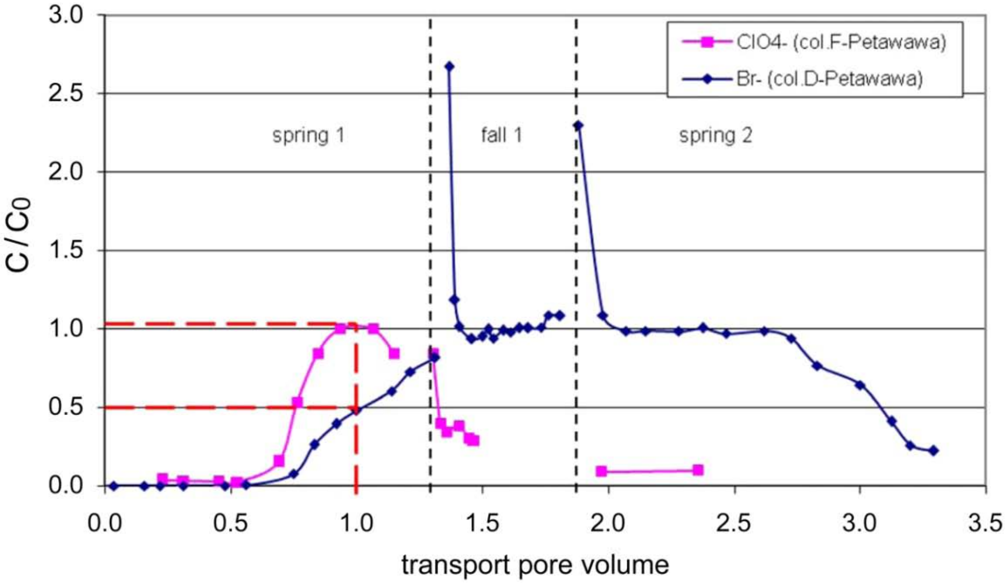

Figure 6-16. Perchlorate (ClO_4^-) and bromides (Br-) vs. transport pore volumes.

6.12.1.3 Nitrites and nitrates

The effluent samples were also analyzed for their nitrite (NO_2^-) and nitrate (NO_3^-) concentrations. In the literature, the degradation of NG does not produce nitrate because experiments were done under anaerobic conditions or under conditions where the optimal mass of bacteria capable of using nitrate as a source of energy were reached (Wendt 1978; White 1996a, b; Christodoulatos 1997; Accashian 2000). Results in the present study differ because the fate and transport processes of NG took place in aerobic conditions and optimal mass of bacteria was not reached.

Nitrate concentrations in effluent from the Valcartier sand Columns B and C followed a similar trend (Figure 6-17). Data collection for Column B ended at the beginning of the first autumn infiltration period because of an unsolvable leakage problem with the column. The nitrate concentration in Column B effluent reached a high peak at the beginning of the experiment at a maximum of 112 mg/L; this exceeds the MCL of 45 mg/L (Health Canada 2007). The possible peak for Column C effluent could not be seen due to the 10-day period with missing data that resulted from a programming error. However, the nitrate concentrations in the effluent from Column C have shown a slight nitrate production probably associated with biodegradation of NG and metabolites during the first fall, after a dry summer and a residence time of 30 days. There was also a slight production of nitrate during the second fall, after a period of drying and a warmer temperatures during the 90-day summer period. For a background value, the average nitrate concentration in effluent samples from Column A, the reference column, was 2.4 mg/L. Relative to the initial concentration in the source term, percentage of nitrates recovery was 136% for Column B and 105% for Column C. These values did not include the possible peak at one transport pore volume for Column C. Evidence of nitrate production is not great in the Valcartier sand. Recharge and the dilution factor for Valcartier have a larger effect, thus implying the residence time in the Valcartier column is too short to have nitrate production.

Nitrate concentrations in Column E effluent for Petawawa sand showed two peaks at the beginning of the experiment during the first spring period (Figure 6-18). A phase of nitrate production was observed during the second spring, producing a maximum concentration of 116 mg/L at approximately 3.1 transport pore volumes. Nitrate concentrations for Column F showed a first nitrate peak at the end of the first spring infiltration period, reaching a maximum of 111 mg/L (Figure 6-19). A second phase of nitrate production was observed with a maximum of 102 mg/L near the end of the first fall, after a longer and warmer summer. The average nitrate concentration in effluent samples from Column D of Petawawa, a background value, was 6.4 mg/L.

The second nitrate peak was clearly the result of a nitrate production from NG or metabolites. Percentage recovery of nitrates in the effluent compare to mass of nitrate in the source term was 698% and 607% for Columns E and F, respectively.

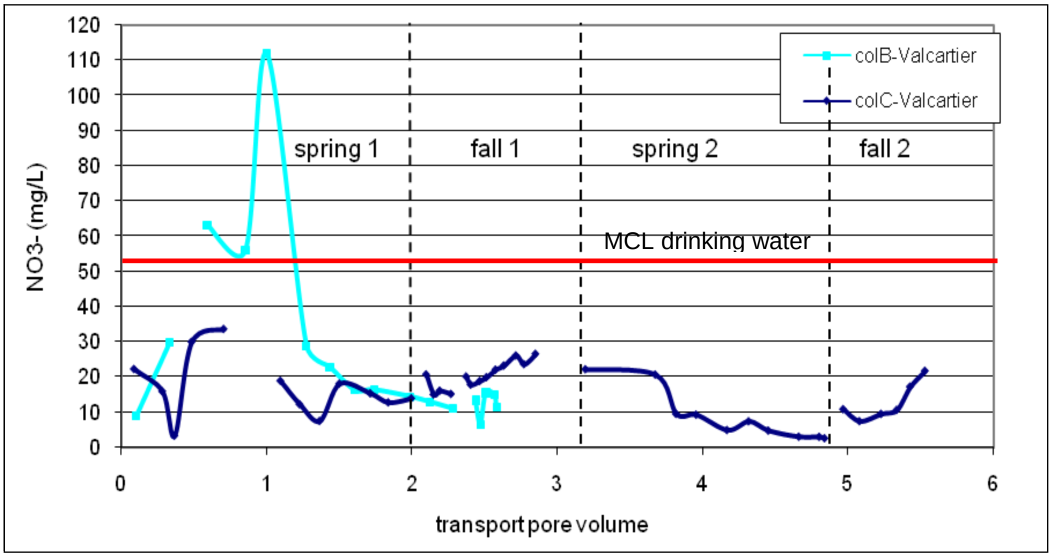

Figure 6-17. Nitrate (NO_3^-) effluent concentration as a function of transport pore volumes for Columns B and C of Valcartier.

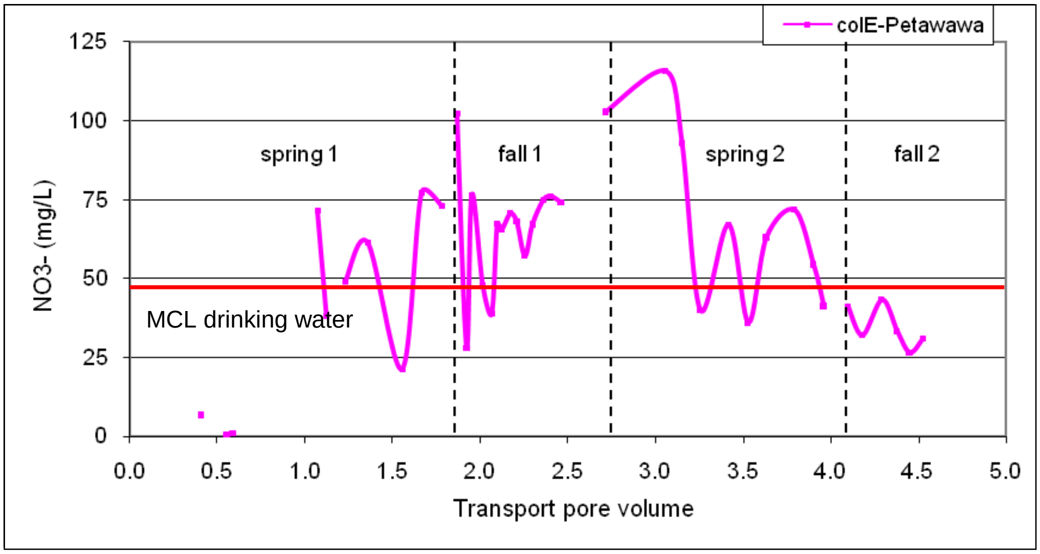

Figure 6-18. Nitrate (NO_3^-) effluent concentration as a function of transport pore volumes from Column E (Petawawa).

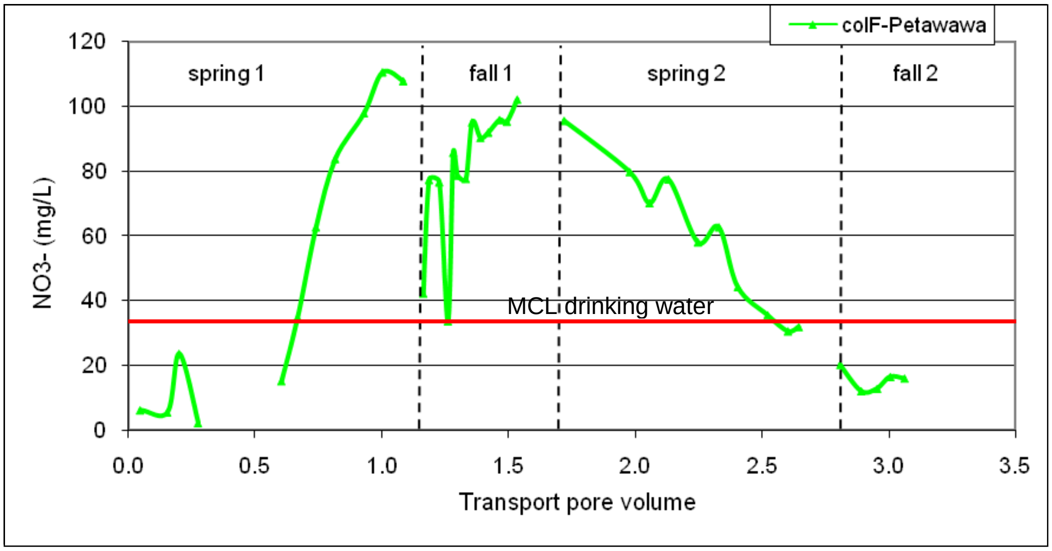

Figure 6-19. Nitrate (NO_3^-) leachate concentration vs. transport pore volumes from Column F (Petawawa).

Differences between the slight nitrate production of Columns B and C and the high production in Columns E and F may be explained by the difference in recharge pattern and residence time in the column. Recharge was more significant for Valcartier, thus nitrates were washed through the unsaturated zone, and NG was less degraded.

Nitrate and perchlorate concentrations were also compared (Figure 6-20). Perchlorate is an ion that is neither retarded nor transformed during its transport through the unsaturated zone; thus, there is no possibility of perchlorate production during the experiment. The first maximum in concentration for nitrate observed at the end of the first spring coincides with the maximum for perchlorate, proving that nitrate can be a good tracer for evaluation of transport pore volume in Petawawa sand. The second nitrate peak observed at the end of first fall is clearly the result of nitrate production from NG because the perchlorate curve included no second maximum.

Nitrite concentrations in effluent of Columns B and C of Valcartier followed a similar trend (Figure 6-21). The Column B nitrite concentration increased to a prominent peak at 45 mg/L during the first spring period. This is significantly above the MCL for nitrite, which is 3.2 mg/L (Health Canada 2007). Percentage of recovery for nitrites was 57% and 21% for Columns B and C (without considering a possible initial peak), respectively. Recovery of nitrites was not complete because nitrites degrade quickly into nitrates in aerobic conditions. Columns E and F of Petawawa have not produced measureable nitrites throughout the test. The lower recharge at Petawawa allows a longer contact time with oxygen so that nitrites can transform into nitrates in these soils.

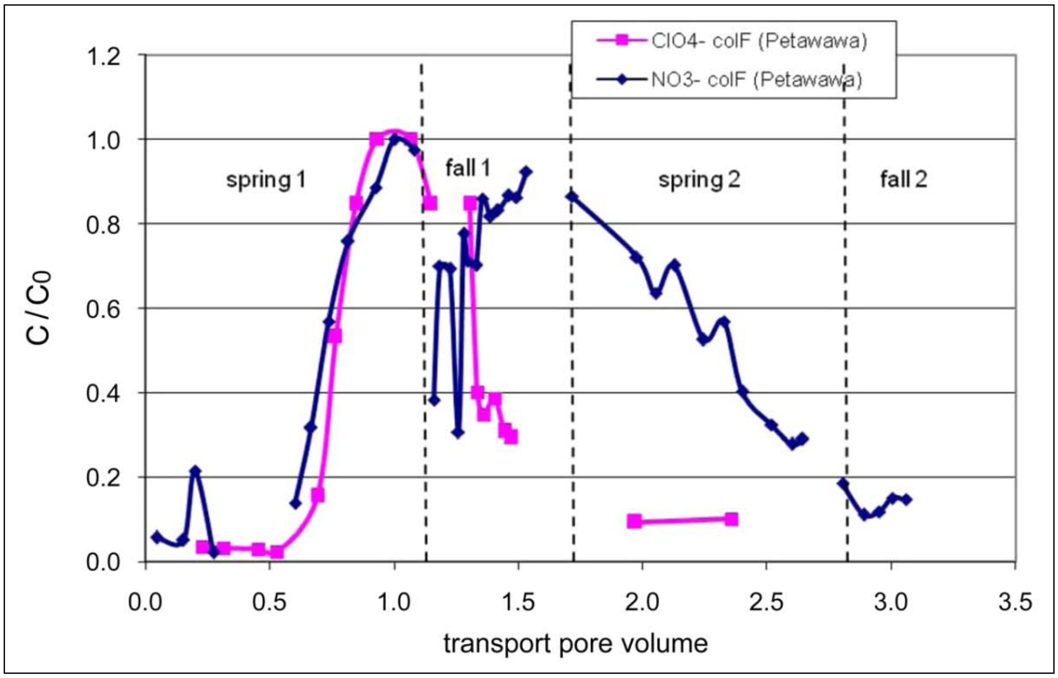

Figure 6-20. Nitrate (NO_3^-) and perchlorate (ClO_4^-) concentration in column effluent as a function of transport pore volume from Column F (Petawawa).

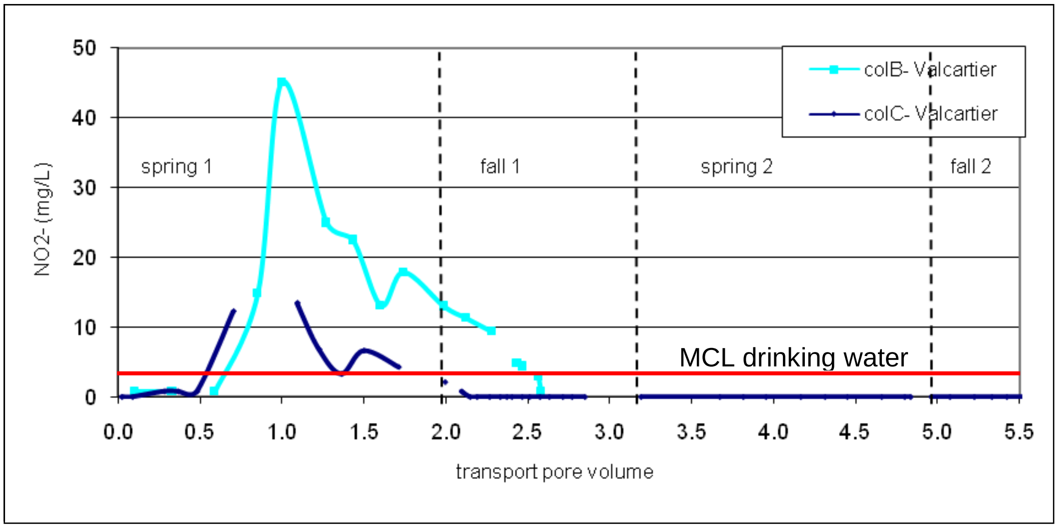

Figure 6-21. Nitrite (NO_2^-) concentration in effluent as a function of transport pore volumes for Columns B and C (Valcartier).

Nitrite and nitrate concentrations were also compared for Column B (Figure 6-22). Both nitrite and nitrate reached their maximum concentrations at the same time. Actually, NO_2^- and NO_3^- are compounds that are quickly washed through the unsaturated zone as shown by the maximum being present at one transport pore volume.

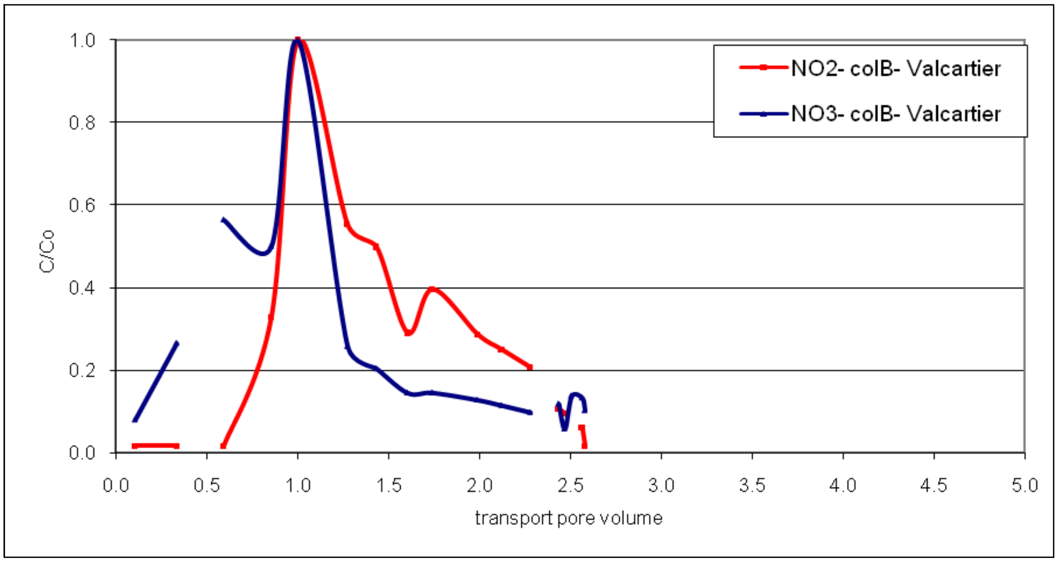

Figure 6-22. Nitrite and nitrate concentration in effluent as a function of transport pore volumes for Column B (Valcartier).

6.12.1.4 NG, DNG, and MNG

NG, 1,2-DNG, 1,3-DNG, 1-MNG, and 2-MNG concentrations were correlated as a function of their percentage of recovery during the solid phase extraction. The concentrations of these compounds for Column B followed a similar trend (Figure 6-23). The dataset is short, because this experiment was stopped at the beginning of the first autumn infiltration period. Also, water sample bottles were broken around 1 and 2 transport pore volumes.

The NG, DNG, and MNG concentration results show a possible peak at one transport pore volume. It would mean that the transport of the NG and its metabolites would not be delayed in the soil as shown by the perchlorate concentration profile in Figure 6-23. A second and third peak seemed to arrive at 2 and 2.5 transport pore volumes. The subsequent peaks could be explained by a release of NG from its NC matrix during the dissolution process. NG concentrations reached a maximum of 174 mg/L, which compares with a MCL of 0.28 mg/L (Robidoux 2006). Percentage of recovery for NG was 23% for Column B. It means that NG is readily degraded through the unsaturated zone. It could also mean that NG is still embedded in the NC matrix and cannot be leached through the unsaturated zone. The 1-MNG and 2-MNG concentrations were very close; however, 1,2-DNG concentrations were higher than 1,3-DNG, contrary to what was described in literature (Christodoulatos 1997). Nevertheless, the MNG and DNG concentrations were two orders of magnitude less than NG concentrations.

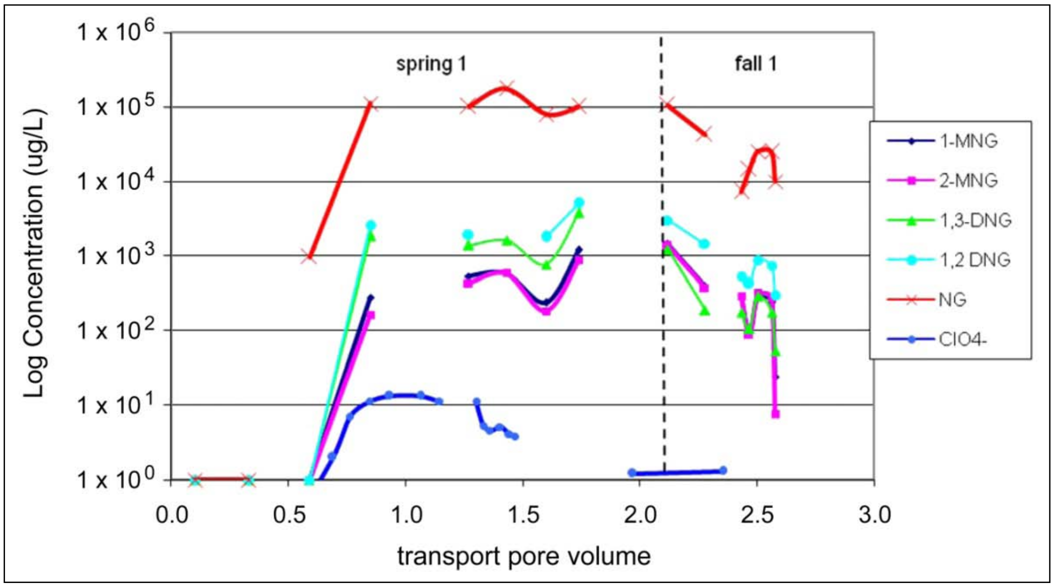

Figure 6-23. NG, DNG, MNG concentration in effluent vs. transport pore volumes from Column B-Valcartier.

Figure 6-24 shows the concentrations of NG, 1,2-DNG, 1,3-DNG, 1-MNG, and 2-MNG in the effluent of Column C (Valcartier). Most of these compounds are flushed out of the sand column within one infiltration year (Figure 6-25). They all reached their first peak at one transport pore volume, which indicates no retardation (no adsorption) as was also observed in Column B. NG concentrations reached a maximum of 110 mg/L. Shortly after the first peak, MNG concentrations behave contrary to NG, i.e., when NG is at a maximum concentration, the MNGs are at a minimum concentration, and vice versa (Figure 6-26; 1.7–2.0 pore volumes). The cyclic behavior of NG and DNGs is observed also after the two dry seasons of the second year (Figure 6-24) and this phenomenon is related to the back diffusion of these compounds embedded into the NC fibers. Percentage of recovery for NG was 12% for Column C.

The 1-MNG concentrations were clearly higher than 2-MNG, and 1,2-DNG concentrations were higher than 1,3-DNG was from Column B Valcartier (Figure 6-27).

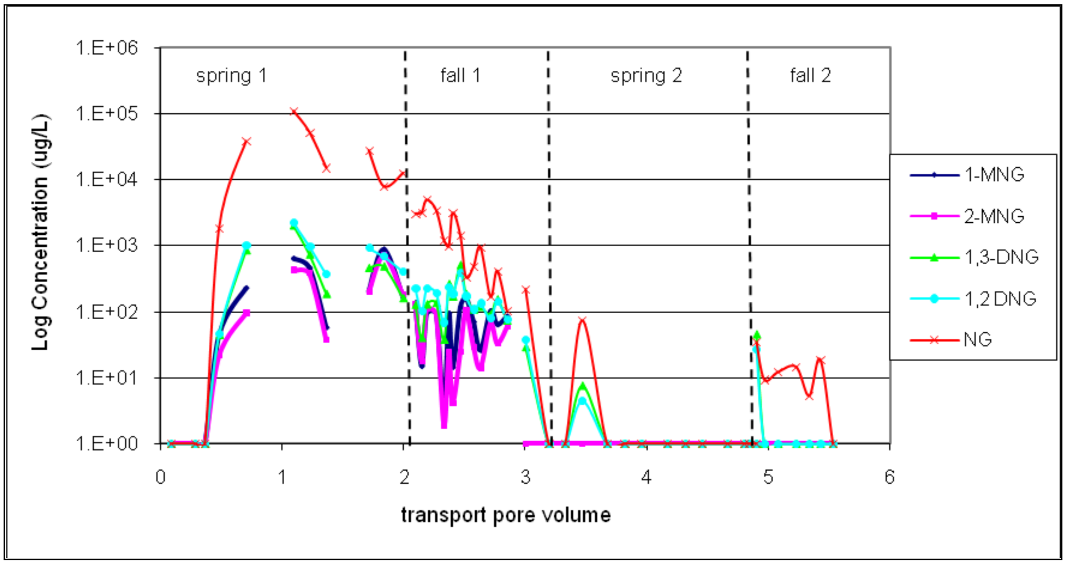

Figure 6-24. NG, DNG, and MNG concentration in effluent vs. transport pore volumes from Column C–Valcartier.

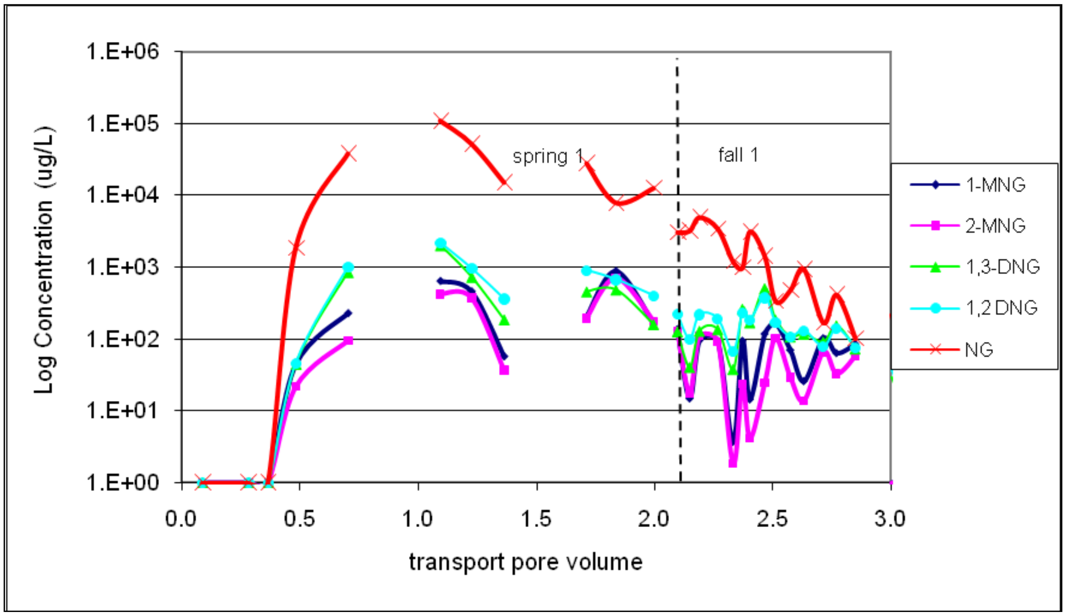

Figure 6-25. NG, DNG, and MNG concentration in effluent between 0 to 3 transport pore volumes from Column C–Valcartier.

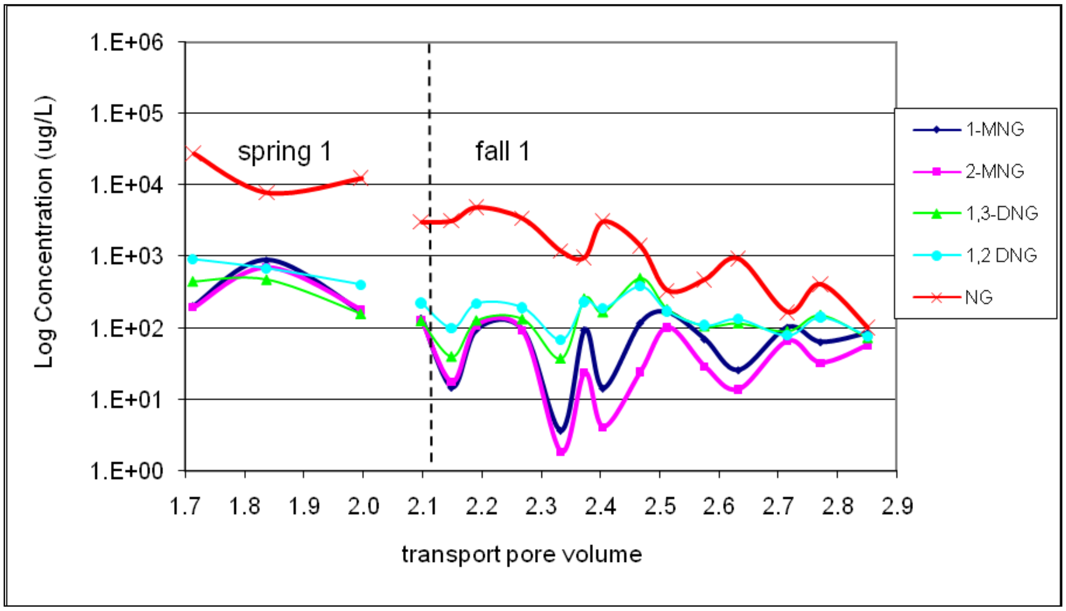

Figure 6-26. NG, DNG, and MNG concentration in effluent between 1.7 to 2.9 transport pore volumes from Column C–Valcartier.

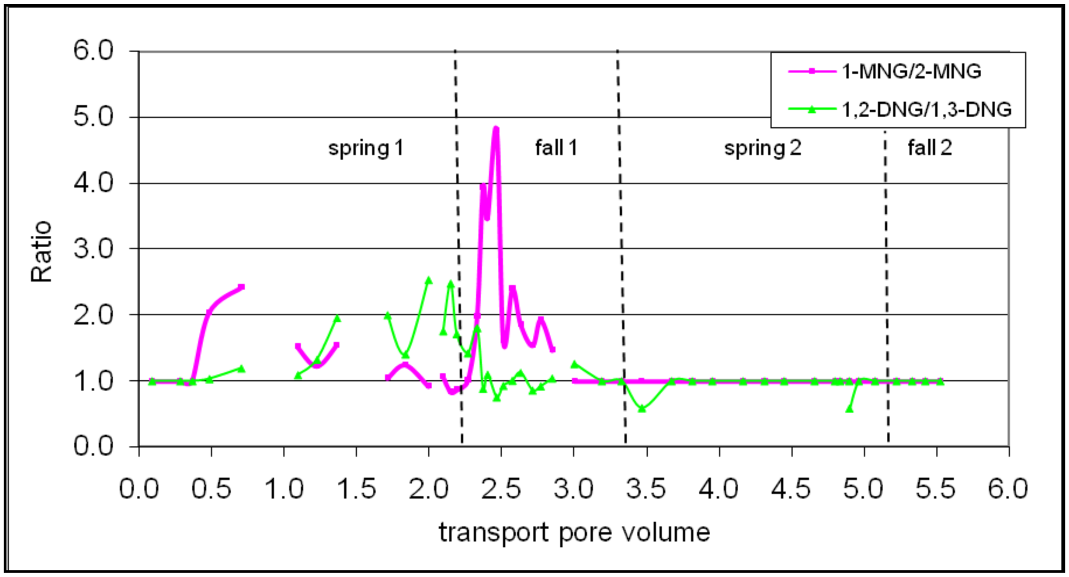

Figure 6-27. Ratio for DNGs and MNGs from Column C–Valcartier.

The maximum concentrations of the studied compounds can be above the MCL for NG, NO_2, and NO_3 in the effluent of the Valcartier columns (the values that exceed limits are noted by bold font in Table 6-4). No concentrations of NG, MNGs, and DNGS were detected in the effluent of the two columns from Petawawa; only nitrate and perchlorate were detected, meaning that the totality of NG, DNGs, and MNGs concentrations were still in the soil or were degraded completely along the flow path in the column before reaching the column outlet. This can be explained by the lower amount of recharge in Petawawa, which gives the water in the column a longer residence time and increases the time available for biodegradation processes. It can also be related to the composition of the Petawawa source term (Table 6-5) that has much more organic matter (six times) than the Gagetown one (on Valcartier soil). All the other parameters are equivalent or not significantly different.

Table 6-4. Maximum concentrations of compounds detected in the column effluent after 2 years of recharge.

Maximum Concentration Detected	NG (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	1-MNG (µg/L)	2-MNG (µg/L)	1,2-DNG (µg/L)	1,3-DNG (µg/L)	ClO_4^- (µg/L)
Valcartier	**174**	**45**	**128**	1417	1377	5040	3758	NA
Petawawa	BDL	BDL	**111**	BDL	BD	BDL	BD	**13**
BDL: below detection limit; **Bold values**: concentration above MCL; NA: not analyzed								

Table 6-5. Physico-chemical composition of the source terms on top (2-cm thick) of the Valcartier and Petawawa columns.

Physico-Chemical Parameter	Valcartier	Petawawa
Classification (USDA)	medium sand	medium sand
Clay (%)	0.1	0.2
Silt (%)	2.6	2.6
Very fine sand (%)	14.6	15
Fine sand (%)	21.2	30.9
Medium sand (%)	39.1	40.3
Coarse sand (%)	22.2	10.7
Very coarse sand content (%)	0.2	0.3
pH	5.35	4.22
Electrical conductivity (ms.cm^{-1})	0.327	1.471
Oxydo reduction potential (mV)	273.75	42.4
Total Organic Carbon (%)	1.189	6.793
Fe (mg/Kg)	1629	2641
CEC (m$_{eq}$/100g)	1.55	2.98
NO_2-NO_3 (mg-N/Kg)	286	863

6.13 Mass balance on source terms and soils

Analyses were performed after the experiment to determine the concentrations of perchlorates, nitrites, nitrates, and NG in the source term spread on top of the columns. The mass lost for each compound was calculated (Table 6-6). Soil from Columns C (Valcartier) and E (Petawawa) will soon be analyzed for their DNG and MNG concentrations.

Nitrites and perchlorates were almost completely washed out through the unsaturated zone for both sites. Moreover, nitrites were not stable and were quickly transformed into nitrates in contact with oxygen. Nitrate concentrations in the source term remained high after the experiment, and losses are about 50%. These findings reinforce the assumption that the degradation products of NG, such as nitrates, are caught in the NC matrix. NC delays the dissolution of compounds and their transport in the unsaturated zone.

The loss of NG was significantly lower than the other compounds in the source term with only 16% removed by watering for Valcartier, proving that NG can be a long-term source in soil because it is embedded in NC. The mass balance of NG in the source term before and after the 2-year infiltration test is confirmed by the mass balance of NG in the effluent recovered at the base of the column (total mass of the NG in the effluent to the initial mass of NG in the source term), which was 12% for Column C–Valcartier and estimated to be 0% for Column E–Petawawa by inference of the lack of NG in the column effluent.

Table 6-6. ClO_4^-, NO_2^- and NO_3^- concentrations in the source term on top of the soil Column C–Valcartier and Column E–Petawawa after the experiment

	Source Term Concentration (mg/kg $_{soil}$)					
	Column C – Valcartier			Column E – Petawawa		
Compound	Initial	Final	Lost (%)	Initial	Final	Lost (%)
ClO_4^-	0.00352	NA	NA	0.05346	0.0058	89
NO_2^-	307	25	92	483	58	88
NO_3^-	296	159	46	634	329	48
NG	3145	2627	16	5652	–	–

NA: Not analyzed (No NG recovered from effluent).

NG concentration in Valcartier soil Column C at the end of the experiment as a function of depth show also that most of the NG is still located in the source term (0–2 cm) on top of the sand column; however, some transport or cross-contamination occurred within the first 0-5 cm below the source term. NG was not detected in any of the soil samples between 5 and 60 cm below the source term.

Based on Column C Valcartier results, NG is a short-term source in groundwater because the available NG at the surface of the NC particles is washed away within a year after its deposition on the ground surface. The remaining NG embedded in NC at the soil surface is not very available for dissolution by precipitation. So, if the training activity stops, no more NG will be flushed through the unsaturated zone even if high concentrations of NG still exist at the soil surface. This observation is confirmed by the Carpiquet study, a site with a firing position that had been abandoned for 30 years (see Chapter 5). In that study, NG or NG degradation products were neither detected in water of the unsaturated zone nor in groundwater of the aquifer below the firing point, even though high concentrations of NG were still present in the surface soil.

Determination of NG concentrations in the soil profile of Petawawa (Column E) at the end of the experiment also show that most of the NG is still in the 0-2 cm source term with some transport or mixing within the first 0-5 cm below the source term (Figure 6-28). In this column, a small slug of dissolved NG was found at the 40–50 cm interval. This slug contains a mass of 35 mg of NG and has a mean NG concentration of 4.0 mg/L or 4000 µg/L. This was calculated using the concentration and physical parameters of the soil column (thickness, radius, soil density) dissolved in 8.8 L of water. The water content of the 10-cm layer of soil at 40-50 cm was 0.325%. This value is above the MCL and in the same range as observed in the effluent of Valcartier column test. This profile also shows that NG is probably highly biodegraded along the pathway because the mass at depth is only 0.1% of the initial NG mass in the source term (35 mg versus 28.26 g). It was concluded that the retardation factor of dissolved NG due to its adsorption in the organic matter of the source term is probably around a value of 6 transport pore volumes. Since the dissolution front in the soil column was located at 45 cm deep after the injection of 4.5 transport pore volumes, it is assumed that at least 6 transport pore volumes will be necessary to flush this front out of the 60-cm-long column.

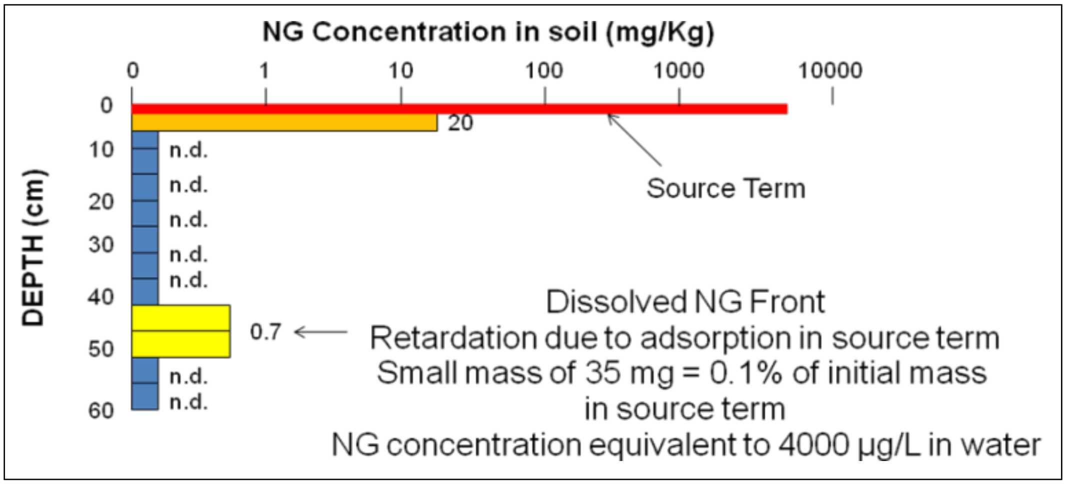

Figure 6-28. NG concentration in Petawawa soil for Column E at the end of the experiment as a function of depth.

Based on Column E–Petawawa results, NG can be adsorbed in the top soil if it contains organic matter. Adsorption slows down the vertical movement of the dissolved NG compared to water velocity and, when adsorption is combined with a lower infiltration rate, according to climatologic data, residence time of dissolved NG in water of the unsaturated zone is increased. A longer residence time gives more time for biodegradation/ degradation processes along the flow path in the unsaturated zone. Massive production of NO_{3-} (six times its initial mass in the source term soil based on mass balance in the effluent) in the column effluent proves that degradation of NG occurs. Therefore, it may be possible to not detect NG deep in the unsaturated zone or in the aquifer below a firing position even if high concentrations of NG exist in the top soil.

6.14 Bacterial analysis

At the end of the sand column experiment, a total cell count was done at different depths in the soil profiles of Column C (Valcartier) and Column E (Petawawa), shown in Figure 6-29. Initial concentrations in the uncontaminated soils from Valcartier and Petawawa were 1,900 and 2,500 colony-forming units (CFUs), respectively. These values are higher than expected for sand with less than 1% of organic carbon.

No bacterial activity was noted at 4 °C. Soils from Columns C and E contained generally uniform bacterial activity at 21 °C throughout their depth. Bacterial activity was higher in soils that were in contact with propellant residues diluted in water than in the initial uncontaminated soil.

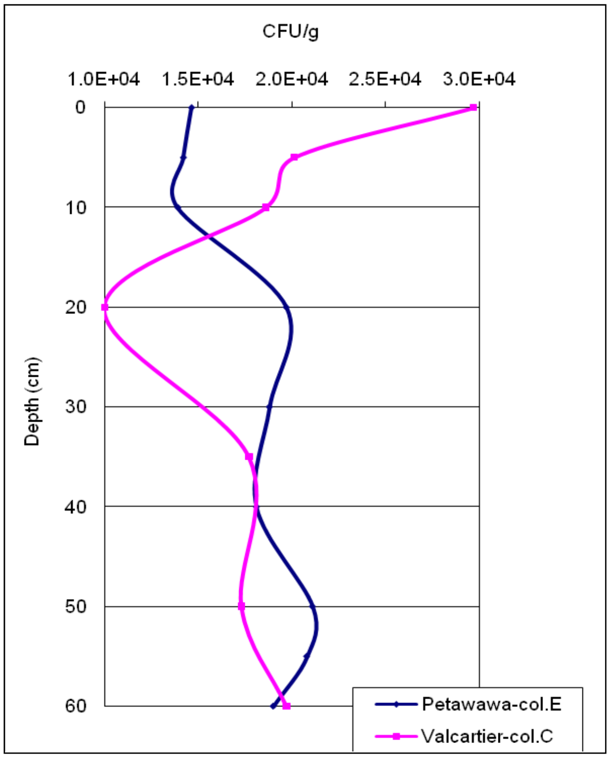

Figure 6-29. Total cell count (TCC) for soils from Column C (Valcartier) and Column E (Petawawa) at 21 °C.

6.15 Surface and groundwater quality at firing positions

Water samples from Valcartier (6 groundwater) and from Petawawa (10 groundwater and 2 surface water) were taken downstream of firing positions in summer 2008. Samples were analyzed for NG, 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG. All samples for NG, DNG, and MNG showed concentrations below the detection limit, even if wells were in an unfavorable position such as near a firing position (< 10 m), where the groundwater was shallow (< 2 m), or the unsaturated zone was mainly sand. Moreover, there have been no reports in the literature of NG in groundwater samples from antitank rocket range areas, or at any other range (Jenkins et al. 2007). However, limit of detection of the analytical method used was high, and all of the above samples needed to be reanalyzed with the analytical method developed (Appendix 6-A), where detection limits of 1.2 µg L^{-1} for NG, 0.3 µg L^{-1} for 1.3-DNG, and 0.4 µg L^{-1} for 1.2-DNG are reached.

6.16 Conclusion

Propellant residues accumulated from soil on two Canadian Forces antitank firing positions were sampled and put on top of 60 cm x 60 cm sand columns filled with unsaturated and uncontaminated soil. The columns were watered, and the fate and behavior of the propellant residues were followed in the effluent of the columns, as well as in the source term on top of the columns and in the soil profiles at the end of this 2-year test. This project shows that propellant residues constituents such as perchlorate, nitrite, nitrate, NG, MNGs, and DNGs are dissolved by precipitation, may be mobile in the unsaturated zone, and may have an impact on groundwater quality. To reach the groundwater table, however, specific conditions have to be present: newly generated propellant residues, a significant amount of recharge by precipitation, shallow permeable unsaturated zone, and low TOC in the surface soil.

The source term contained initially high concentrations of nitrite and nitrate. For both types of sand columns tested (Petawawa and Valcartier) 90% of nitrite and 47% of nitrate initially associated to the NC matrix of the source term were washed through the unsaturated zone after 2 years of watering. These compounds, when diluted into the upper part of the aquifer, may not be a concern. A fraction of nitrite was transformed into nitrate in contact with oxygen.

For the Valcartier column test, 16% of NG and its degradation products initially in the source term were dissolved in water during the first year of watering (369 mm) and were not retarded through the sandy unsaturated zone. This means that, if there is no addition of new propellant residues at a firing position (no more firing), no more dissolved concentrations of NG and its degradation products will be detected in water under the firing position after a year because the remaining NG, MNGs and DNGs, nitrite, and nitrate are embedded within the NC.

Petawawa column tests, which have a source term with high organic matter (6%) and a low watering rate (237 mm per year), show a massive production of dissolved nitrate in the effluent equivalent to more than six times its initial mass in the source term. During this 2-year test, no nitrite, NG, or degradation products were detected in the columns' effluent. Most of the NG and its degradation products remained in the source term, but some of them were located in the soil close to its exit indicating a retardation factor of 6 associated with the organic matter in the source term. The biodegradation of dissolved NG, MNG, and DNG into nitrite that was transformed into nitrate along the flow path may explain the high nitrate content in the column effluent.

6.17 Acknowledgements

We wish to thank the financial support from Director General Environment , from Director Land Environment, from the Ministry of National Defense in Canada, and from SERDP through research project ER-1481. We appreciated the technical support of INRS-ETE staff: Richard Léves-que and Michelle Bordeleau (chemical analysis technicians) and Sébastien Lange (post-doctoral fellow) at INRS-ETE for his in soil sampling and chemical analysis on soil.

6.18 References

Accashian, J.V., B.F. Smets, and B.J. Kim. 2000. Aerobic biodegradation of nitroglycerin in a sequencing batch reactor. *Water Environment Research* 72 (4):499-506.

Christodoulatos, C., Bhaumik, S., Brodman, B.W. 1997. Anaerobic biodegradation of nitroglycerin. *Water Research* 31 (6):1462-1470.

Dubé, P., S. Thiboutot, G. Ampleman, A. Marois, and M. Bouchard. 2006. *Preliminary Assessment of the Dispersion of Propellant Residues from the Static Live Firing of 105 MM Howitzer*. DRDC Valcartier TM 2005-284.

Environnement Canada centre Saint Laurent. 1992. *Guide méthodologique de caractérisation des sédiments.* Gouvernement du Québec, Ministère de l ‘environnement et Environnement Canada. 81-86.

Faucher, D., S. Brochu, I. Poulin, and M.R. Walsh. 2008. *Assessment of Gaseous and Particulate Propellant Residues Resulting From Small Arms Live Firing, Chapter 5, in Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges*. ERDC TR-08-1. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Gillman and Sumpter. 1986. Modification to the compulsive exchange method for measuring exchange characteristics of soil. *Aust. J. Soil Res.* 24: 61-66.

Health Canada. 2007. http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/sum_guide-res_recom/index_e.html.

Hewitt, A.D., and S. Bigl. 2005. *Elution of energetic componds from propellant and composition B residues*. ERDC/CRREL TR-05-13. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Jenkins, T.F., C. Bartolini, amd T.A. Ranney. 2003. *Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil.* ERDC/CRREL TR-03-7. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Jenkins, T.F., J.C. Pennington, G. Ampleman, S. Thiboutot, M.R. Walsh, E. Diaz, K.M. Dontsova, A.D. Hewitt, M.E. Walsh, S.R. Bigl, S. Taylor, D.K. MacMillan, J.L. Clausen, D. Lambert, N. Perron, M.C. Lapointe, S. Brochu, M. Brassard, R. Stowe, R. Farinaccio, A. Gagnon, A. Marois, T. Gamache, B. Quémerais, L. Melanson, R. Tremblay, Y. Cuillerier, G. Gilbert, D. Faucher, S. Yost, C. Hayes, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, and S.P. Saari. 2007. *Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges. Interim Report 1, SERDP Project ER-1481*, ERDC TR 07-1. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Keeney, D.R., and D.W. Nelson. 1982. Nitrogen-inorganic forms. *In:* Methods of soil analysis. Part 2- Chemical and microbiological properties Second Edition (eds. Page, A.L., Miler, R.H. and Keeney, D.R.), pp 643-698. Madison, WI: Soil Science Society of America, Inc.

Lewis, J. 2007. *The transport and fate of detonation residues originating from cracked unexploded ordnance in the vadose zone.* Thèse de doctorat, INRS-ETE.

Martel, R. 2007. *Gestion et restauration des nappes et des sols contaminés.* Université du Québec. Institut national de la recherche scientifique. Centre Eau, Terre, Environnement Notes de cours.

Martel, R., G. Comeau, S. Brochu, and D.A. Hewitt. 2008. Propellant Residues in Surface Soils and Groundwater at Firing Positions at Canadian Force Base Petawawa, Ontario. *ERDC TR-08-1, Chapter 9*. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Martel, R., and P.J. Gélinas. 1996. Surfactant solutions developed for NAPL recovery in contaminated aquifers. *Ground Water* 34 (1):143-154.

Mirecki, J.E., B. Porter, and C.A. Weiss. 2006. *Environnemtal transport and fate process descriptors for propellant compounds.* ERDC TR-06-7. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Robidoux, P.Y, B. Lachance, L. Didillon, F.O. Dion, and G.I. Sunahara. 2006. *Development of ecological and human health preliminary soil quality guidelines for energetic materials to ensure training sustainability of Canadian Forces.* National Research Council Canada, Applied Ecotoxicology Group, Biotechnology Research Institute.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of Gun Propellant Residues from 84-mm Carl Gustav Rocket Firing*. DRDC Valcartier TR 2007-408.

Thomas, G.W. 1996. Soil pH and soil acidity. *In*: Methods of soil analysis. Part 3- Chemical methods (eds. Sparks, D.L.), pp 475-490. Madison, WI: Soil Science Society of America, Inc.

Thiboutot, S., G. Ampleman, A. Marois, A.Gagnon, and D. Gilbert. 2009. *Nitroglycerine Deposition from M-72 Antitank Rocket Firing*. DRDC Valcartier TR 2009-003.

Tipton, D.K., D.E. Rolston, and K.M. Scow. 2003. Transport and biodegradation of perchlorate in soils. *Journal of Environmental Quality* 32 (1):40-46.

U.S. Environmental Protection Agency (EPA). 1994. Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC).

Wendt, T.M., J.H. Cornell, and A.M. Kaplan. 1978. Microbial degradation of glycerol nitrates. *Applied and Environmental Microbiology* 36:693-699.

White, G.F., J.R. Snape, and S. Nicklin. 1996a. Bacterial biodegradation of glycerol trinitrate. *International Biodeterioration & Biodegradation* 38(2):77-82.

White, G.F., J.R. Snape, and S. Nicklin. 1996b. Biodegradation of glycerol trinitrate and pentaerythritol tetranitrate by Agrobacterium radiobacter. *Applied and Environmental Microbiology* 62(2):637-642.

Appendix 6-A: Determination of Nitroglycerin (NG) and its Degradation Products by Solid-Phase Extraction/Liquid Chromatography UV

Richard Martel, Aurélie Bellavance-Godin, Richard Lévesque,
*and Sébastien Côté**

Abstract

The usual U.S. Environmental Protection Agency (EPA) analytical method (EPA 8330B) cannot properly separate the four degradation products of NG (1-MNG, 2-MNG, 1,2-DNG, and 1,3-DNG). An analytical method for the determination of the degradation products of NG in water using LC/MeOH was developed at 205 nm. The most suitable solid phase extraction (SPE) cartridge was selected in order to reach the required detection level of these products in water. The combination of the extraction and liquid chromatography (LC) analysis is sensitive and allows detection of NG and its products at µg L-1 level. The technique is straightforward and can help to understand the environmental fate of NG.

Introduction

Nitroglycerin is industrially important as a result of two major applications. First, it is widely used as a powerful explosive [1] and second, it is an effective vasodilator in the treatment of heart disease [2]. Degradation products of NG include dinitroglycerine (DNG; such as 1,2-dinitroglycerine [1,2-DNG], 1,3-dinitroglycerine [1,3-DNG]), and mononitroglycerine (MNG; such as 1-mononitroglycerine [1-MNG], and 2-mononitroglycerine [2-MNG]) [2]. These compounds can be detected in waste water and soil at production sites and soil at storage sites. The environmental monitoring of the degradation products of NG is also important because DNG and MNG are much more soluble than NG and potentially more toxic [3]. A sensitive technique is necessary for their monitoring in the environment because they are usually present at trace levels (µg L-1).

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* This appendix was previously published in the Feb 2010 issue of *Chromatographia* (see bibliography in Chapter 10).

Currently used analytical methods for the determination of explosives [4] include gas chromatography that is equipped with a thermal conductivity detector analyzer [1], electron capture [1; 5; 6], nitrogen phosphorus detector [7] or mass spectrometry detector [8]. Liquid chromatography may be also used with an ultraviolet (UV) detector [9-17] or mass spectrometry (MS) detector [18].

Current methods for extracting explosives are liquid-liquid extraction (LLE) [20], salting-out liquid-liquid extraction (SOE) [21; 22], solid-phase microextraction (SPME) [23–25] and solid-phase extraction (SPE) [20; 22; 26-28]. LLE and SOE are time consuming, require large volumes of solvents, and can lead to different extraction efficiencies depending on the compounds investigated [23]. SPE is a robust method, which offers the advantage of a lower consumption of organic solvent. Moreover, detection limit of the SPE method is significantly lower than the SPME method [23].

In this study, the potential use of SPE/LC-UV to analyze nitroglycerin and its degradation products was investigated. To our knowledge, no publications exist that deal with the use of extraction methods for the quantification of NG degradation products. The well-known EPA Method 8330B analyzes NG but not its degradation products [29]. Octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX) and 1,3,5-Trinitrobenzene (1,3,5-TNB) can be analyzed with EPA method 8330B even if 1,2-DNG and 1,3-DNG are present. However, DNG analyses cannot be achieved because of the interference of HMX and 1,3,5-TNB at 205 nm (Figure 6-A1). Furthermore, the two MNGs are not adequately separated from each other in this EPA method.

Experimental materials and procedures

Chemicals and reagents

LC-MS grade methanol, acetonitrile, and acetone were from Sigma-Aldrich (St. Louis, MO) and filtrated before use. Distilled water was further purified by flowing it through a milli-Q Plus apparatus. The control solution for EPA 8330B was a standard solution containing 14 explosives at a concentration of 1 mg mL-1 each in AcN:MeOH (1:1) (Accustandard, New Haven, CT). Control solutions were prepared with a standard solution of 0.1 mg mL-1 of 1-MNG, 2-MNG, 1,2-DNG, 1,3-DNG in AcN:MeOH (1:1) and a solution of 1 mg mL-1 of NG in EtOH:MeOH (97:3) (Accustandard, New Haven, CT).

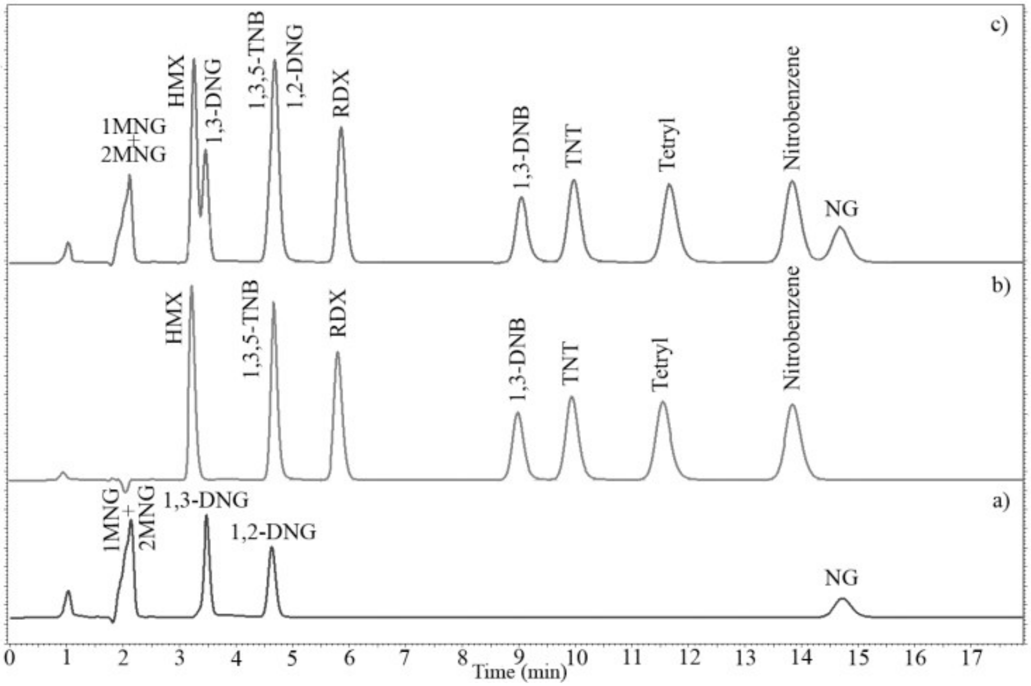

Figure 6-A1. Method EPA 8330B with and without the degradation products of NG at 205 nm in water:i-PrOH (85:15) by LC-UV : a) Detection of NG, MNG, and DNG standard; b) Detection of EPA method 8330B standard; c) Detection of NG, MNG, and DNG standard combine with the EPA method 8330B standard (Martel et al.).

Model water samples

Three model water samples were studied to determine the lowest analytical concentration of each compound using SPE: (1) model water sample A (MWS-A) for NG and its degradation products detection limits evaluation from 40 mL of deionized water spiked with NG, MNG, and DNG in a concentration of 100 µg L^{-1} for each compound; (2) model water sample B (MWS-B) for MNG detection limits evaluation from 20 mL of deionized water spiked with NG, MNG, and DNG in a concentration of 200 µg L^{-1} for each compound, and (3) model water sample C (MWS-C) for very low NG and DNG detection limits from 400 mL of deionized water spiked with NG, MNG, and DNG in a concentration of 10 µg L^{-1} for each compound.

LC-UV system

NG and its degradation products were analyzed separately using a liquid chromatograph (Agilent 1200 series) equipped with a Zorbax Eclipse XDB-C18 column (4,6 mm × 150 mm, 5µm; Whatman, Inc.). A first eluting method for the degradation products was developed using an isocratic mobile phase of 5% methanol and 95% deionized water (Figure 6-A2). Then, a second eluting method was developed for the analysis of NG using an isocratic mobile phase containing 50% methanol and 50% deionized water due to the long time needed to elute NG with the first method.

The analyses were conducted at a flow rate of 1 mL min^{-1}, and the column temperature was kept at 25 °C. A 20-µL sample was injected into the chromatographic column. NG eluted with the second method was observed within 10 minutes; 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG were eluted with the first method within 20 minutes. The UV-detector wavelength was set at 205 nm. Quantification was carried out using calibration curve and peak area measurements.

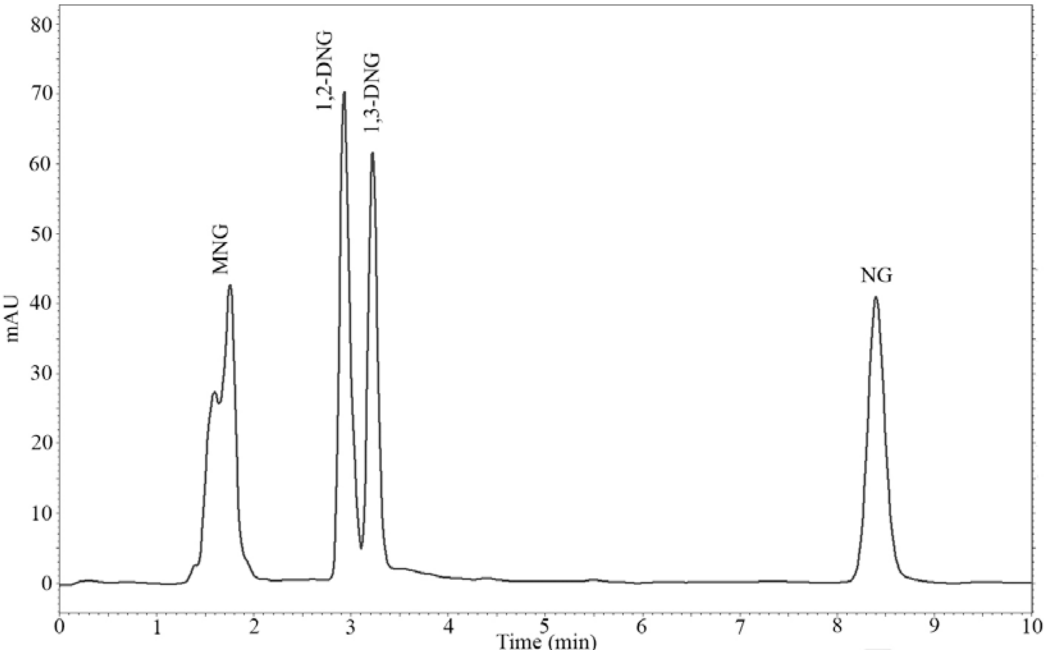

Figure 6-A2. LC separation of MNG and DNG with UV detection at 205 nm in water:MeOH (95:5).

Extraction procedure with SPE cartridges

Various sorbents and solvents were tested to compare their interaction properties in the extraction process of NG and its degradation products in water sample. The following SPE cartridges were tested: Water Oasis Max 6 cc 500 mg, C-18 Plus, Water Diol, Prapak RDX 500 mg, and Water HLB 200 mg and 500 mg (Water: Milford, MA). The general sample preparation procedure for SPE cartridges was as follows: (1) conditioning the SPE cartridge by successive washing with 3 mL of methanol and two times 3 mL of deionized water; (2) loading the Model Sample waters (MWS-A or MWS-B or MWS-C) in the cartridge; (3) eluting the analytes with 2 mL of solvent (methanol or acetonitrile or acetone) off the SPE cartridge; (4)

completing this solution to 4 mL with deionized water in order to have a solvent: water ratio of 1:1; and (5) injecting 20 µL of this solution into the LC-UV system.

Results and discussion

First, the LC method was validated and tests were carried out to determine the best SPE cartridge, solvent, and sample volume.

LC method validation

Calibration curves were created ranging from 0.2 to 4 mg L^{-1} (0.2, 0.5, 1, 2, and 4 mg L-1) for all analytes. A five-point calibration curve was created for each analyte. Good linearity was observed for all the analytes in 0.2 to 4 mg L^{-1} ranges ($r^2 = 0.999$). The precision and accuracy of the method were evaluated intra- and inter-day by analyzing six replicates. The accuracy of the method was determined as percent of error, while precision was evaluated by intra- and inter-day relative standard deviation. All parameters were in acceptable range of 1-5% depending on the analyte.

The LOQ was the lowest concentration that can be determined in a sample with acceptable precision under stated operational conditions of the method. The LOD was the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value). The LOD was determined by analysis of ten replicates of concentration, which gave signals equal to 10 times the noise level of the chromatograph. The LODs for the NG and its degradation products (2-MNG, 1-MNG, 1,3-DNG, and 1,2-DNG) obtained were 120, 5.5, 15, 29, and 35 µg L^{-1}, respectively. The LOQs were about three times the LODs with 390, 18, 49, 96, and 120 µg L^{-1} respectively for NG and its degradation products.

SPE optimization

Extraction recoveries with various SPE cartridges

The selection of the SPE with the most suitable sorbent material plays an important role in achieving high and reproducible recovery of NG and its degradation products. Several types of SPE sorbents were tested for extraction of NG and its degradation products from model water sample A (MWS-A) at different pH (neutral and acid). Basic pH was disregarded because energetic materials are known to degrade or react under basic conditions. Methanol was used as elution solvent in tests. The best extraction for all analytes was obtained with Water Oasis HLB 500-mg cartridges (Figure 6-A3) at acid pH of 3. So, Water Oasis HLB copolymer cartridges were chosen to be used for further testing. The use of water diol cartridges at pH 3 and 7 did not trap any of the analytes and was discarded.

Elution with different solvents

The recovery of analytes by SPE cartridges was highly dependent on the polarity of the eluents. Acetone, acetonitrile, and methanol as eluents were tested for the elution of NG and its degradation products with MWS-A and Waters Oasis HLB 500-mg cartridge. Comparison of these extraction recoveries with all solvents is shown in Figure 6-A4. The best extraction recovery for the tested cartridge was observed with methanol as eluent. Acetone showed no recovery for the two MNGs.

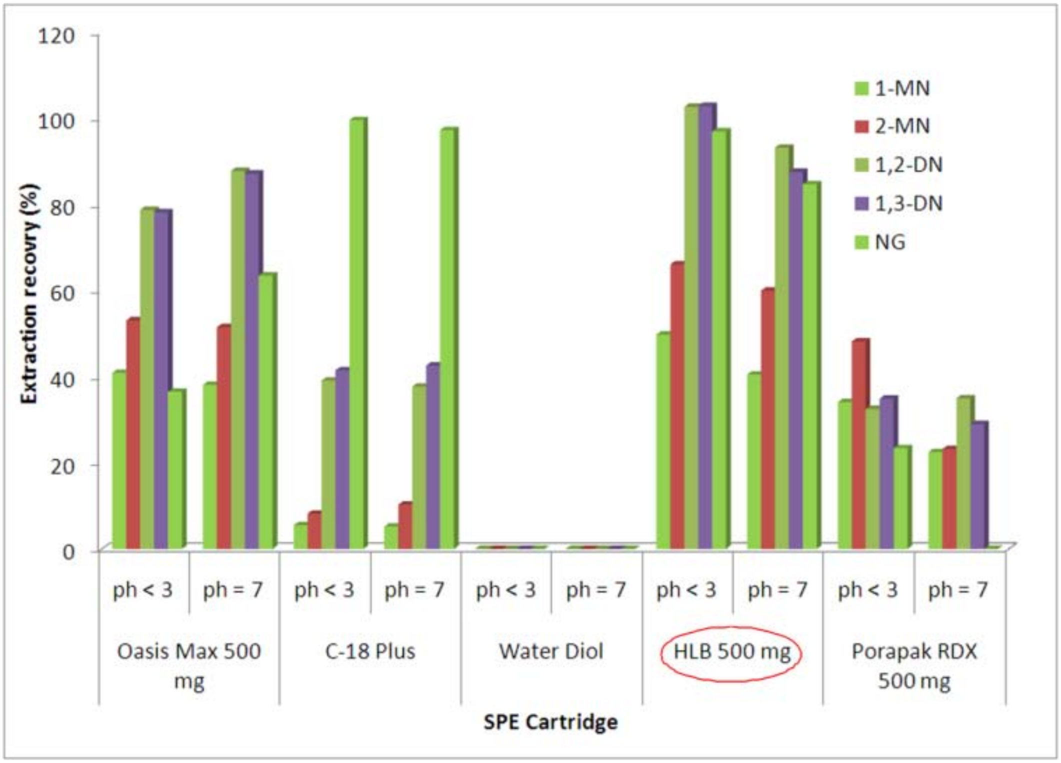

Figure 6-A3. Extraction recoveries obtained with tested SPE cartridges (Martel et al.).

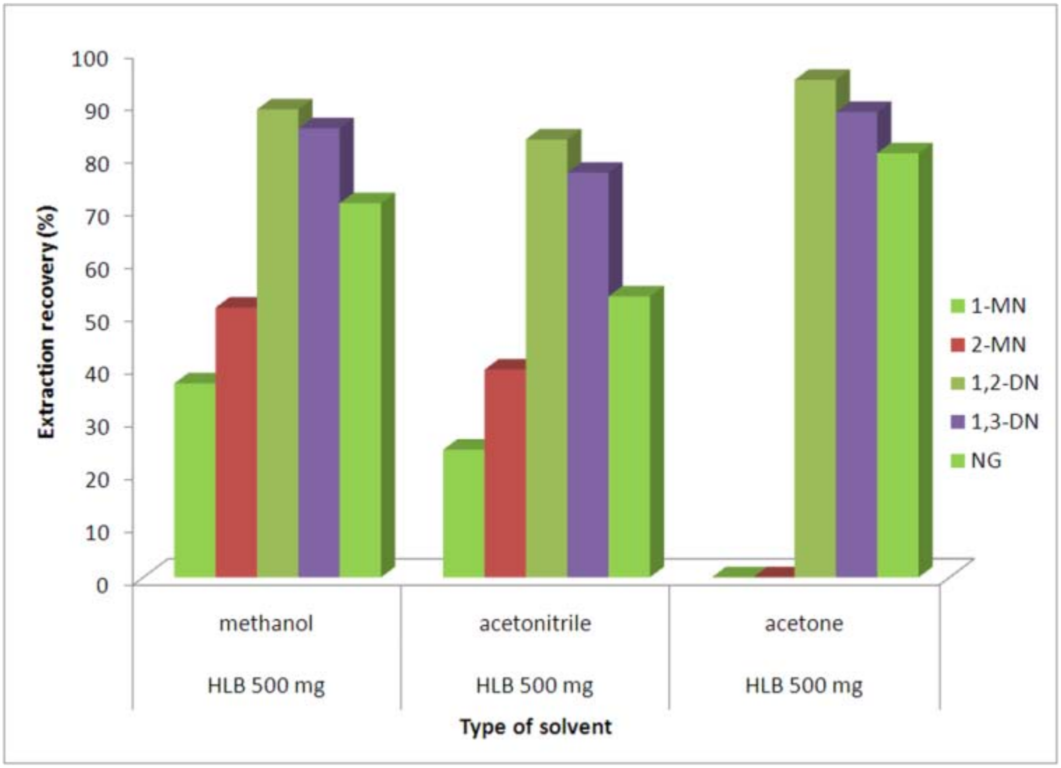

Figure 6-A4. Comparison of extraction recoveries for various elution solvents (Martel et al).

Affinity between the SPE cartridge and the tested compounds

The quantity of water sample that can be loaded in the SPE cartridge determined the sensitivity of the analytical method. The affinity of the sorbent in the SPE cartridge with each analyte limited the total quantity of analytes that can be trapped in the cartridge. Testing was done to determine the optimal volume of water sample that can be eluted in the SPE cartridge without eluting some of the tested analytes. With a model water sample of 40 ml (MWS-A), some of the MNG that had less affinity with the sorbent was lost from the SPE cartridge, as indicated by the low recovery (less than 60%). Acceptable recovery above 60% was observed for MNG with a model water sample of 20 ml (MWS-B). Also with this injected volume in the Waters Oasis HLB 500-mg SPE cartridge, a recovery above 80% was observed for NG, DNG, and 2-MNG. Methanol as elution solvent in combination with Waters Oasis HLB 500-mg SPE cartridge was chosen for the analysis of 20 mL of model water sample (MWS-B) and for the determination of the limit of detection (LOD).

Comparison between model water samples

The LOD values for MWS-A and MWS-B water samples were not adequate for a proper quantification of NG and its degradation products in water samples at the low µg L^{-1} considering that a 5 µg L^{-1} threshold value is required for drinking water quality. MWS-A has an LOD of 24 µg L^{-1} for NG whereas MWS-B has an LOD of 12 µg L^{-1} for NG. The model water sample C (MWS-C) of 400 mL was then extracted with the Water Oasis HLB 500-mg cartridge in order to lower the LOD for NG and also for both DNGs. The model sample was concentrated and analyzed in replicate. Increasing the volume of the sample from 20 mL (MWS-A) to 400 mL (MWS-C) decreased the limit of quantification (LOQ) and the LOD by 20.The percentage recovery for NG and both DNGs is excellent within 2.5% of error in average for two samples.

Analyses of groundwater samples

Groundwater samples were collected at the base of a sand column where propellant residues were spread on top and then watered following an existing infiltration rate according to spring snowmelt and autumn rainfall data in Valcartier, Québec, Canada. More than 250 water samples were successfully analyzed with the method developed as shown in an earlier paper [30]. Groundwater samples from observation wells located in training areas of some Canadian Force Bases were also analyzed with this technique at the µg L^{-1} detection levels.

Conclusions

An analytical method for the quantification of NG and its degradation products using SPE cartridge and an LC-UV system was successfully developed. The operating optimal conditions for NG and its degradation products in one-extraction were achieved with an SPE cartridge Water Oasis HLB 500 mg, methanol as the eluent, and 20 mL as the sample volume. This procedure achieved LODs of 24 µg L^{-1} for NG, 2 µg L^{-1} for 2-MNG, 3 µg L^{-1} for 1-MNG, 6 µg L^{-1} for 1,3-DNG, and 6 µg L^{-1} for 1,2-DNG. For lower detection limits of 1.2 µg L^{-1} for NG, 0.3 µg L^{-1} for 1.3-DNG, and 0.4 µg L^{-1} for 1.2-DNG, the extraction was made with an SPE cartridge Water Oasis HLB 500 mg, methanol used as the eluent, and 400 mL of sample volume.

Appendix 6-A References

1. Yinon, J., and S. Zitrin. 1993. *Modern methods and applications in analysis of explosives*. New York, NY: Wiley, 163-188.

2. Wendt, T.M., J.H. Cornell, and A.M. Kaplan. 1978. Microbial degradation of glycerol nitrates. *Appl. Environ. Microbiol* 36 (5): 693-699.

3. Ellis III,.H.V., J.R. Hodgson, S.W. Hwang, L.M. Halpap, and D.O. Helton. 1978. Disposition and metabolism and Ames test of additional compounds. Kansas City, MO: Midwest Resources Institute.

4. Gaurav D, A.K. Malik, and P.K. Rai. 2007. *Critical reviews in analytical chemistry*. Abington, Oxford, UK: Taylor & Francis, 227-268.

5. Jenkins, T.F., D.C. Leggett, P.H. Miyares, M.E. Walsh, T.A. Ranney, J.H. Cragin, and V. George. 2001. Chemical signatures of TNT-filled land mines. *Talanta* 54 (3):501-513.

6. Furton, K.G., J.R. Almirall, M. Bi, J. Wang, and L. Wu. 2000. Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens. *J. Chromatogr. A* 885 (1-2): 419-432.

7. Batlle, R., H. Carlsson, P. Tollback, A. Colmsjo, and C. Crescenzi. 2003. Enhanced detection of nitroaromatic explosive vapors combining solid-phase extraction-air sampling, supercritical fluid extraction, and large-volume injection-GC *Anal. Chem*. 75:3137-3144.

8. Yinon, J. 1996. Trace analysis of explosives in water by gas chromatography-mass spectrometry with a temperature-programmed injector. *J. Chromatogr. A* 742(1-2):205-209.

9. Oh, S.Y., P.C. Chiu, and D.K. Cha. 2008. Reductive transformation of 2,4,6-trinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine, and nitroglycerin by pyrite and magnetite. *J. Hazard. Mater*. 158(2-3):652-655.

10. Oh, S.Y., D.K. Cha, B.J. Kim, and P.C. Chiu. 2004. Reduction of nitroglycerin with elemental iron: pathway, kinetics, and mechanisms. *Environ. Sci. Technol.* 38(13): 3723-3730.

11. Accashian, J.V., B.F. Smets, and B.J. Kim. 2000. Aerobic biodegradation of nitroglycerin in a sequencing batch reactor. *Water Environ. Res*. 72(4):499-506.

12. Marshall, S.J., and G.F. White. 2001. Complete denitration of nitroglycerin by bacteria isolated from a washwater soakaway. *Appl. Environ. Microbiol.* 67(6):2622-2626.

13. Christodoulatos, C., S. Bhaumik, and B.W. Brodman. 1997. Anaerobic biodegradation of nitroglycerin. *Water Res*. 31(6): 1462-1470.

14. Zhang, Y.Z., S.T. Sundaram, A. Sharma, and B.W. Brodman. 1997. Biodegradation of glyceryl trinitrate by Penicillium corylophilum Dierckx. *Appl. Environ. Microbiol.* 63(5):1712-1714.

15. White, G.F., J.R. Snape, and S. Nicklin. 1996. Biodegradation of glycerol trinitrate and pentaerythritol tetranitrate by agrobacterium radiobacter. *Appl. Environ. Microbiol.* 62(2): 637-642.

16. Bhaumik, S., C. Christodoulatos, G.P. Korfiatis, and B.W. Brodman. 1997. Aerobic and anaerobic biodegradation of nitroglycerin in batch and packed bed bioreactors. *Water Sci. Technol.* 36(2-3):139-146.

17. Meng, M., W.Q. Sun, L.A. Geelhaar, G. Kumar, A.R. Patel, G.F. Payne, M.K. Speedie, and J.R. Stacy. 1995. Denitration of glycerol trinitrate by resting cells and cell extracts of bacillus thuringiensis/cereus and enterobacter agglomerans. *Appl. Environ. Microbiol.* 61(7):2548-2553.

18. Gates, P.M., E.T. Furlong, T.F. Dorsey, and M.R. Burkhardt. 1996. Determination of nitroaromatic explosives and their degradation products in unsaturated-zone water samples by high-performance liquid chromatography with photodiode-array, mass spectrometric, and tandem mass spectrometric detection. *TrAC Trends Anal. Chem.* 15(8):319-325.

19. Casetta B, Garofolo F. 1994. Characterization of explosives by liquid chromatography/mass spectrometry and liquid chromatography/tandem mass spectrometry using electrospray ionization and parent-ion scanning techniques. *Org. Mass Spectros* 29(10):517-525.

20. Feltes, J., K. Levsen, D. Volmer, and M. Spiekermann. 1990. Gas chromatographic and mass spectrometric determination of nitroaromatics in water. *J. Chromatogr.* 518(1):21-40.

21. Leggett, D.C., T.F. Jenkins, and P.H. Miyares. 1990. Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. *Anal. Chem.* 62(13):1355-1356.

22. Jenkins, T.F., P.H. Miyares, K.F. Myers, E.F. McCormick, A.B. Strong. 1994. Comparison of solid phase extraction with salting-out solvent extraction for preconcentration of nitroaromatic and nitramine explosives from water. *Anal. Chim. Acta* 289(1):69-78.

23. Monteil-Rivera, F., C. Beaulieu, S. Deschamps, L. Paquet, and J. Hawari. 2004. Determination of explosives in environmental water samples by solid-phase microextraction-liquid chromatography. *J. Chromatogr. A* 1048(2):213-221.

24. Jezová, V., J. Skládal, A. Eisner, P. Bajerová, and K. Ventura. 2007. Determination of nitrate esters in water samples: comparison of efficiency of solid-phase extraction and solid-phase microextraction. *J. Chromatogr. A* 1174(1-2):13-19.

25. Calderara, S., D. Gardebas, and F. Martinez. 2003. Solid phase micro exraction coupled with on-column GC/ECD for the post-blast analysis of organic explosives. *Forensic Sci. Int.* 137(1):6-12.

26. U.S. Environmental Protection Agency. 1998. Method 8535A SW-846, solid-phase extraction (SPE). Washington, DC: Office of Solid Waste.

27. Cassada, D.A., S.J. Monson, D.D. Snow, and R.F. Spalding. 1999. Sensitive determination of RDX, nitroso-RDX metabolites, and other munitions in ground water by solid-phase extraction and isotope dilution liquid chromatography-atmospheric pressure chemical ionization mass spectrometry. *J. Chromatogr. A* 844(1-2): 87-95.

28. Smith, M., G.E. Collins, and J. Wang. 2003. Microscale solid-phase extraction system for explosives. *J. Chromatogr. A* 991(2):159-167.

29. U.S. Environmental Protection Agency. 2006. Method 8330B, Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC) http://www.epa.gov/osw/hazard/testmethods/pdfs/8330b.pdf

30. Bellavance-Godin, A., R. Martel, G. Ampleman, and S. Thiboutot. 2008. Sustainable use of military training areas: Environmental fate and transport of nitroglycerin from propellant residues at firing positions in the unsaturated zone. Paper presented at 9th Joint IAH-CNC and CGS Groundwater Specialty Conference, 61th Canadian Geotechnical Conference, October 21-24, Edmonton, session W2-B Source Water Protection IV and Hydrogeology of the Great Lakes Basin and St. Lawrence Lowlands II.

7 Energetic Residues from the Expedient Disposal of Artillery Propellants

Michael R. Walsh, Marianne E. Walsh, and Alan D. Hewitt[*]

7.1 Abstract

Military live-fire training missions utilizing mortars and howitzers frequently generate excess propellant charges. Disposal of this propellant is often done on site and is referred to as expedient disposal. Investigations into energetics residues resulting from expedient disposal of propellants began in 2002 with the collection of residues inside and outside a propellant burn structure. These residues contained very high concentrations of 2,4-Dinitrotoluene, an indication that the burning process was not complete. Other informal tests were conducted, indicating the same results. In 2006 and 2008, a series of tests were conducted on snow using propellants from various mortar cartridges. In one test, 10 charges of mortar propellant were burned on snow and the residues collected and analyzed. Over 15% of the original nitroglycerin content was recovered. In 2008, two series of tests were conducted, one involving winter disposal of mortar propellants, the other summer disposal of howitzer propellants. These tests, conducted under controlled conditions, indicate that the environmental setting and climatic conditions can influence the efficiency of expedient propellant disposal by three orders of magnitude.

7.2 Introduction

Military ranges provide soldiers the opportunity to train using a variety of munitions. When training with artillery, a full complement of propellant charges is provided with each round and, depending on the need of the exercise, excess propellant charges may be generated. These charges contain a nitrocellulose (NC) matrix combined with energetic materials such as nitroglycerin (NG), 2,4-dinitrotoluene (2,4-DNT), and nitroguanidine (NQ). Characterization studies conducted at various firing points (FP) have demonstrated that propellants are not completely consumed during

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[*] Portions of this chapter were previously published as ERDC/CRREL TR-09-8 (see bibliography in Chapter 10).

live-fire exercises (USACHPPM 2000; Ogden EES 2000; Jenkins et al. 2001; M.E. Walsh et al. 2004, 2007; Dubé et al. 2006; Thiboutot et al. 2007). We thus hypothesized that significant energetic residues would be generated by the open burning of excess propellant charges at these training sites.

In June of 2002, Marianne Walsh and Arthur Gelvin conducted a test to determine if measurable amounts of energetics remained after burning of excess M1 propellant from 105-mm howitzer cartridges in a sand-filled burn pan (Walsh et al. 2004). The measured concentration of 2,4-DNT in the sand collected from within the burn pan following the tests was 2.3 g/kg and the concentration of 2,4-DNT found in soil samples collected on the ground downwind of the burn pan was 0.12 g/kg. In addition, concentrations of 2,6-DNT of approximately 5% of the 2,4-DNT were also found. The obvious conclusion is that the open burning of excess propellants will generate significant amounts of energetics residues.

The State of Alaska has listed 2,4-DNT as a Class 2 carcinogen. The U.S. Army Alaska was thus interested in knowing the possible extent and sources of this compound on their training ranges. In addition, a Strategic Environmental Research and Development Program project (ER-1481) under Dr. Thomas Jenkins of the U.S. Army Engineer Research and Development Center — Cold Regions Research and Engineering Laboratory (ERDC–CRREL) was investigating propellant residues from the use of munitions. Leveraging both interests, a series of tests were performed starting in the winter of 2006 in Alaska to estimate the deposition rate of energetics residues resulting from the open burning of excess propellants.

7.3 Field test methods

7.3.1 Field sites

The project’s three test series were conducted at field sites within either the Eagle River Flats Impact Area (ERF) of Fort Richardson, Alaska (FRA), or at Observation Point 7 (OP 7) in the Donnelly Training Area (DTA) near Fort Greely, Alaska.

The first series of tests occurred January 2006 at Firing Point (FP) Upper Cole (M.R. Walsh et al. 2006). FP Upper Cole is an open, gravelly area atop a bluff overlooking ERF. At the time of the test, it was covered with 25–35 cm of snow (Figure 7-1).

a. Winter 2006

b. Spring 2006

Figure 7-1. Firing Point Upper Cole adjacent to Eagle River Flats at Fort Richardson, AK.

The second series of tests were conducted from February through July 2008 in a basin area adjacent to the open burning/open detonation pad at ERF (Figure 7-2.). The basin was used in the mid-1990s as a containment structure and settlement area for a dredge operation conducted at ERF. Thus, soil in the basin is a peaty loam liner over the underlying native, compacted, unsorted gravel. The 716th Explosive Ordnance Disposal (EOD) detachment at Fort Richardson has used this site on occasion to dispose of unexploded ordnance found in ERF. Detonation of munitions in the basin had not occurred that winter and the nearest legacy (pre-snowpack) detonation point is over 30 m from the test site. None of these prior detonations involved munitions containing materials addressed in the propellant burn tests. At the time of the tests in February 2008, snow depth was 40 cm. Sampling in 2008 at this site occurred once in the winter and twice over the course of the following summer.

The final test included in this report was conducted at OP 7 in July 2008 (Figure 7-3.). OP 7 occupies the top of a bluff looking south over the Delta River. The soils are glacial, unsorted till. For the test, clean sand was spread 40-cm wide x 1.8-m long x 4-cm deep over the ground near the existing burn pan to separate our tests from the existing ground contamination.

Figure 7-2. Basin adjacent to the Eagle River Flats Impact Area.

Figure 7-3. Propellant disposal area at Observation Point 7, Donnely Training Area, AK. Burn pan is in center of image.

7.3.2 Propellants

The tests used excess propellant charges from three different munitions. In the first series of tests, we burned 10 M185 propellant charges from M301A3 81-mm illumination rounds. Each charge contained 13.3 g of M9 double-base propellant. For the second series of tests, 10 to 11 M230 propellant charges from M933 120-mm high-explosive (HE) rounds were burned for each of the three different physical conditions, all with the same meteorological conditions. Each charge contained 130 g of double-base propellant. For the third series of tests, five sets of Charge 6 and Charge 7 propellant bags containing M1 single-base propellant were burned for each condition. Table 7-1 lists the energetics constituents for each test. Appendix 7-A contains complete munitions data for these tests.

Table 7-1. Energetic constituents for propellants used during tests.

Test	Propellant	Constituent	Weight (g)
81-mm burn (10 M185 charges)	M9		13.3
	(each)	NC	7.65
		NG	5.31
		Other	0.34
120-mm winter burn (2 x 11, 1x10 M230 charges)	M45		130
	(each)	NC	112
		NG	13
		Other	5
105-mm summer burn (2 x 5 sets of Increment 6 & 7 M67 charges)	M1	Charges 6 & 7	655
	(per set of 2)	NC	557
		DNT	65
		Other	33

7.4 Tests

Our tests were conducted in association with the 1st Battalion, 501st Parachute Infantry Regiment and the 716th EOD detachment at FRA, and an artillery battery training at DTA. All tests involved standard-issue live munitions. In all tests, a few unburned grains were collected prior to the tests for analysis and confirmation of propellant formulation.

7.4.1 January 2006 test: Mortar propellants on snow

In mid-January of 2006, our first controlled field-expedient burn test of a mortar propellant was conducted. The propellant was excess to the requirement for the training mission and was originally issued with 81-mm M301A3 illumination rounds. No background surface snow sample from the test area was collected because the area had previously been sampled as part of a different test, and background propellant residue levels were known. Ten propellant bags were piled on the snow surface and initiated with a butane lighter (Figure 7-4 and Figure 7-5). Following the burn, all the surface snow in the affected area was collected down to clean snow by following standard snow sampling practices developed at CRREL (M.R. Walsh et al. 2007). A 30-cm annulus surrounding the main sampled area was also collected for analysis. All samples were placed in clean polyethylene (PE) bags for transport to the field lab for processing.

Figure 7-4. 81-mm propellant burn test on snow.

Figure 7-5. 81-mm propellant burn residues.

7.4.2 February 2008: Disposal of M45 mortar propellants under various conditions

The 120-mm burn test was conducted in association with blow-in-place testing of high-explosives cartridges on 14 February 2008. Thirty-two propellant charges were separated from their cartridges prior to detonation. Three setups were assembled. The first setup consisted of 11 charges placed on the snow surface (Figure 7-6). For the second setup, the 40-cm deep snow cover was removed from a 30- x 30-cm area to expose the frozen ground (Figure 7-7); eleven charges were then placed in the center of the cleared area. For the third test, a stainless steel bowl 27 cm across at the bottom, 34 cm across at the top, and 11 cm deep was pressed into the snow surface up to its rim and 10 charges were placed in the center bottom of the bowl. For all three tests, one of the charges was cut open enough to insert a section of M700 time-blasting fuze, which shot a delayed burst of flame into the charges to ignite the propellant.

Figure 7-6. 120-mm propellant burn tests, charges on snow.

Figure 7-7. 120-mm propellant burn tests, charges on frozen soil.

Following the test burns, the residues within the bowl were collected (Figure 7-8) and bagged and the bowl itself placed in a clean PE bag. A 1-m diameter area of the snow surrounding the bowl location (Figure 7-9) was then sampled to a depth of 2.5 cm and sealed in a PE bag for further processing and analysis (see next section). The other two test locations were marked and left for sampling the following spring.

Figure 7-8. Aftermath of 120-mm propellant burn, residues in burn bowl.

Figure 7-9. Aftermath of 120-mm propellant burn, residues surrounding bowl after burn.

7.4.3 June and July 2008: Sampling of M45 burn points

In early June 2008, the two 120-mm propellant burn locations (one with snow and the other with snow removed to the frozen ground) were sampled for propellant residue. First, each location was visually inspected. Both locations had intact propellant grains on the surface (Figure 7-10).

Individual 3-cm diameter cores were obtained to a depth of 2.5 cm within the center portion of the burn points for subsequent laboratory analysis. Then, all of the soil within the top 2.5 cm that had visible grains at each burn point was collected using a stainless steel scoop and placed in a PE bag. A 1-m diameter area was marked at each burn point using survey tape (Figure 7-11) and a 50-increment sample was obtained outside the previously sampled area using a 3-cm corer to a depth of 2.5 cm. Both burn locations were sampled in this manner. All samples were shipped to the analytical lab at Hanover, NH, for chemical analysis.

a) February 2008 following burn.

b) June 2008 prior to first sampling.

c) June 2008 recovered unburned propellant.

d) July 2008 prior to second sampling.

Figure 7-10. M45 mortar propellant grains after burn tests.

Figure 7-11. Sampled area: 120-mm prop burn on frozen ground (June 2008).

Based on the results of analyses from the June sampling, further sampling was conducted at the snow and frozen ground propellant burn sites in July 2008. At each burn point, a 0.5–1.0 m annulus and a 1.0–1.5 m annulus were marked with survey tape (Figure 7-12). Within each annulus, duplicate multi-increment samples were taken. Samples were collected using a 3-cm diameter CRREL-designed coring tool that was set to a depth of 2.5 cm. The number of increments per sample ranged from 20 to 26. Closer examination of the center of the burn points revealed that some grains were missed in the June sampling, so these grains and the underlying soil were collected. Finally, three soil profiles were taken below the locations of the July propellant grains in 2-cm increments (lifts) through the peaty loam to the underlying gravel (Figure 7-13). All samples again were shipped to the analytical lab at Hanover for final processing and analysis.

Figure 7-12. July resampling of 120-mm mortar prop burn sites, showing sampling areas.

Figure 7-13. July resampling of 120-mm mortar propellant burn sites, showing depth samples.

7.4.4 July 2008 test: Howitzer propellants on soil

The final series of tests was conducted in July 2008 (Figure 7-14). An artillery unit was training with 105-mm howitzers at DTA while we were at the site, and we were able to obtain 10 Charge 6 and 10 Charge 7 propellant bags to use in a burn test. Two separate cells consisting of clean sand (1.8-m long x 40-cm wide x 4-cm deep) were placed over the ground. One test cell was wetted, and five Charge 6 and five Charge 7 propellant bags were lined up alternately in the center of the cell. The end bag was cut and the propellant grains spread out in a line for about 5 cm. The end grains were then lit with a butane lighter, and the line of charges proceeded to burn.

For the second test, the 10 bags were lined up as above, only this time on the dry sand cell and ignited by lighting the end bag with the lighter. For both test cells, the burn areas were completely sampled to a depth of about 1.5 cm, followed by sampling outside the burn areas and sampling below the burn areas (Figure 7-14c and Figure 7-14d). Each sample was placed in a clean PE bag for later processing and analysis at the analytical lab in Hanover.

a. Start of burn.

b. Propellant burning on wet sand.

c. Residues after burn.

d. Depth samples.

Figure 7-14. Burning of 105-mm howitzer propellants.

7.5 Sample processing and analysis

7.5.1 Sample preparation

7.5.1.1 Snow samples

Snow samples were melted in a nearby field lab where they were vacuum filtered to separate the solids from the aqueous fraction. The 90-mm ø glass microfiber filters (Whatman Grade GF/A) containing the solid residues were stored in refrigerated 120-mL clean amber jars (one sample per jar). A 500-mL aliquot of the aqueous fraction was passed through a solid-phase extraction cartridge (Waters Porpak RDX Sep-Pak, 6 cm^3, 500 mg) to pre-concentrate the energetics. For the January 2006 tests, the cartridges were wrapped in aluminum foil, bagged, and placed in a refrigerator for storage prior to shipment overnight to the analytical chemistry laboratory at CRREL for final processing and analysis. For the February 2008 test, the cartridge was eluted with 5 mL of acetonitrile (AcN), resulting in a 100:1 concentration of the analytes. The soot samples and a 3.5-mL aliquot of the solid phase extracts were shipped overnight to the analytical laboratory at CRREL for final processing and analysis. Energetics were extracted from the solid residues captured on the filters using AcN by shaking each sample with the solvent for 18 hours.

7.5.1.2 Burn bowl samples

Cleaning of the bowl from the 120-mm propellant burn test proved to be quite a challenge. The loose, solid residue (not adhered to the bowl) was weighed in a tared 250-mL wide mouth jar (Figure 7-15). A 50-mL aliquot of AcN was added to extract the NG from the residue. Much of the AcN was absorbed by the residue, so an additional 50 mL of AcN was added. The jar was placed on a platform shaker and shaken at 150 rpm for 18 hours prior to analysis.

Figure 7-15. Processing of the burn bowl residues; loose residues from bowl.

Figure 7-16. Cleaning the char from the burn bowl.

The bowl had charred residue adhering to the bottom and sides (Figure 7-16). To extract the NG from the residue, the following sequential procedure was used:

1. 50-mL aliquots of AcN were added to the bowl and the bowl swirled to allow contact between the solvent and the residue that was fixed to the inside surfaces of the bowl. Each aliquot, which was very yellow, was then poured into a 250-mL graduated cylinder until a 200-mL volume of AcN was obtained for analysis by HPLC.
2. A metal spatula was used to scrape all inside surfaces of the bowl (Figure 7-16), and the solid residue was transferred to a 120-mL wide mouth amber jar. A 20-mL aliquot of AcN was added to the jar and the contents shaken for 1 hour. Then, one drop of the extract was tested for the presence of

NG using the EXPRAY kit (as described below). The EXPRAY indicated that the concentration of NG was high, so an additional 20-mL of AcN was added to the jar and the jar was shaken overnight (~ 18 hr).

3. More 50-m aliquots of AcN were used to rinse the bowl until the solution was colorless. The final sample volume totaled 180 mL.
4. A 50-mL aliquot of AcN was added to the bowl and the inside of the bowl was wiped with a glass fiber filter. The filter was squeezed to remove as much solvent as possible and placed in a 250-mL wide mouth jar. The AcN was poured into a 250-mL graduated cylinder. The same process was repeated with more AcN, and a second glass fiber filter used to wipe the bottom and sides of the bowl. The bowl was rinsed until a 200-mL volume of AcN was collected in the graduated cylinder. The AcN was then poured into the jar with the filters.
5. Finally, additional 50-mL aliquots of AcN were used to rinse the inside surfaces of the bowl. All AcN remaining after the analysis of the sample was disposed of by following strict laboratory standards.

7.5.2 Soil samples

At the lab, the > 2-mm fraction was sieved out of each sample and retained. The < 2-mm fraction was then ground, sub-sampled, and analyzed according to EPA SW-846 Method 8330B (USEPA 2006). The > 2-mm fraction was extracted using whole sample extraction and analyzed.

7.5.3 Propellant grain composition

To determine the actual amount of NG in the double base grains of the M9 and M45 propellant and the amount of 2,4-DNT in the single-based M1 propellant, approximately 100 mg of unburned grains of each type of propellant were dissolved in AcN. The M45 grains that were isolated from cores taken in June at the frozen ground and snow-covered burn points were also dissolved in AcN. The masses of NG or 2,4-DNT were determined by high performance liquid chromatography (HPLC) analysis.

7.6 Analytical methods

7.6.1 EXPRAY

An EXPRAY kit (Plexus Scientific Corporation) was used to test for the presence of NG or 2,4-DNT in the AcN extracts and to estimate the dilution needed prior to HPLC analysis (Bjella 2005). (Note: this test also responds to NC.) One drop of each extract was placed on the paper supplied with the EXPRAY kit. Then the paper was sprayed sequentially with two reagents. The first reagent is alkaline and forms a blue-green product if 2,4-DNT is present. The first reagent in combination with the second reagent forms nitrate ions from NG, resulting in a pink colored product as a result of Griess reaction. The color intensity is proportional to the concentration of 2,4-DNT or NG (and other nitroaromatic, nitrate esters, and nitramines, if present) in the AcN aliquot, with a more intense color corresponding to a higher analyte concentration.

7.6.2 HPLC

Prior to analysis, each extract was diluted with AcN based on the intensity of the color from the EXPRAY test so that the injected concentration would be less than 10 mg/L. The AcN was then mixed with reagent-grade water (1:3 v/v) and filtered through a Millex-FH filter unit (Millipore, PTFE, 0.45 µm).

Determinations were made on a modular system from Thermo Electron Corporation composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector (cell path 1 cm), set at 210nm (to detect NG) and 254 nanometers (nm) (to detect other energetics), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15-cm X 3.9-mm (4-µm) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28 °C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

Calibration standards for NG and 2,4-DNT were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The concentration of each analyte was 10 mg/mL in AcN in the solutions used to calibrate the HPLC-UV.

7.7 Results

7.7.1 NG content of M9 and M45 propellant and 2,4-DNT content in M1 propellant: unburned state

Unburned propellant grains were analyzed to determine if the analytes of interest were present in specified concentrations. Each type of propellant was found to be within military specifications for NG or DNT content

(Table 7-2). The analytically derived mass percentages were used to better estimate the energetics residue resulting from our tests.

Table 7-2.Analysis results for propellant grains prior to burn tests.

Propellant	Actual Mass of Grains (mg)	Mass of Analyte Recovered (mg)	Analyte Mass %	Military Specified Analyte %
M9	117	46 (NG)	39%	40±1.5%
M45	114	12 (NG)	10%	10±2%
M1	115 (one grain)	11 (DNTs)	9.7%	10±2%

7.7.2 Winter tests

7.7.2.1 M9 propellant

The results of the analysis of the 81-mm mortar cartridge propellant burn are presented in Table 7-3. Characterization of the site prior to the test indicated a residue level of <200 µg NG / m^2 from mortar firing during the previous two days. The area influenced by the burn test was less than 1 m^2. Because of the small quantity of charges involved in the test, the propellant burned only a few centimeters into the snow. Approximately 870 mg (1.7 %) of the NG in the original charges was recovered from the sampled area. This is equivalent to about 87 mg NG per charge. The background concentration of NG due to the firing exercise was insignificant, three orders of magnitude less than the final concentrations of the snow samples following the burn test.

Table 7-3 Results of analyses for NG following disposal of M185 propellant charges on snow.

Sample	DU† Size (m^2)	Recovered Mass (mg)	Recovered Mass (%)
Background*	0.56	0.11	–
Burn Point	0.063	840	1.6%
Annulus	0.50	33	0.06%

*Background mass estimated from background concentration of 200 µg/m^2

†Decision Unit (Total area from which sample was taken)

7.7.2.2 M45 propellant

As discussed earlier, the 120-mm mortar cartridge propellant burn experiment in February 2008 involved several activities. These included the immediate post-burn sampling of the snow at the site as well as processing of the burn bowl residues, the initial soil sampling in June 2008, and the follow-up soil sampling in July 2008. Both the June and July samplings addressed the snow and frozen ground burn residues.

7.7.2.3 NG remaining in the burn bowl

The burn bowl and associated loose, solid residues were processed as described earlier in this chapter. The mass of loose residues within the bowl contained 2.3 mg of NG. Residues that were scraped from the bowl contained 23 mg of NG. The bowl cleaning process yielded an additional 48 mg of NG, with 0.26 mg NG recovered with the final rinse (Appendix 7-B). The snow surrounding the burn bowl contained 200 mg of NG. The total mass recovered was 270 mg, 73% of which was found outside the burn bowl. The per-charge NG residues are thus 27 mg/charge, or 0.21% of the original load.

7.7.2.4 NG remaining from the burns on snow and frozen ground

The mass of NG remaining after the snow and frozen soil burns indicated that large quantities of propellant remained after both experiments. The results are divided into three zones for both experiments. The center zone encompasses the burn location and the surrounding area out to 0.5 m. This zone contained the recovered propellant grains. The other two zones were the two annuli surrounding the central areas. Estimates of the mass per charge and percentage of mass per charge for all three experiments with M45 propellant, including the burn bowl, are shown in Table 7-4. The residues from the propellant that was burned on the snow pack contained an estimated 18% of the initial NG mass, indicating a very inefficient burn. Residues from the burn on frozen ground had 5% of the initial NG mass. Both of these unconfined burns left numerous propellant grains on the soil surface; these grains are included in the totals. The burn bowl experiment, as stated above, had residues containing 0.21% of the original mass of NG. The relative percent differences (RPDs) for the four annular samples taken around the snow and frozen ground burns averaged 49%, higher than we like to see, but not unusual when trying to measure areas containing a few propellant grains kicked out during a deflagration process. Appendix 7-C contains the analytical data leading to these results.

Table 7-4. Results of M45 propellant burn experiments.

Sample Description	NG (mg)
Burn Bowl	
Within Bowl	73
Residue on snow surrounding bowl	200
Total NG Mass Remaining for Bowl Burn	270
Initial NG Mass in 10 M45 Charges	130,000
NG Recovered (%)	0.21%
Frozen Soil Burn	
Center 0.5 m radius	7,200
Annulus 0.5 to 1.0 m	140
Annulus 1.0 to 1.5 m	<10
Total NG Mass Remaining for Frozen Soil Burn	7,340
Initial NG Mass in 11 M45 Charges	140,000
NG Recovered (%)	5.2%
Snow Burn	
Center 0.5 m radius	22,300
Annulus 0.5 to 1.0 m	2,100
Annulus 1.0 to 1.5 m	560
Total NG Mass Remaining for Snow Burn	25,000
Initial NG Mass in 11 M45 Charges	140,000
NG Recovered (%)	18%

7.7.2.5 Soil depth profiles from burns on snow and frozen ground

Propellant grains from the tests conducted in February remained on the ground through June and, for some not collected in June, they remained on the ground until follow-up sampling in July. Three soil profile samples were taken to determine if any transport had occurred during the initial snowmelt and subsequent summer months. One profile was taken in the center of each burn location that was sampled in June, and a third was taken in July beneath a cluster of grains remaining after the June sampling event at the snow burn location. Results are shown in Table 7-5 and Figure 7-17.

The NG concentrations were in the µg/g range for the shallowest soil samples. The mass that is present in these soil samples was small compared to that in the surface 1.5- or 2.5-cm bulk samples that were taken above the profile locations. The profile taken in July beneath the cluster of grains at the snow burn location gives an extended view of the effect of propellant weathering. A comparison can be made between this area and the area of the same burn location that was sampled in June. In July, the soil profile taken below the recently removed grains and surface soil contained 31% of the NG mass estimated in the surface and grains (7.4 mg vs. 24 mg). In June, it was 1.2% (0.6 mg vs. 50 mg). Although this is only a rough estimate of the effect of the additional weathering of the surface grains and residues, it indicates that leaching of NG into an organic surface soil will occur.

Table 7-5: Results of analyses of soil column profiles for M45 propellant burn.

Sample Description	NG Soil Concentration (µg/g)	Total NG Recovered (mg)
Frozen Soil Burn – Center of pit		
Original surface sample (Top 2.5 cm)	990	16*
0–2 cm from new surface	52	2.2
2–4 cm	<0.1	
4–6 cm	<0.1	
6–8 cm	<0.1	
8–10 cm	<0.1	
Total mass for profile samples		2.2
Snow Burn – Center of pit		
Original surface sample (Top 2.5 cm)	3,100	50*
0–2 cm from new surface	23	0.60
2–4 cm	<0.1	
4–6 cm	<0.1	
6–8 cm	<0.1	
8–10 cm	<0.1	
10–12 cm	<0.1	
12–14 cm	<0.1	
Total mass for profile samples		0.60
Snow Burn – Below grain mass		
Original surface sample (Top 1.5 cm)	2,500	24*
0–2 cm from new surface	180	5.8
2–4 cm	46	1.3
4–6 cm	9.0	0.30
6–8 cm	<0.1	
8–10 cm	<0.1	
10–12 cm	<0.1	
12–14 cm	<0.1	
Total mass for profile samples		7.4

Note: Original surface samples (top 2.5 and 1.5 cm) contained propellant grains

*Estimated for equivalent sample area as taken for profile lifts (2 cm x 2 cm).

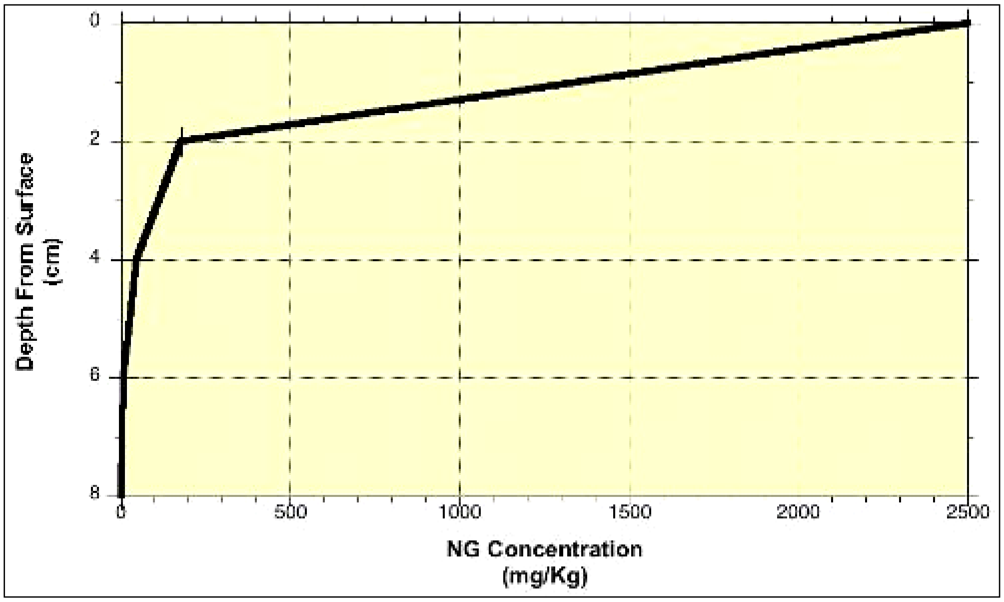

Figure 7-17. Graph of NG concentration as a function of depth of the soil profile taken beneath unburned M45 propellant grains, July 2008.

7.7.2.6 NG in unconsumed propellant grains

Finally, we analyzed the mass of NG in grains remaining on the soil surface. In June, grains were isolated from three core samples from the snow burn and frozen ground burn tests (3-cm ø). The grains were counted and analyzed for percent NG remaining. Table 7-6 shows the results of the analyses. The NG mass remaining in the weathered grains was 56% of the mass expected for unburned grains, based on laboratory analyses of propellant grains collected prior to the burn test (Appendix 7-D).

Table 7-6: Results of analyses of propellant grains collected from sample cores.

Sample	# Grains	Theoretical NG Mass (mg)†	NG Mass Recovered (mg)	% Mass Recovered
Frozen Ground	977	410	230	56%
Snow Burn	741	310	170	55%
† Based on the analysis that each grain contains 10.4% NG on average and the grains are 4 mg each.				

It is interesting to note that the mass of NG recovered from a single 3-cm ø core sample can be quite high. Six 2.5-cm deep core samples were examined for the number of intact grains on the surface, the NG content in the weathered grains, and the concentration of NG in the soil (Table 7-7). The recovered NG averaged 95 mg per core sample, with sample concentrations averaging 5.4 mg/g. This average concentration is almost three orders of magnitude higher than the concentrations found on a nearby firing point heavily used by units training with the 120-mm mortar using M45 propellant at Fort Richardson (8.7 µg/g - Walsh, M.E., et al. 2007). The effect of a single core or increment containing burn point propellant grains can have a pronounced effect on a multi-increment sample collected to characterize a firing point. The effect on a discrete sample is even greater.

Table 7-7. Results of analyses of core samples containing propellant grains.

Core #	Grains in Sample	NG in Grains (mg)	Soil Mass (g)	NG Conc. in Soil (µg/g)	NG in Soils (mg)	Total NG (mg)	NG Conc. in Sample (µg/g)
1-Frozen Ground	366	84	17	2,500	42	120	6,800
2- Frozen Ground	351	84	16	1,200	19	100	6,000
3- Frozen Ground	260	59	19	1,200	22	81	4,100
1-Snow Burn	330	64	16	2,700	45	110	6,300
2- Snow Burn	140	37	18	1,400	25	62	3,400
3- Snow Burn	271	67	16	1,300	21	89	5,600

7.7.3 Summer tests

7.7.3.1 M1 propellant

Samples for the two test burns utilizing M1 single-based howitzer propellant were processed and analyzed in two steps. The <2-mm fraction was ground using a ring-and-puck mill, sub-sampled using the multi-increment technique (n≈40), extracted with AcN, and analyzed. The >2-mm fraction was extracted using whole-sample extraction and then analyzed (Appendix 7-C). A summary of the results is given in Table 7-8. From this table, the total recovered DNT is 3,100 mg for the burn on dry sand and 3,300 mg for the burn on wet sand. Of these totals, ≈18% of the mass is from the >2 mm fraction. For the dry burn, 87% of the mass was found in the initial sampling of the plume, 13% was recovered from the subsurface samples, and <0.5% was recovered from outside the initial sample area. For the wet burn, the corresponding averages were 73%, 26%, and <0.5%, respectively. Combined DNT in the residues is 0.94% of the original load for the dry burn and 0.99% for the wet burn.

The background sample taken for the 105-mm M1 propellant burn test showed a slight amount of analytes: <2 mg of 2,4-DNT and <0.1 mg 2,6-

DNT in a 430-g sample. The source of these analytes was found to be from cross-contamination due to co-storage of the background and residues samples. The background levels for DNT are thus <0.07% for both burns.

Table 7-9 summarizes all the propellant burn tests conducted for this report. Only the final total estimated mass is given for each test. These totals include the results of the soil profiles and both June and July surface sampling for the 120-mm mortar tests on snow and frozen ground.

Table 7-8: Results of analyses of M1 propellant burn tests.

Sample	Fraction	Recovered Mass: 2,4-DNT (mg)	Recovered Mass: 2,6-DNT (mg)	Total Recovered Mass: DNT (mg)	Total % Mass Recovered: DNT
Background	<2 mm	1.6	0.064	1.7	
	>2 mm	0.37	0.013	0.38	
	Totals	2.0	0.077	2.1	
Dry Burn	<2 mm	2,400	103	2,500	(81% of total)
	>2 mm	570	28	600	(19% of total)
	Totals	3,000	130	3,100	0.94%
Wet Burn	<2 mm	2,600	98	2,700	(82% of total)
	>2 mm	550	27	580	(18% of total)
	Totals	3,100	130	3,300	0.99%

Table 7-9 Summary of test results.

Test	Estimated Total NG Mass in Residues	Percent original NG Mass in Combined Charges
Winter Tests		
81-mm Mortar		
Snow surface	870 mg	1.7%
120-mm Mortar		
Burn bowl	270 mg	0.21%
Frozen soil	7,300 mg	5.2%
Snow surface	25,000 mg	18%
Summer Tests		
105-mm Howitzer		
Dry sand	3,100 mg	0.94%
Wet sand	3,300 mg	0.99%

Over the course of these experiments, many QA procedures were conducted to ensure the quality of the data. Replicate logs were maintained for all samples from the point of collection through the final analyses. Background (baseline) samples were taken, where necessary, to ensure that any background contamination was not significant. Multi-increment sampling was carried out when sampling the larger decision units. In most cases where discrete (whole area or bulk) samples were taken, subsurface samples and samples outside the burn areas were obtained. In the processing lab, replicate sub-samples of the ground samples and the snow sample aqueous fractions were obtained. Blanks and spikes were run through the processing equipment to check for cross-contamination and to verify procedural efficacy. Whole-sample extraction was done on the >2-mm fraction for the 105 propellant burn tests. In the analytical lab, blanks and spikes were run to verify instrument output. The lab replicates of ground soil and of melted snow samples were processed and analyzed to verify repeatability. All QA procedure results indicate sampling and data fidelity.

7.8 Discussion

The impact of environmental factors on the efficacy of field-expedient disposal of excess propellants from training exercises is quite significant. The mass remaining following the burning of the M45 propellant on snow and on frozen ground surrounded by snow was much larger than expected, based on the small-quantity test conducted in 2006 with M185 mortar propellant. However, the original test did not generate the heat and violence of burning seen with the larger-quantity tests. There is a phenomenon that occurs that our Canadian colleagues term the “popcorn effect” in which gasses generated by the deflagrating propellant will eject material during the disposal process. This was evident during the burn bowl test in which nearly 75% of the recovered energetics fell outside the bowl. Ejected, unburned propellant grains can constitute a cumulative environmental hazard, especially with propellants that contain DNT, RDX, or heavy metals such as lead. We often find propellant grains scattered about fixed burn points, even those with burn pans, and especially when improper disposal methods are employed. The presence of propellant grains can also pose health and security risks. When ignited, even a small amount of propellant will burn furiously, posing a risk to the unaware. Larger quantities pose a security risk as well, because confined propellants can detonate when initiated.

7.9 Conclusions

This set of experiments demonstrates that environmental factors and climatic conditions will have a strong effect on the efficacy of the field-expedient disposal of excess propellants. Results showed that the use of a properly designed and utilized burn pan is critical in the disposal of propellants in winter, especially when snow cover is present. The presence of large quantities of unburned propellants at disposal sites can constitute both an environmental hazard and a security risk.

7.10 Nomenclature

2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
AcN	acetonitrile
CRREL	Cold Regions Research and Engineering Laboratory
DNT	dinitrotoluene
DoD	U.S. Department of Defense
DTA	Donnelly Training Area
DU	decision unit
EOD	Explosive Ordnance Disposal
EPA	Environmental Protection Agency
ER	environmental restoration
ERDC	Engineer Research and Development Center
ERF	Eagle River Flats
FP	firing point
FRA	Fort Richardson, Alaska
HE	high explosives
HPLC	high performance liquid chromotography
NC	nitrocellulose
NG	nitroglycerin
NQ	nitroguanidine
OP	observation point
PE	polyethylene
QA	Quality Assurance
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RPD	relative percent difference
SERDP	Strategic Environmental Research and Development Program

SW	solid waste
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet

7.11 References

Bjella, K. L. (2005) *Pre-screening for explosives residues in soil prior to HPLC analysis utilizing Expray*. ERDC/CRREL TN-05-2. Hanover, NH: U. S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TN-05-2.pdf

Dubé, P., S. Thiboutot, G. Ampleman, A. Marois, and M. Bouchard. 2006. Preliminary assessment of the dispersion of propellant residues from the static live firing of 105 mm howitzer. DRDC Valcartier TM 2005-284. Valcartier, Quebec, Canada: Defence Research and Development Canada.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M. R. Walsh, D. J. Lambert, N.M. Perron, N.H Collins, and R. Karn. 2003. *Estimates for explosives residue from the detonation of army munitions.* ERDC/CRREL TR-03-16. Hanover, NH: U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-03-16.pdf

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N.M. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren. 2001. *Characterization of explosives contamination at military firing ranges*. . ERDC/CRREL TR-01-5. Hanover, NH:U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-01-5.pdf

Jenkins, T.F., M.E. Walsh, P.H. Miyares, A.D. Hewitt, N.H. Collins, and T.A. Ranney. 2002. Use of snow-covered ranges to estimate explosives residues from high-order detonations of army munitions. *Thermochimica Acta* 384 (1-2): 173-185.

Ogden Environmental and Energy Services (EES). 2000. *Client Draft IAGS Technical Team Memorandum 00-3: Evaluation of gun and mortar firing positions for the Camp Edwards impact area groundwater quality study, Massachusetts Military reservation, Cape Cod, Massachusetts*. Westford, MA: Ogden Environmental and Energy Services.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, D. Gilbert, V. Tanguay, and I. Poulin. 2007. *Deposition of gun propellant residues from 84-mm Carl Gustav rocket firing*. DRDC Valcartier TR 2007-408, Unclassified. Valcartier, Quebec, Canada: Defence Research and Development Canada.

U.S. Army Center for Health Promotion and Preventative Medicine (USACHPPM). 2000. *Training range site characterization and risk screening, Camp Shelby, MS, 7-23 September 1999*. Geohydrologic Study No. 38-EH-8879-99. Aberdeen Proving Ground, MD: U.S. Army Center for Health Promotion and Preventative Medicine.

U.S. Environmental Protection Agency (USEPA). 2006. *Method 8330B: Nitroaromatics, nitroamines, and nitrate esters by HPLC, Revision 2*. Part of SW846: *Standard methods of analysis test methods for evaluating solid wastes, physical and chemical methods*. Washington, D.C.: USEPA Office of Solid Waste. Available at (accessed July 2009): http://www.epa.gov/sam/pdfs/EPA-8330b.pdf

Walsh, M.E., C.M. Collins, C.A. Ramsey, T.A. Douglas, R.N. Bailey, M.R. Walsh, A.D. Hewitt, and J.L. Clausen. 2007. ERDC/CRREL TR-07-9. Hanover, NH: U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-07-9.pdf

______, C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T.S. Douglas, N. Perron, D. Lambert, R. Bailey, and K Meyers. 2004. *Range characterization studies at Donnelly Training Area, Alaska: 2001 and 2002*. ERDC/CRREL TR-04-3. Hanover, NH: U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-04-3.pdf

Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari. 2006. *Energetic residues deposition from 60-mm and 81-mm mortars*. ERDC/CRREL TR-06-10. Hanover, NH: U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-06-10.pdf

______, M.E. Walsh, and C.A. Ramsey (2007) *Measuring energetics residues on snow*. ERDC/CRREL TR-07-19. Hanover, NH: U.S. Army Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory. Available at (accessed July 2009): http://libweb.wes.army.mil./uhtbin/hyperion/CRREL-TR-07-19.pdf

Appendix 7-A: Munitions Data

The following information on the rounds used in the propellant burn tests was taken from munitions packing crates at the site of the training mission or test. All munitions are standard issue for live-fire training and are commonly used by the military. No lot data was obtained for the105-mm munitions, although a loaded date was obtained and is listed in Table 7-A1. Propellant data can be found in Table 7-1.

Table 7-A1. Munitions data.

NSN	DODIC	Nomenclature	Lot No.	Drawn for tests
1315001437048	C226	Cartridge, 81-mm IL, M301A3, w/Fuze, Time, M84A1	LOW85C108013	61*
1315013431941	C623	Cartridge, 120 MM HE, M933, W/Fuze, PD, M745	MM97K025002	8
1315000284857	C445	Cartridge, 105MM HE M1 Dualgran	(Loaded Mar 2002)	10**

*Drawn for training mission.

**Number of rounds from which propellant bags were used in tests.

Mortar rounds and howitzer rounds are packaged differently. There are variations and differences in the general rules of their packaging, the following descriptions give a general guide for how these munitions are handled. Mortar rounds are packed as cartridges and howitzer rounds are packed as projectiles. The difference is in how the propellant is handled. A mortar cartridge can often be fired “out of the box” without the addition of propellant.

Each mortar round is assembled with an integral ignition cartridge in the tail assembly, capable of ejecting the round out of the mortar tube and arming most fuzes. The cartridges come with additional propellant charges attached to the tail assembly. The number of charges can be adjusted (by removal) to vary the range of the round. Charges not used are excess and are disposed of following a training mission either by burning on the ground (or snow surface) or in a burn pan.

The howitzer rounds are handled differently. The 105s are composed of a projectile, a fuze (sometimes attached), a supplementary charge in the fuze well (optional based on the fuze type), a brass cartridge case, and propellant charges. All elements are separate components. The charges consist of a series of bags containing varying amounts of propellant, with the first two charges containing single-perforated cylindrical grains and the remaining five containing 7-hole, multi-perforated, cylindrical grains. As above, the charges are adjusted to get the required range for the projectile. They are used in the order of the charge numbers, with the lower charge numbers used prior to the higher charge numbers for the standard charge load. Charges not used are excess and are disposed of (by burning, as described previously) at the end of the training exercise. For our tests, we utilized five each of Charges 6 and 7, containing 250 g and 408 g of multi-perforated M1 propellant respectively. Thus, each test incorporated $5 \cdot (250+408\text{g}) = 3.3$ kg of multi-perforated M1 propellant containing 10 ± 2.0% DNT.

Appendix 7-B: Results of Burn Bowl Analyses for NG

Processing of the burn bowl residues was a multi-step process, as outlined in this report's Section 3 (Processing and Analysis). The following table (Table 7-B1) presents the results from analyses for each step of that process. As previously pointed out in the Results section of this chapter, the final rinse of the bowl contained very little NG, two orders of magnitude less than the first rinse and less than 0.1% of the total recovered NG. This is a good indication that very little NG was missed in processing residues in the bowl. Results from the snow samples taken outside the bowl are also included in this table.

Table 7-B1. Results of burn bowl test analyses.

Sample	NG Mass (mg)
Contents of bowl	
First rinse	44
Second rinse	2.4
Third rinse	0.59
Fourth rinse	0.26
Loose solid residue (11.8 g)	2.3
Adhered solid residue (5.17 g)	23
Subtotal	73
From snow outside the bowl	
Snowmelt	7.7
Soot	190
Subtotal	200
Total – All sources	**270**

Appendix 7-C: M45 Propellant Analytical Data and Results

Tables 7-C1 and 7-C2 contain analytical data and results for the samples run for the winter test burning of M45 propellant. The table is divided into the different sampling events and tasks. Some samples were rerun to verify results. Table 7-C3 contains data and results for the summer M1 propellant burn tests.

Table 7-C1. Analytical data and results for June samples, February M45 propellant tests.

CRREL #	Sample Description	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution Factor	2,4-DNT (mg/Kg)	NG µg/g
June Propellant Burn												
08FRA-S-01	Core#1 BP SR	17.04				30.00		14.0		100		2465
08FRA-S-02	Core#2 BP SR	15.69				30.00		6.28		100		1201
08FRA-S-03	Core#3 BP SR	18.67				40.00		5.52		100		1183
08FRA-S-04	Core#4 BP SR	15.99				30.00		36.7		10		689
08FRA-S-05	Core#5 BP SR	17.89				40.00		15.1		10		338
08FRA-S-06	Core#6 BP SR	14.88				30.00		1.87		10		37.7
08FRA-S-07A	Bulk BP SR	2597.69	71.69	(5) 60 s	10	20		4.96		100		992
08FRA-S-07B	Bulk BP SR				10	20		5.08		100		1016
08FRA-S-07C	Bulk BP SR				10	20		4.79		100		958
08FRA-S-08A	OTP BP SR	829.98	38.29	(5) 60 s	10	20		11.1		10		222
08FRA-S-08B	OTP BP SR				10	20		11.5		10		230
08FRA-S-08C	OTP BP SR				10	20		11.1		10		222
08FRA-S-09	Core#1 BP S	16.34				30.00	0.124	14.9		100	22.8	2736
08FRA-S-10	Core#2 BP S	17.68				40.00	0.080	6.37		100	18.1	1441
08FRA-S-11	Core#3 BP S	16.25				30.00	0.264	70.8		10	4.87	1307
08FRA-S-12A	Bulk BP S	4613.40	568.68	(5) 60 s	10	20	0.0707	15.9	Rerun @ 10 dil.	100	14.1	3180
08FRA-S-12B	Bulk BP S				10	20	0.0781	15.2	Rerun @ 10 dil.	100	15.6	3040
08FRA-S-12C	Bulk BP S				10	20	0.0746	16.1	Rerun @ 10 dil.	100	14.9	3220

CRREL #	Sample Description	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution Factor	2,4-DNT (mg/Kg)	NG µg/g
08FRA-S-13A	OTP BP S	962.52	43.38	(5) 60 s	10	20	0.0892	19.0	Rerun @ 1 dil.	10	1.78	380
08FRA-S-13B	OTP BP S				10	20	0.0702	19.0	Rerun @ 1 dil.	10	1.40	380
08FRA-S-13C	OTP BP S				10	20	0.0688	19.7	Rerun @ 1 dil.	10	1.38	394
June Propellant Grains		Grain Mass (mg)				Amt. of AcN (ml)		NG (mg/Kg)		Dilution Factor		NG (µg)
CRREL #	No. of Grains											
08FRA-S-01 P	366	1464				100		8.39		100		83900
08FRA-S-02 P	351	1404				100		8.36		100		83600
08FRA-S-03 P	260	1040				100		5.92		100		59200
08FRA-S-09 P	330	1320				100		6.41		100		64100
08FRA-S-10 P	140	560				100		3.69		100		36900
08FRA-S-11 P	271	1084				100		6.74		100		67400

Table 7-C2. Analytical data and results for July samples, February M45 propellant burn tests.

CRREL #	Sample Description/ Depth	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution factor	2,4-DNT (mg/Kg)	NG (mg/Kg)
July Propellant Profiles after removing top 2.5 cm												
Snow - Center of pit												
08-FRA-64	0–2 cm	26.1				50		0.121	Rerun 1:1	100	<4	23.2
08-FRA-65	2–4 cm	33.6				70	0.036		Rerun 1:1	10	0.750	<1.0
08-FRA-66	4–6 cm	33.1				60	0.073			1	0.132	<0.10
08-FRA-67	6–8 cm	29.4				60				1	<0.04	<0.10
08-FRA-68	8–10 cm	18.6				40				1	<0.04	<0.10
08-FRA-69	10–12 cm	39.0				80				1	<0.04	<0.10
08-FRA-70	12–14 cm	28.3				60	0.111			1	0.235	<0.10
Snow - North Wall of pit												
08-FRA-71	0–2 cm	32.5				70		0.829	Rerun 1:1	100	<4	179
08-FRA-72	2–4 cm	28.3				60	0.028	2.19	Rerun 1:1	10	0.594	46.5
08-FRA-73	4–6 cm	33.94				70	0.312	4.35		1	0.643	8.98
08-FRA-74	6–8 cm	30.37				60	0.100			1	0.198	<0.10
08-FRA-75	8–10 cm	46.18				90	0.021			1	0.041	<0.10
08-FRA-76	10–12 cm	41.49				80				1	<0.04	<0.10
08-FRA-77	12–14 cm	43.38				80				1	<0.04	<0.10
08-FRA-78	14–16 cm	16.33				30		3.43		1	<0.04	6.31

CRREL #	Sample Description/ Depth	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution factor	2,4-DNT (mg/Kg)	NG (mg/Kg)
Snow Removed - center pit												
08-FRA-79	0–2 cm	42.7				90		0.212	Rerun 1:1	100	<4	44.7
08-FRA-80	2–4 cm	41.95				80			Rerun 1:1	10	<0.4	<1
08-FRA-81	4–6 cm	33.98				70				1	<0.04	<0.10
08-FRA-82	6–8 cm	36.36				70				1	<0.04	<0.10
08-FRA-83	8–10 cm	28.71				60				1	<0.04	<0.10
08-FRA-84	10–12 cm	24.98				50	1.09	0.145		1	2.19	0.29
08-FRA-85	North side mass: Snow	182.03				360	0.021	12.8		100	4.15	2533
08-FRA-86	Grains from Periphery: Snow	263.56				520	0.057	17.5		100	11.2	3447
08-FRA-87	East side SR: Missed grains	281.12				560		17.0		100	<2.0	3386
FRA-Blk	Blank						<0.02	<0.02		1		
FRA-LCS	Lab Control						0.510	0.521		1		
08-FRA-64	Rerun	26.1				50	0.768	12.0		1	1.47	23.0
08-FRA-65	Rerun	33.6				70	0.392			1	0.817	<0.1
08-FRA-71	Rerun	32.5				70	0.919	82.8		1	1.98	178
08-FRA-72	Rerun	28.3				60	0.328	21.7		1	0.695	46.1
08-FRA-79	Rerun	42.7				90		24.8		1	<0.04	52.3
08-FRA-80	Rerun	41.95				80				1	<0.04	<0.1

CRREL #	Sample Description/ Depth	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution factor	2,4-DNT (mg/Kg)	NG (mg/Kg)
July OTPs												
08FRA-S-56	1.0–1.5, REP 1, Frozen Ground Test	1167.48		580(2)	10	20		<0.1				
08FRA-S-57	1.0–1.5, REP 2, Frozen Ground Test	1188.30		595(2)	10	20		<0.1				
08FRA-S-58	1.0–1.5, REP 1, Snow Test	1035.64		520(2)	10	20		3.72				
08FRA-S-59	1.0–1.5, REP 2, Snow Test	992.86		495(2)	10	20		6.84				
08FRA-S-60	0.5–1.0, REP 1-A, Frozen Ground Test	849.98		425(2)	10	20		4.19				
08FRA-S-60	0.5–1.0, REP 1-B, Frozen Ground Test	849.98			10	20		3.95				
08FRA-S-60	0.5–1.0, REP 1-C, Frozen Ground Test	849.98		464(2)	10	20		4.68				
08FRA-S-61	0.5–1.0, REP 2, Frozen Ground Test	928.86			10	20		0.97				
08FRA-S-62	0.5–1.0, REP 1, Snow Test	778.30		390(2)	10	20		44.8				

CRREL #	Sample Description/ Depth	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Weight (g)	Amt. of AcN (ml)	2,4-DNT (mg/Kg)	NG (mg/Kg)	Notes	Dilution factor	2,4-DNT (mg/Kg)	NG (mg/Kg)
08FRA-S-63	0.5–1.0, REP 2, Snow Test	870.28		435(2)	10	20		52.1				
BLK 2 (JUL)	Blank grind	500.00		500	10	20		0.00				
FRA LCS	Lab Control	10.00				20		0.96				
FRA LCS	Lab Control	10.00				20		0.93				

Table 7-C3. Analytical data and results for August samples, M1 propellant burn tests.

							Injected Concen.			Extract Concen.		Soil Concen.	
CRREL # 08DTA-S–	Sample Description	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Wt. (g)	AcN (ml)	2,4DNT (mg/L)	2,6-DNT (mg/L)	Dilution factor	2,4DNT (mg/L)	2,6DNT (mg/L)	2,4DNT (µg/g)	2,6DNT (µg/g)
<u>Less than 2 mm</u>													
165A	Background (Different bag)	432.52		90s	10	20	1.80	0.079	1	1.803	0.079	3.6	0.2
165B	Background (Different bag)	432.52		90s	10	20	1.79	0.070	1	1.793	0.07	3.6	0.1
Dry burn													
166A	Dry burn - Sand plume	2306.22		90s	10	20	4.39	0.191	100	438.7	19.1	877	38.2
166B	Dry burn - Sand plume	2306.22		90s	10	20	4.41	0.197	100	440.5	19.7	881	39.4
164A	Dry burn - Subsurface	2180.22		90s	10	20	7.57	0.293	10	75.68	2.93	151	5.9
164B	Dry burn - Subsurface	2180.22		90s	10	20	7.53	0.303	10	75.27	3.03	151	6.1
168A	Dry burn-OTP scoop width	735.8		90s	10	20	6.49	0.166	1	6.485	0.166	13.0	0.3
168B	Dry burn-OTP scoop width	735.8		90s	10	20	5.55	0.128	1	5.553	0.128	11.1	0.3
Wet burn													
169A	Wet burn - Sand plume	1366.42		90s	10	20	7.10	0.259	100	710	25.9	1420	51.8
169B	Wet burn - Sand plume	1366.42		90s	10	20	6.86	0.252	100	686.2	25.2	1372	50.4
167A	Wet burn - Subsurface	1740.77		90s	10	20	18.9	0.798	10	188.78	7.98	378	16.0
167B	Wet burn - Subsurface	1740.77		90s	10	20	18.5	0.797	10	184.91	7.97	370	15.9
163A	Wet burn - OTP	477.86		90s	10	20	12.2	0.297	1	12.232	0.297	24.5	0.6
163B	Wet burn - OTP	477.86		90s	10	20	11.8	0.221	1	11.776	0.221	23.6	0.4
NOTE: Table continued on next page													

							Injected Concen.			Extract Concen.		Soil Concen.	
CRREL # 08DTA-S–	Sample Description	<2mm (g)	>2 mm (g)	Type of Grind	Sub-sample Wt. (g)	AcN (ml)	2,4DNT (mg/L)	2,6-DNT (mg/L)	Dilution factor	2,4DNT (mg/L)	2,6DNT (mg/L)	2,4DNT (µg/g)	2,6DNT (µg/g)
<u>Greater than 2 mm</u>													
165R	Rocks - Background		336.87	WSE*		340	1.08	0.037	1	1.081	0.037	1.1	0.0
Dry burn													
166R	Rocks - Dry Sand-plume		1943.3	WSE		1940	25.1	1.30	10	250.62	13	250	13.0
164R	Rocks - Dry -Subsurface		1599.9	WSE		1600	4.82	0.176	10	48.15	1.76	48.2	1.8
168R	Rocks - Dry burn - OTP		585.35	WSE		580	9.22	0.369	1	9.217	0.369	9.1	0.4
Wet burn													
169R	Rocks - Wet Sand-plume		1342.8	WSE		1340	3.02	0.155	100	302.3	15.5	302	15.5
167R	Rocks – Wet- Subsurface		1413.05	WSE		1400	10.0	0.452	10	99.7	4.52	98.8	4.5
163R	Rocks - Wet burn - OTP		384.78	WSE		400	6.20	0.141	1	6.2	0.141	6.4	0.1
BLK-4	Blank	500			10	20	<0.020	<0.020	1				
LCS-4	Spike				10	20	0.500	0.500	1	0.5	0.5		

Appendix 7-D: Analysis Results of Unburned Propellant Grains Recovered after M45 Tests.

Table 7-D1. Mass (mg) of individual M45 double-base grains and collective mass of 20 grains.

Grain #	Mass (mg)	Grain #	Mass (mg)
1	4.1	11	4.1
2	3.5	12	4.2
3	4.0	13	3.6
4	4.3	14	3.9
5	3.6	15	3.6
6	3.4	16	3.2
7	4.0	17	4.2
8	4.1	18	3.4
9	3.4	19	4.2
10	4.0	20	3.6
Statistics for Mass (mg) Minimum: 3.2 Maximum: 4.3 Mass of 20 grains: 76 Mean mass: 3.8			

8 Detection of Dioxins and Furans in the Residues from the Open Burning of Artillery Propellants

Isabelle Poulin, Sonia Thiboutot, and Sylvie Brochu[*]

8.1 Abstract

Burning bags of excess gun propellant left after an artillery exercise is a common practice on Canadian Forces Bases (CFBs) ranges and training areas. Bags are aligned and burned on the ground. This operation is known to leave significant quantities of energetic residues. It was also suspected to produce among its combustion products dioxins and furans, two structurally and chemically related chlorinated compounds that are known to be toxic and persistent in the environment. At CFB Petawawa, dioxins and furans were detected in some soil and water samples. The work reported here was aimed at studying the potential production of dioxins and furans from the burning of gun propellants using a flare as an igniter. The results indicated that this production was not related to the combustion patterns, chemical composition, or the mass of gun propellant, but to the presence of the igniter. The accepted procedure published by the Canadian Forces requires the use of a railroad fusee or flare (same as that used for signaling at night) as the ignition source of the gun propellant. As this railroad fusee was shown to be the source of dioxins and furans, the disposal procedure for excess gun propellant by open burning should be modified.

8.2 Introduction

Training with weapons, including live-fire training, is an important part of military activity. Training ensures the troops are always in a high degree of preparedness for any potential mission. Among the weapons used, the large caliber howitzers such as 105 mm and 155 mm are common. At the end of most military exercises involving large-caliber weapon systems, unused bags of gun propellant remain. This is due to the fact that the propelling charges for many large-caliber ammunitions are composed of incre-

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[*] This chapter previously published as DRDC-Valcartier TR 2009-365 (see bibliography in Chapter 10).

ments, the number of which is chosen to fit the target distance. The excess propellant charges are disposed of by open burning. This disposal method is accomplished by positioning the charges on the surface of the ground, in a shallow trench, on a concrete slab, or in metal trays, and igniting them from a safe distance by means of an ignition train of combustible material [1].

Although this procedure is well established, its impacts on the environment are not fully understood. The burning, either on snow cover, on the ground, or on a burning plate (concrete or steel) does not lead to complete combustion. Few studies on the characterization of these residues have been reported in the literature.

In the work of Walsh et al. [2-3], several mortar gun propellant expedient burn sites in the field were studied to determine the deposition of gun propellant residues resulting from these disposal activities. Both energetics-containing residues and “kicked-out” raw propellant grains have been found at burn and test sites, mostly occurring on wet and snow-covered ground. The quantities were significant, greater than 1% of the original nitroglycerin load for mortar propellants. It was stressed that energetic residues from field-expedient disposal burns on the ground at firing points will be problematic for range sustainment. In Diaz et al. [4], gun propellant bags from 105-mm howitzers (M1 single-base composition) and from 155-mm howitzers (white bag, M1 single-base composition) were burned in various configurations, and it was found that the burning on snow cover led to the dispersion of 0.08% by total weight of unburned 2,4-dinitrotoluene (2,4-DNT) (or 0.8% of the original 2,4-DNT load). This value is thought to be an underestimation since the entire plume was not collected. Other contaminants, such as lead, can be spread during the excess gun propellant burning activities. The complete list of combustion by-products remaining on the surface soil is not known at this time.

Among the contaminants found in various ranges, dioxins and furans are some of the most problematic. These families of compounds are highly toxic and their source is very difficult to determine. For example, at CFB Petawawa [5], dioxins and furans were detected in a scrap pit, and the source was clearly anthropogenic, without being easily identifiable.

Also, the Old Grenade Range at CFB Petawawa contained dioxins and furans at concentrations over the regulations in soil samples. For example, in the profile sample collected between 0 and 10 cm, dioxins were present at the level of 6.1 nanograms of toxic equivalent quantity (TEQ) per kilogram (ng TEQ/kg) and at 5.3 ng TEQ/kg in the sample collected between 10 and 20 cm. They were also found in water outside the range and up gradient. The source is still unknown, but it was not associated with Agent Orange, a chemical used at this location [6].

Since it is well known that the combustion of many compounds produces dioxins and furans, one of the hypotheses raised to explain the presence of these compounds in Petawawa was that they may be produced during the burning of excess gun propellant.

This report presents the trials conducted in September 2008 and February 2009 to verify the hypothesis according to which dioxins and furans may be produced during the combustion of excess propellants. This work was sponsored by Director of Land Environment, Department of National Defence, Canada and the U.S. Strategic Environmental Research and Development Program through project Environmental Restoration project 1481.

8.3 Dioxins and furans

Polychlorodibenzo-p-dioxins (PCDDs or dioxins) and polychlorodibenzofuranes (PCDF or furans) are two groups of planar aromatic chlorinated compounds that present similar physicochemical properties. The basic chemical structure of dioxins is presented in Figure 8-1 and of furans in Figure 8-2. There are 210 different congeners of dioxins and furans. From one to another, they vary slightly in toxicity, but their exposure has been associated with a wide range of adverse health effects in laboratory animals and humans, including: skin disorders and lesions such as chloracne, liver problems, stomach cancer, impairment of the immune system, the endocrine system, the reproductive functions, effects on the developing nervous system, other developmental events, and certain types of cancers [7, 8]. Many of the effects are mediated through an interaction with the aryl hydrocarbon receptor [8].

Dioxins and furans are mainly produced by human activities. Multiple sources exist and long-range transport can occur. The major identified sources of dioxins have been grouped into four categories as shown in Table 8-1. They are persistent and bio-accumulate in the environment. Scientists have shown that they are highly resistant to biodegradation due to their very low water solubility and high octanol-water partition coefficients [8].

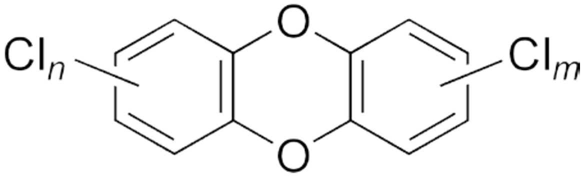


Figure 8-1. General structure of PCDDs (n and m range 0–4).

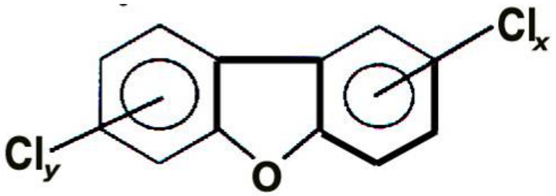


Figure 8-2. General structure of PCDFs (x and y range 0–4).

Table 8-1. Sources of dioxins in the environment [8].

Source	Examples
Incineration	Municipal waste Hospital waste Hazardous waste Sewage sludge
Combustion	Cement kilns Wood burning Diesel vehicles Coal fired utilities Crematoria facilities
Industrial processes	Pulp and paper mills Chemical manufacturing Metal industry
Other	Biochemical processes Photolytic processes Forest fires Accidental releases

8.4 Regulations for dioxins and furans and calculation of the toxic equivalent quantity

Dioxins and furans are regulated in terms of concentration in soils and waters as well as daily intake by humans. Because they are rarely encountered individually in the environment, but are present in varying mixtures, the way to compare the toxicity of samples is by using a TEQ. The congeners are standardized to a toxicologically equivalent amount of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic congener. In other words, the most toxic congener TCDD is rated 1.0 and the less toxic congeners are rated as fractions [8]. The TEQ is calculated using Equation 1. The use of the TEF assumes that the toxic effects are additive and act via a common mechanism to cause toxicity [8].

$$\text{Total} \quad \text{TEQ} = \sum_{i=1}^{n} (C_i \times TEF_i) \tag{1}$$

Where :

TEQ : Toxic equivalent quantity is the concentration of the mixture of congeners, expressed as equivalent of 2,3,7,8-TCDD

n : number of congeners [with available toxic equivalency factors (TEFs)]

C_i : concentration of congener i

TEF_i : toxic equivalency factor for the congener i (can be found in Appendix 8-A)

In Canada, the Canadian Council of Ministers of the Environment [9] has stated that the recommendation for all land uses (agricultural, residential, commercial, and industrial) is 4 ng TEQ/kg (4 pg TEQ/g). For drinking water, Health Canada has not issued any regulation for this parameter, but Quebec province, through the Sustainable Development, Environment and Parks ministry, published a criteria of 15 pg TEQ/L (0.015 ng TEQ/L) for groundwater for drinking [10a]. In the United States, the Environmental Protection Agency (EPA) stated that the national regulation in drinking water is 0.03 ng TEQ/L [10b].

8.5 Dioxins and furans in residues from the burning of excess gun propellant: preliminary studies

As presented in the introduction, Diaz et al. [4] conducted a trial in winter 2005 to study the accumulation of residual dinitrotoluenes from the open burning of gun propellant (155-mm caliber, M4 series, white bags) on pristine snow cover. As the residues collected during this trial were kept in a freezer after Diaz's work, it was decided to analyze five samples coming from various burning scenarios for dioxin and furan detection. As the complete description of the trial can be found in Reference [4], it will not be duplicated entirely here. As a brief summary, each burn was carried out separately on a fresh snow cover, each with their own railroad fusee for ignition. A portion of the residue (roughly 80% of the plume for most trials) was collected with the snow and placed into bags. Snow was melted and the residue recovered. The total mass of the residues was quite high, so only a small aliquot (10 g) was sent to a private company (Bodycote, Pointe-Claire, QC, Canada), which subcontracted to another laboratory (Pacific Rim Laboratories Inc., Surrey, BC, Canada) for dioxins and furans analysis. The masses of gun propellant burned and of residues collected as well as the results obtained for dioxins and furans analyses are included in Table 8-2.

For three of the five samples, the TEQ was significantly higher than the regulation: 29.5, 31.8, 10.9 pg TEQ/g, compared with the criteria of 4 pg TEQ/g. These results led Defence Research and Development Canada (DRDC) scientists to believe that the production of dioxins and furans by the open burning of excess gun propellant may be possible but should be investigated in more detail. The tests will be described in the next section.

Table 8-2. Results of the preliminary tests for dioxins and furans in solid residues from open burning of excess gun propellant on snow.

Sample	Mass of gun propellant (kg)	Mass of residue collected (kg)	Concentration of PCDD-PCDF (pg TEQ/g)
1	73.176	1.648	ND
2	18.294	0.162	ND
3	18.294	0.130	29.5
4	36.588	0.652	31.8
5	1.261	0.057	10.9
ND: not detected			

8.6 Experimental materials and procedures

This section will describe the material as well as the setups used for the two trials conducted. Sampling and analysis for dioxins and furans will also be described.

8.6.1 Gun propellant

Gun propellant from 105- and 155-mm caliber howitzers was used. The M67 propellant for the 105-mm caliber howitzer [11] consists of a total of seven bags of gun propellant, for a total weight of approximately 1.28 kg, filled with grains of single-base composition M1. Table 8-3 lists the chemical constituents of the gun propellant. The gun propellant for each charge increment is loaded into a polyester-viscose rayon cloth bag marked with the increment (charge) number and the lot number of the enclosed propellant. Charges #1 and #2 use 0.38 mm (FNH.015 inch) single perforation type II propellant for quick burning. Charges #3 to #7 use 0.71 mm (FNH.025 inch) multi-perforated (7 holes) type I propellant for slower burning. Figure 8-3 shows a picture of bags #6 and #7. For the trial, only bags of charges #5, #6, and #7 were used; they are the bags that are mostly burned in the field. Table 8-4 lists the masses of gun propellant in each bag.

During the trials, gun propellant bags from the 155-mm caliber howitzer, namely the M3A1 green bag propelling charges [12], were also burned. The full charge consists of approximately 2.5 kg of single-perforated (0.381 mm/0.015 in.) cylindrical gun propellant of composition M1. The propellant is contained in bolt-shaped cartridge cloth bags, dyed green, and is divided into a base charge and four increment charges.

Table 8-3. Chemical composition of gun propellant M1.

Constituents	Proportions (weight/weight %)
Nitrocellulose	85 ± 2
2,4-dinitrotoluene	10 ± 2
Dibutylphtalate	5 ± 1
Diphenylamine (added)	0.9 ± 1.2
Potassium sulfate (added)	1 ± 0.3

Figure 8-3. Propellant bags (M67, 105-mm caliber).

Table 8-4. Masses of gun propellant in the propelling charges of M67 (Weight Zone 2) [11].

Charge	Mass of gun propellant (kg)
1	0.245
2	0.040
3	0.072
4	0.110
5	0.114
6	0.260
7	0.406

The mass of propellant charge in each bag is given in Table 8-5, while the propellant's chemical composition was presented in Table 8-3. An igniter charge consisted of 99 g of clean burning igniter (CBI) powder in a red cloth bag sewn to the rear of the base charge (Charge #1). The composition of CBI is a minimum of 98% nitrocellulose, 1.5% ± 1.0 of diphenylamine, up to 0.1% of potassium nitrate, and 0.2% of added graphite glaze. A flash reducer pad containing 57 g of potassium nitrate was assembled forward of the base charge. Similar 28.4 g pads were assembled forward of increments 4 and 5. A picture of bags of Charges #4 and #5 plus the flash reducer pad of potassium nitrate is shown in Figure 8-4. A schematic of the complete M3A1 propellant is shown in Figure 8-5.

Table 8-5. Masses of propelling charge M1 in the M3A1 (green bags) [12].

Charge	Mass of gun propellant (kg)
1	0.864
2	0.227
3	0.298
4	0.425
5	0.709

Figure 8-4. Gun propellant bags: M3A1, 155-mm caliber.

All the gun propellant bags for both 105- and 155-mm calibers were obtained from the Canadian Forces via the Munitions Experimental Test Center (METC). They were accumulated from various live-firing exercises held at CFB Valcartier. The excess gun propellant bags, instead of being burned after the exercises, were stored in plastic bags deposited in thick cardboard boxes (triwall), brought back to METC, and kept in storage.

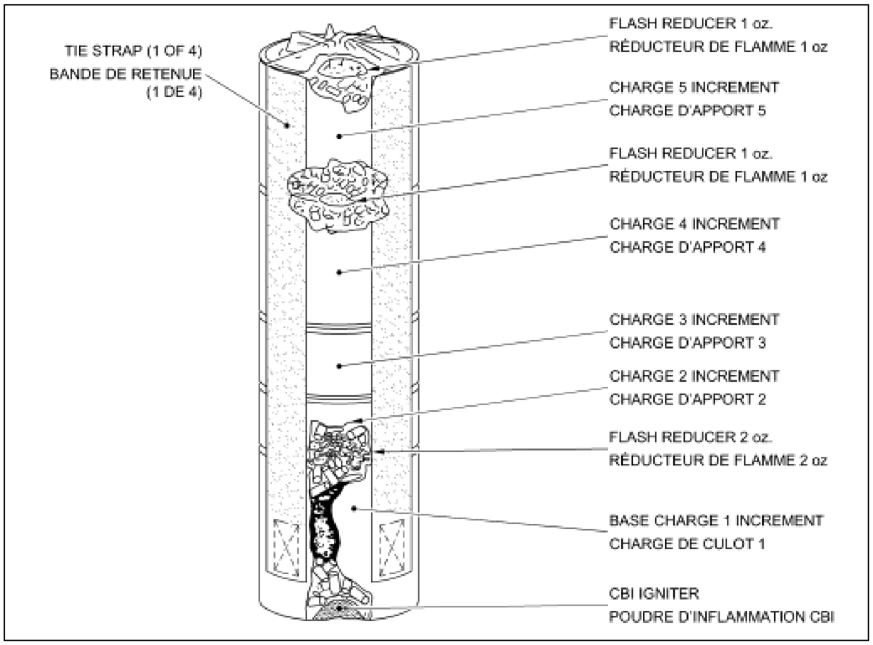


Figure 8-5. Schematic of the complete propelling charge M3A1 (155-mm caliber) [12].

8.6.2 Experimental setup: gun propellant burning trial on surface soil

The first trial involved burning excess gun propellant bags directly on the soil surface. It was conducted at the 2500-m firing corridor on the METC area located within CFB Valcartier on 23 September 2008. The Global Positioning System position of the setup site was 0307269 – 5198999 (7 m precision). This position was chosen considering that this site was probably not contaminated with dioxins and furans since the site was used almost exclusively for live-firing tests. The presence of a nearby groundwater sampling well was considered a potential asset. If a significant quantity of dioxins and furans were to be created during the trial, this well could be monitored for a period of time to verify any leaching. The setup was placed upstream from the well, as shown in Figure 8-6.

Figure 8-6. 2500-m firing corridor, METC Valcartier.

8.6.3 Gun propellant line configurations

The experimental setup included a total of six lines of gun propellant bags. They were disposed for the burning in three different configurations for the 105- and 155-mm caliber. Figure 8-7 shows the setup. The nomenclature includes the caliber and a letter, which indicates the type of line. The first line for each caliber was named “a” (105a and 155a for the 105- and 155-mm caliber, respectively). The “a” lines were composed of a single line of bags. An enlargement is shown in Figure 8-8. The bags were slightly overlapping to make sure that the fire would travel over the entire line. The second line for each caliber was named “b”; it was a double-bag line (Figure 8-9). Two bags were placed one beside the other, and they were slightly overlapping in the other direction to ensure flame propagation. The last line for each caliber was named “c”; it was a triple-bag line, in which two bags were placed on the ground and the third was placed on top of the other two, in the center (Figure 8-10). Table 8-6 describes the lines. Table 8-7 lists the number of each bag type used for the 105-mm caliber lines; Table 8-8 lists them for the 155-mm caliber lines.

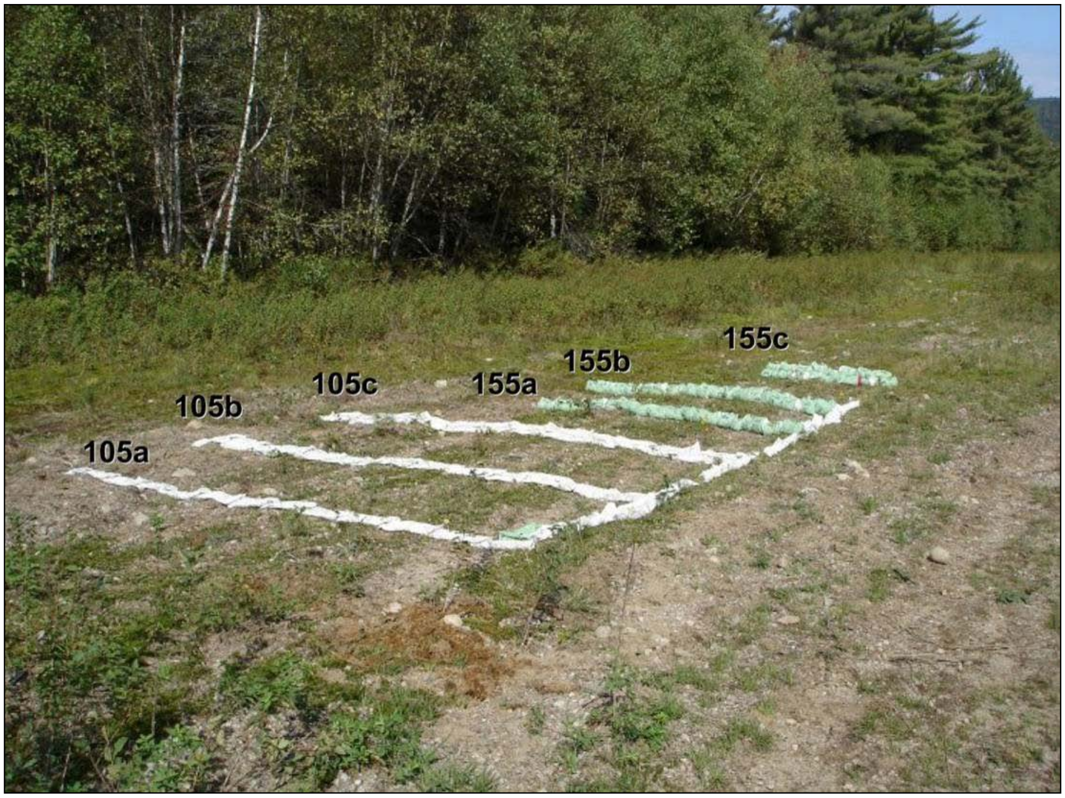


Figure 8-7. Line setup for the burning of gun propellant on the ground.

a) Line 105a (105-mm caliber)

b) Line 155a (155-mm caliber)

Figure 8-8. Setup for single-bag lines.

a) Line 105b (105-mm caliber) b) Line 155b (155-mm caliber)

Figure 8-9. Setup for double-bag lines.

a) Line 105c (105-mm caliber) b) Line 155c (155-mm caliber)

Figure 8-10. Setup for triple-bag lines.

Table 8-6. Description of each line.

Line	Type	Length (cm)	Width (cm)	Total mass of gun propellant (kg)
105a	Single-bag	304	10	5.278
105b	Double-bag	306	17	9.908
105c	Triple-bag	319	19	14.812
155a	Single-bag	209	14	10.49
155b	Double-bag	214	26	20.412
155c	Triple-bag	130	22	16.556

Table 8-7. Number of each bag type for the 105-mm caliber lines.

	Number of propellant bags		
Line	Charge 5 (0.114 kg/bag)	Charge 6 (0.260 kg/bag)	Charge 7 (0.406 kg/bag)
105a	0	0	13
105b	0	10	18
105c	1	5	33

Table 8-8. Number of each bag type for the 155-mm caliber lines.

	Number of propellant bags				
Line	Charge 1 (0.864 kg/bag)	Charge 2 (0.227 kg/bag)	Charge 3 (0.298 kg/bag)	Charge 4 (0.425 kg/bag)	Charge 5 (0.709 kg/bag)
155a	0	0	0	8	10
155b	0	0	0	18	18
155c	1	1	1	14	13

8.6.4 Ignition method

The lines were ignited using a railroad fusee (or flare) [13] connected to approximately 4 ft (1.22 m) of safety fusee, as seen in Figure 8-11. The flare used was the same as those used to indicate obstacles or advise caution on roadways at night. The flares burn with a bright red light and are commonly found in roadside emergency kits. The safety fusee gives enough time for the explosive expert to walk away to a safe distance from the setup area before the ignition of the flare and the gun propellant. This procedure of igniting the excess of gun propellant is a common practice in the Canadian

Forces. It is described in Department of National Defence literature [1]. The flare is composed of strontium nitrate, sulfur, potassium perchlorate, sawdust, and paraffin wax (unknown proportions) [14].

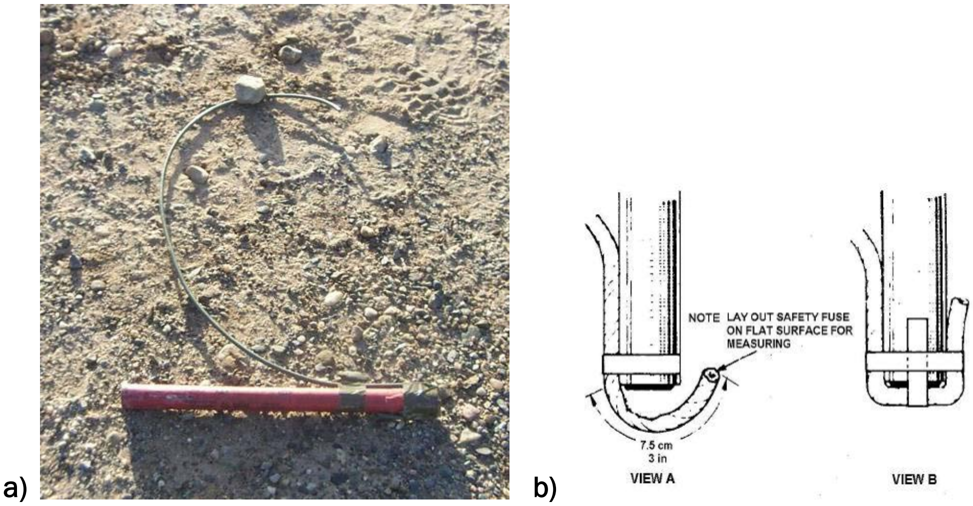
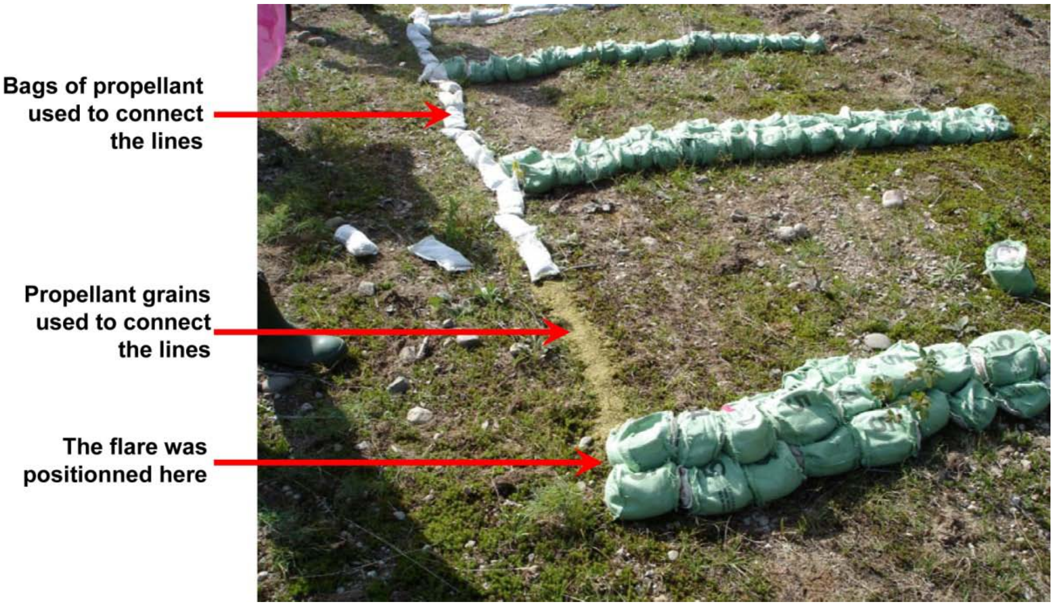


Figure 8-11. Typical flare with a safety fusee for ignition of the gun propellant: a) picture of the setup; b) schematic of preparing the railroad fusee for ignition.

The lines of gun propellant were positioned parallel to each other on the ground. Since only a single flare was available for ignition, the lines were thus connected with propellant, either in bags or as free grains to ensure that all the lines would be ignited (Figure 8-12). At the time of the trial, the fact that the flare was the source of dioxins and furans was unknown. The flare was inserted below the first gun propellant line and the safety fusee was ignited with a match. All personnel went to a secure distance (50 m) from the setup and waited for ignition. As shown in Figure 8-13, the fire was intense but only lasted for approximately 30 seconds.


Bags of propellant used to connect the lines

Propellant grains used to connect the lines

The flare was positionned here

Figure 8-12. Lines of propellant bags before ignition.


Figure 8-13. Burning of gun propellant lines.

8.6.5 Experimental setup: the flare trial

After obtaining the results from the burning on surface soil trial described previously and subsequent discussions with Mr. Michael Walsh from Cold Regions Research and Engineering Laboratory, Hanover, NH, a second trial was organized to determine if the flare was needed to produce dioxins and furans. Two trials were carried out: (1) burning on sand; (2) burning on stainless steel plates. The test on sand was prepared to collect samples in three conditions:

1. Gun propellant burned near the railroad fusee.
2. Gun propellant burned far from the fusee.
3. A railroad fusee was ignited alone, without gun propellant.

The test on stainless steel plates was prepared to collect samples in two conditions:

1. Gun propellant burned near the railroad fusee.
2. Gun propellant burned far from the fusee.

8.6.6 Setup description for the burning on sand

This trial was conducted in winter (9–10 February 2009). Because the combustion of propellant on soil differs from that on snow [2-4], a layer of clean sand approximately 5 cm thick was poured over the snow cover and the propellant and flare were placed on top. Three samples were taken during this trial.

A schematic of the setup is shown in Figure 8-14. Lines #1 and #2 were composed of four bags each of 105-mm caliber M67 propellant (previously described in section discussing gun propellant), two bags of Charge #6, and two of Charge #7, for a total of 1.332 kg of gun propellant. Line #1 was equipped with a railroad fusee for ignition. A line of propellant grains spread between Lines #1 and #2 connected them to ensure proper ignition of Line #2. Photographs of the trials are shown in Figure 8-15 and Figure 8-16.

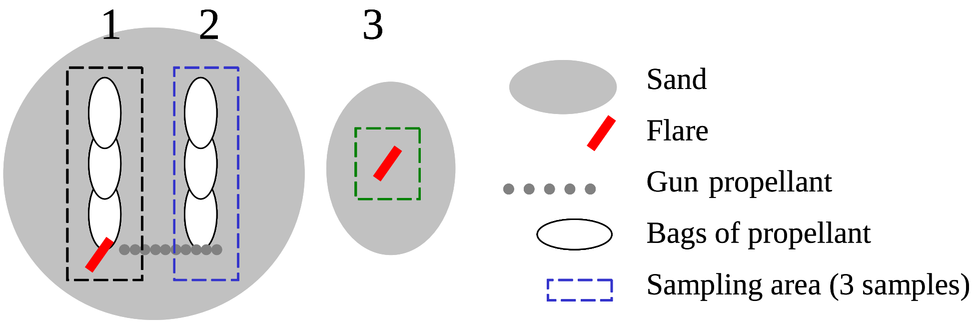
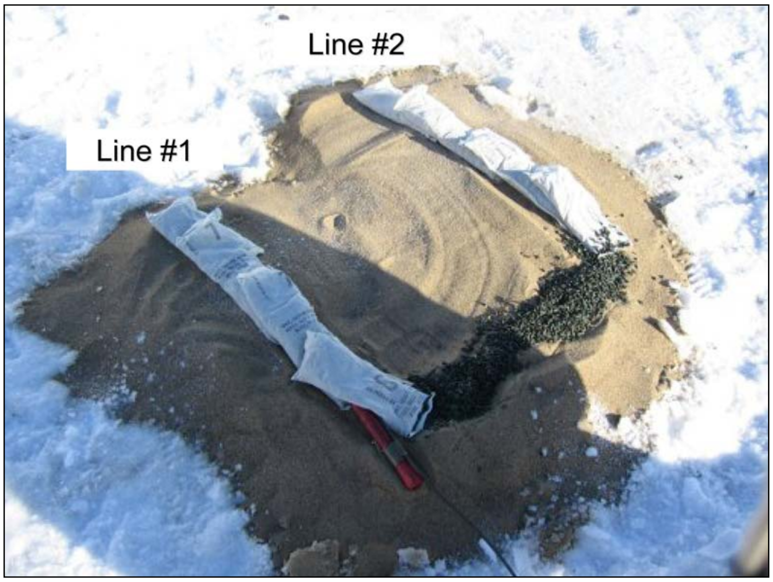
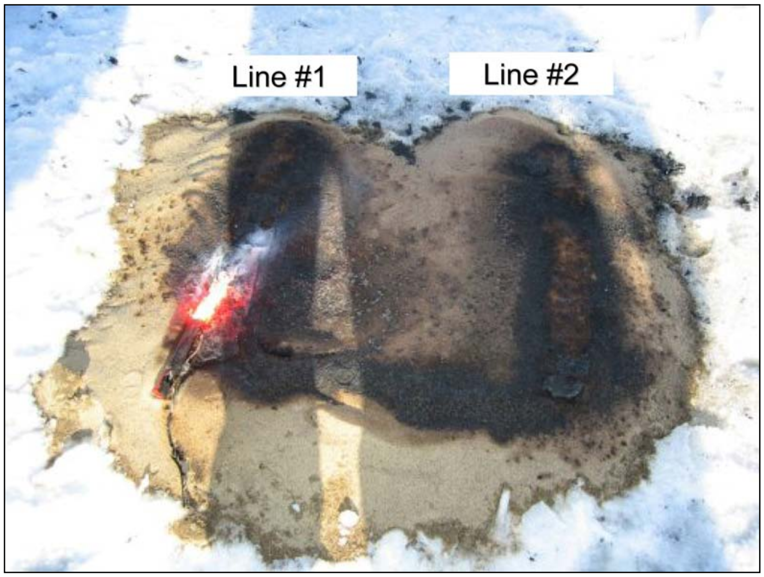


Figure 8-14. Schematic of the setup for the flare trial.



a) Before combustion.



b) After combustion.

Figure 8-15. Setup for flare trial (Lines #1 and #2).

Figure 8-16. Setup for flare trial (part for the flare only: Line #3).

8.6.7 Setup description for the burning on stainless steel plates

In order to avoid any dilution of the samples due to the sampling of sand with the burning residues, burnings were also conducted on stainless steel plates. The setup used was developed by Dr. Sonia Thiboutot from DRDC Valcartier (unpublished results and [15]). The setup consisted of a large stainless steel table measuring 3 × 1.5 m (Figure 8-17 and Figure 8-18) on which the excess bags of gun propellants were placed and ignited with the same type of railroad fusee as used in the other trials. The flare was put in a corner and propellant was placed on the table (Figure 8-18). Propellant bags with a total mass of 150 kg (105-mm caliber, unknown number of bags #5 to #7) were used for the two trials, as seen in Figure 8-19.

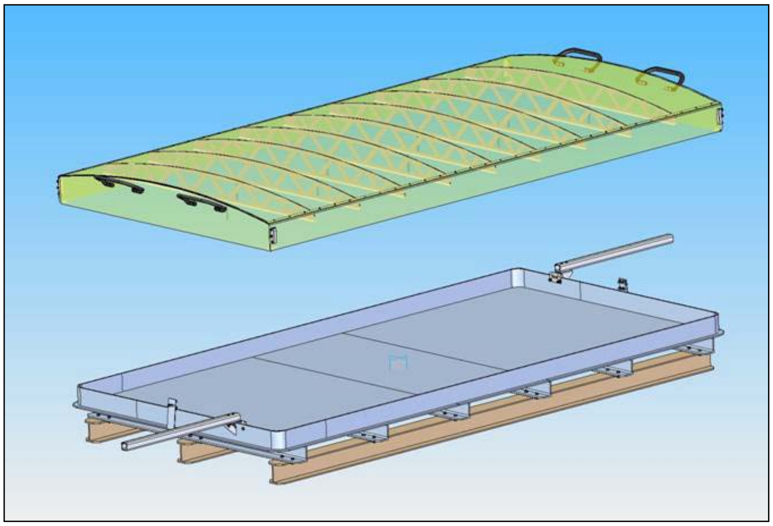


Figure 8-17. Schematic of the stainless steel burning table.

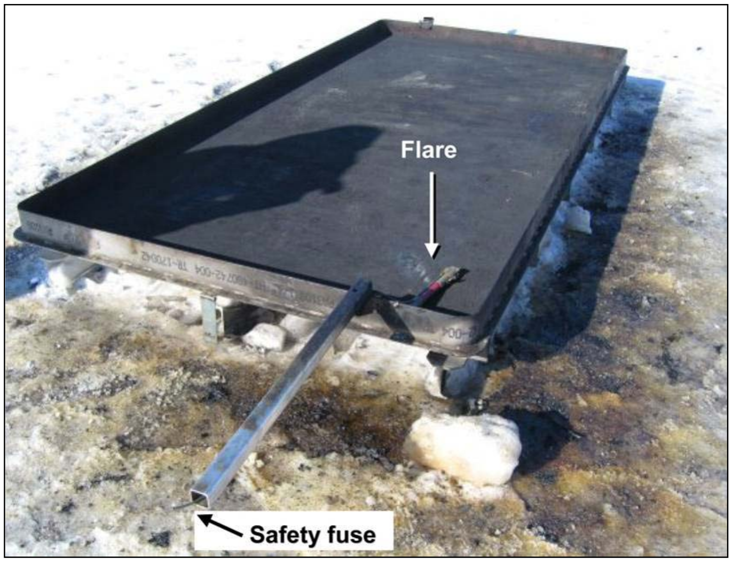


Figure 8-18. The flare in one corner of table.

Figure 8-19. Gun propellant bags on table before ignition.

8.7 Sampling

8.7.1 Sampling for the propellant burning trial on soil

For the initial trial, two soil samples were taken at the burning site before the lines were set up to determine if there was a background of dioxin and furans at the trial location. Figure 8-20 shows the area where the background was taken and where the setup would be placed. Most of the soil was free from vegetation, but some very short grass and moss were present. Two samples were built by collecting 25 increments of the surface soil throughout the entire area of the future burning at a depth of 0 to 1 cm.

a) Before installation of the propellant lines.

b) After the burning.

Figure 8-20. Setup area for the burning trial on soil.
Flags indicate the position of the future gun propellant lines.

After the fire (Figure 8-20b), the burn marks were obvious, outlined with black lines of soot. It is recognized that, after events of gun propellant burning, intact grains are often “kicked-off” from the fire and are found intact after the end of the burning [2-4]. No intact gun propellant grains were observed after this trial at any position.

Figure 8-21 shows a close-up of a line after burning was complete. Once the lines cooled down, the sampling began. One surface sample was taken in the burning path for each line, taking care to sample only the soot residue, with as little soil as possible. Another sample was taken under the burning path (i.e., 0–1 cm deep). A duplicate was taken for some samples. A small shovel was used (as seen in Figure 8-21) and was cleaned with solvent and paper towel between each sampling to reduce sample cross contamination (acetone-water-acetone). Samples were put in a 250-mL amber glass jar and placed in a cooler with ice after the sampling. Samples were kept at 4 °C until their analysis.

Figure 8-21. Close-up of a line after the burning.

8.7.2 Sampling for the flare trial: sand and stainless steel table

For the trial on sand, three samples were collected after the burning (Figure 8-14) and sent for analysis (following section). The shovel was carefully washed with acetone between samples. Samples were composed of burning residues (gun propellant and/or flare) and a portion of sand.

For the trial on the stainless steel table, samples were taken after the combustion at three different locations on the table after the burning (Figure 8-22). The first sample was composed of the flare residue (white solid), the second was composed of the black gun propellant residues around the flare, and the third was taken in the middle of the table, away from the ignition point (see arrows in Figure 8-22). No background sample could be taken for the burning on the stainless steel table because there was no material to sample.

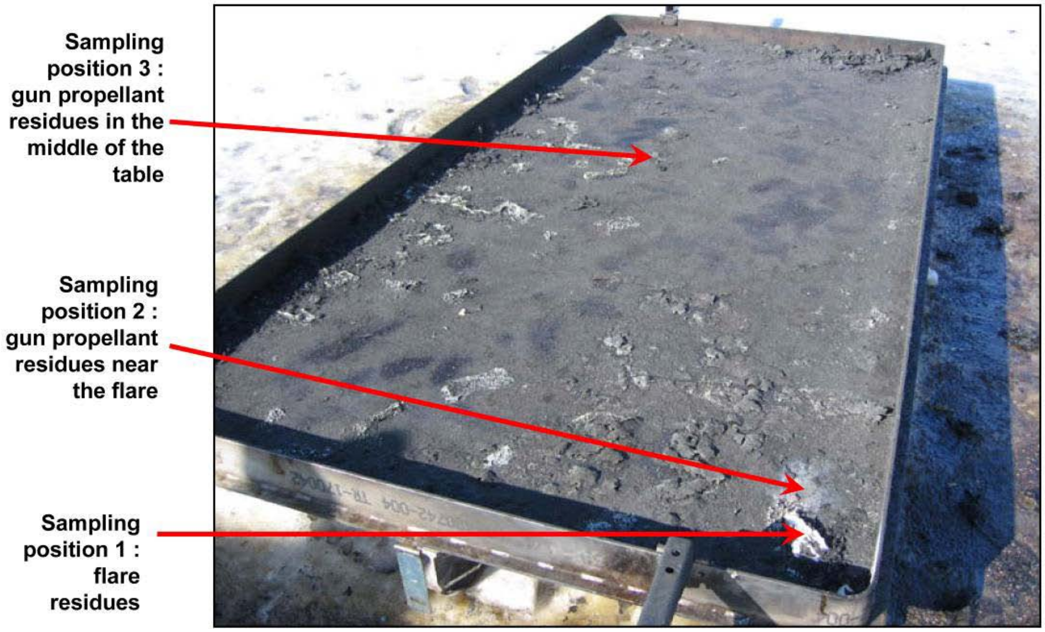


Figure 8-22. Table after burning and sampling positions.

8.8 Analytical method for dioxin and furan determination in solid samples

All the samples were sent to a private company (Biolab, Thetford Mines, Quebec) for analysis. The dioxins and furans were extracted from the solid samples by liquid extraction with toluene in a Soxhlet apparatus. After purification, dioxins and furans were concentrated and analyzed by gaseous phase chromatography coupled to a high resolution mass spectrometer (GC-MS). The method was developed by the *Centre d'expertise en analyse environmentale du Québec* (method MA.400 – D.F. 1.0) [16]. For chlorinated dioxins and furans, it is not possible to express a limit of quantification in TEQ. The method detection limit was 0.1 pg/g for each of the congeners measured. The concentrations obtained were then transformed into the TEQ using Equation (1).

8.9 Results

8.9.1 Dioxins and furans in residues after propellant burning trial on soil

Table 8-9 shows results obtained from the dioxin and furan analyses. In the following discussion, samples will be referred to by using numbers

(BOP-1 to BOP-16) according to Table 8-9. The analyses of the background samples (BOP-1 and 2) demonstrated that the soil chosen for the experiment was not free from dioxins and furans. Contamination can be anthropogenic and/or natural (unknown at this moment). An average of 0.33 pg TEQ/g was detected in the first cm of soil. The amount of soil in the background samples was not the same as for the samples taken in the burn areas. In the burning marks, the sample was mostly composed of burning residues. Due to this fact, the concentration of TEQ of PCDD/PCDF in the background samples was not subtracted from the concentration in the other samples. The discussion presented in the next section uses the raw data in order to compare the lines among them.

Table 8-9. Concentration of dioxins and furans in the samples of gun propellant burned on soil, reported in toxic equivalent quantity,.

Sample #	Line identification and sampling type *	Toxic equivalent quantity for dioxins and furans (TEQ) (pg/g)
BOP-1	Background (surface)	0.34
BOP-2	Background (0-1 cm deep)	0.33
BOP-3	105a (surface)	0.073
BOP-4	105b (surface)	0.06
BOP-5	105c (surface)	0.1
BOP-6	155a (surface)	0.086
BOP-7	155b (surface)	0.094
BOP-8	155c (surface)	0.098
BOP-9	105a (0-1 cm deep)	0.24
BOP-10	105b (0-1 cm deep)	0.15
BOP-11	105c (0-1 cm deep)	0.26
BOP-12	155a (0-1 cm deep)	0.26
BOP-13	155b (0-1 cm deep)	0.18
BOP-14	155c (0-1 cm deep)	0.17
BOP-15	105a (surface) duplicate	0.11
BOP-16	155a (surface) duplicate	0.33

* Surface = sample taken directly in the burning path, collection of residue with as little soil as possible.

0-1 cm deep = sample taken under the burning path (0 to 1 cm soil depth)

For the burning of the 105-mm caliber gun propellant on surface soil, the samples taken directly on the soot line were mostly residue and a low quantity of soil. For example, samples BOP-3, 4, and 5 presented values of 0.073, 0.06, and 0.1 pg TEQ/g, respectively. These values, lower than the background, were not expected. The values for the samples taken under the burning path (0 to 1 cm soil depth; samples BOP-9, 10, 11) presented values of 0.24, 0.15, and 0.26 pg TEQ/g. This value is closer to the value obtained for the background samples. A possible explanation for this result is that the concentration in the residue is very low and this simply dilutes the concentration of dioxins and furans in the soil that is already contaminated from previous trials at this site.

Regarding the lines where 155-mm caliber propellant bags were burned, the values for the residues in samples BOP-6, 7, 8 were 0.086, 0.094, and 0.098 pg TEQ/g, respectively. Again, these values are lower than the values in the background samples. The results for the samples taken under the burning pads (0 to 1 cm soil depth, samples BOP-12, 13, 14) presented values of 0.26, 0.18, and 0.17 pg TEQ/g. The explanation provided previously for the 105-mm burning also applies here. These results will be talked about further in the Discussion section.

8.9.2 Dioxins and furans in residues after the flare trial: sand and stainless steel table

Results of the flare trial on sand are presented in Table 8-10. In this case, the TEQs measured in the samples were very low (0.00006 to 0.04 pg/g) making it hard to draw a conclusion from them.

The TEQ in the samples from the burn trial on the stainless steel table are presented in Table 8-11. The sampling carried out directly on steel avoids any dilution of the residues. Results of this test clearly show that the concentration of dioxins and furans (reported as TEQ) were higher in the area near the flare (5.182 pg/g) than in the area away from it (middle of the table, 0.068 pg/g). The residues of the flare itself showed an intermediate value (0.337 pg/g). Discussion of these results will be presented in the next section.

Table 8-10. Concentration of dioxins and furans, reported in toxic equivalent quantity, in samples of the flare trial on sand.

Sample #	Description	Toxic equivalent quantity for dioxins and furans (TEQ) (pg/g)
1	Propellant + flare residues + sand	0.00006
2	Propellant residues + sand	0.00009
3	Flare residues + sand	0.04006

Table 8-11. Concentrations of dioxins and furans, reported in toxic equivalent quantity, in samples of the flare trial on the stainless steel table.

Sample #	Description	Toxic equivalent quantity for dioxins and furans (TEQ)(pg/g)
1	Flare residue	0.337
2	Propellant residues near flare	5.182
3	Middle of table (propellant residues only)	0.068

8.10 Discussion

8.10.1 Dioxins and furans in residues after the gun propellant burning trial on soil

The results obtained from the burning of propellants on soil made it seem that this combustion did not produce dioxins and furans as expected. As presented in the description of previous studies, a preliminary analysis was carried out on samples taken from burnings of gun propellant on snow, and in three out of five samples analyzed, dioxins and furans were detected at values that exceeded the regulations. One logical explanation is that the production of dioxins and furans is possible only when the flare is present with the organic material to be burned (i.e., gun propellant in this case). One of the main ingredients in the flare is potassium perchlorate. At high temperature, it is believed to react with the gun propellant to form dioxins and furans. This is consistent with the EPA statement [17] according to which the formation of dioxins and furans requires the presence of a chlorine donor (a molecule that provides a chlorine atom to the pre-dioxin molecule), and the formation and chlorination of a chemical intermediate that is a precursor. During the experiment performed on snow [4], one flare was used for every trial (i.e., one flare for each propellant line; no lines connected with grains to assure flame propagation), and most of the plume of residues was collected and combined into one single large sample. In the trial of propellant burning on surface soil presented in this report, only one flare was used to ignite all the six lines, and when taking the samples, care was taken not to sample in the flare residue, because at that time, the flare was not suspected to be the source of dioxins and furans. That would explain the low levels of TEQ measured.

As the dioxins and furans seem to be created when the flare is present, it would have been normal to detect these compounds in most of the samples that were produced in Diaz's trial (burning of propellant on snow [4] and discussed in this report under previous studies). As presented previously, no dioxins and furans were detected in samples #1 and #2 (see Table 8-2), this being still unexplained at the time. This result may be explained by a much larger amount of residue, as compared to the other samples (Table 8-2), thus diluting too much to allow their detection. Following this hypothesis, for the burning on surface soil trial, after the burning of six lines of gun propellant on soil, only one line could have presented some dioxins and furans (line 155c, because the flare was put at its end), but the value detected was still below the background value. This can be explained by the fact that the residue was not taken entirely, but by increments, and also by the fact that the samples near the flare were avoided. As stated earlier, at the time when this first trial was organized, the flare was not suspected to be necessary to produce dioxins and furans during the combustion. Once suspected, the flare trial was conceived and performed to collect samples closer to the position of the flare for analysis.

8.10.2 Dioxins and furans in residues after the flare trial: sand and stainless steel table

In the case of the flare trial on sand (results in Table 8-10), it is believed that the very small quantities measured were due to a dilution factor, which was caused by sampling of the sand along with the residues. In the initial trial, burning of gun propellant on surface soil, sampling was also performed on soil; however, since it was more compact (natural soil vs. loose sand for the flare trial), the analyzed samples likely contained a higher proportion of residues. Overall, the results of the flare trial on sand were considered non-conclusive, and using the stainless steel table for the burning trial was the best approach for sample collection.

The results from the flare trial on the stainless steel table were more conclusive. The presence of the flare clearly was accountable for the production of dioxins and furans. Since no replicate was performed for this trial, these values should be taken only as indications that the flares produce dioxins and furans during combustion with gun propellant and should not be used for any further calculation. The values obtained in the residue are much lower than those of the burnings on snow cover ([4] and description in this report of earlier studies). As previously indicated, dioxins and furans were detected in three out of five samples (29.5, 31.8, 10.9 pg/g) (Table 8-2). These values were obtained from a large sample, while the values obtained for the samples of burned propellant on the steel table were obtained from a much smaller sample. The quantity of dioxins and furans produced with a single flare was clearly higher during the burning on snow. This can be explained by the fact that these molecules were produced during incomplete combustion, such as that of on-snow burning of gun propellant [2–4]. It is believed that the combustion was slowed down by the presence of melted snow, and the perchlorate in the flare reacted with the carbon-based molecules in the propellant to form a precursor of dioxins and furans and then dioxins and furan themselves. These molecules probably were not further decomposed into other molecules, such as gases for example, and were kept in the residue, probably due to the lower temperature in the combustion zone.

8.10.3 Alternative methods to reduce production of dioxins and furans

Results presented in this report showed that burning of excess gun propellant produces dioxins and furans due to the presence of a railroad fusee as the ignition source. This production was worse when the burning was performed on snow cover due to a more incomplete combustion. Combustion performed on a stainless steel table demonstrated that, even if the combustion is more complete, dioxins and furans are still produced, again due to the presence of the igniter. The procedure of burning excess gun propellant bags should be modified in order to reduce or avoid the production of dioxins and furans.

One way to achieve this goal would be to remove the chlorine source (i.e., the railroad fusee that contains perchlorate). Ignition could be done using a chlorine-free device that can be delayed, in order to give enough time for the Soldiers to withdraw from the burning site to a safe distance. The procedural manual for destruction of duds and misfired ammunition on CF ranges and training areas [1] should be modified to account for the findings in this report. Other procedures to ignite the burning should be investigated.

It also has to be noted that burning of excess gun propellant produces other residues considered hazardous for the environment because they contain energetic materials [2-4] such as 2,4-DNT and heavy metals such as lead present in bag #5 of the M67 charge for the 105-mm howitzer [11]. The whole concept of open burning on the ground should be revised to avoid contamination of surrounding soils. Moreover, it is believed that the burning of excess gun propellant on snow cover should be completely avoided; the combustion is incomplete due to the presence of melted snow, which results in the production of a higher quantity of pollutants such as 2,4-DNT. Acceptable alternative methods, such as use of modular charges or recycling of excess gun propellant, were proposed by Diaz et al. [4] and should be considered. More research and development is needed for these two options, but both would avoid burning of excess propellant and also prevent the use of flares for ignition. If combustion of excess propellant bags is unavoidable, the associated environmental risks could be decreased by burning the bags in an incinerator equipped with a gas treatment system to reduce the toxic emissions. The future construction of a demilitarization capability at CFB Dundurn [18] could offer a very interesting solution, but this will not be available in the next few years, so a short-term solution must be considered. One of these short-term solutions is the development of a portable stainless steel table to conduct the burnings, a concept that is currently under investigation by Dr. Sonia Thiboutot from DRDC Valcartier (unpublished results and [15]). This table would avoid any contact between the soil and the residues and prevent any leaching in the soil and groundwater. For these last options, the ignition should not be carried out with a flare to avoid the production of dioxins and furans, and the residues produced should be treated as hazardous materials according to environmental regulations.

8.11 Conclusion

The procedure of burning excess gun propellant produced after an artillery exercise is performed on many ranges and training areas across Canada. The work presented in this report demonstrated that the destruction of excess propellant by open burning on the ground using a railroad fusee (flare) for ignition produces polychlorodibenzo-p-dioxins (PCDD, dioxins) and polychlorodibenzofuranes (PCDF, furans). These compounds are known to be toxic and to persist in the environment. The use of a flare containing perchlorate for ignition was identified as the cause of formation of dioxins and furans. Moreover, the burning of propellants on snow cover produced more contaminants than burning on ground, so these procedures should be revised to account for the results presented in this report.

Replacement of the flare by another device without perchlorates will prevent the formation of dioxins and furans. One short-term solution proposed is to perform future burnings of excess gun propellant without a flare and on stainless steel tables (ongoing work by Dr. Sonia Thiboutot from DRDC Valcartier unpublished results; [15]). This would also prevent contact of the burning residue with the soil and leaching in the environment. Development of a demilitarization system, including an incinerator equipped with gas treatment, is also considered a solution. Further testing with the stainless steel table will include measurements of dioxins and furans using various ignition methods to confirm the results of the present study and to seek an alternative ignition method free of perchlorates.

In the case of using a flare alone, such as for road signalization, it is not believed that the process would produce an important quantity of dioxins and furans if there is a limited amount of organic material in the combustion zone. The thin paper wrap around the flare as well as the presence of paraffin and sawdust in the composition should not produce a significant quantity of dioxins and furans. Also, the combustion should be almost complete because the flare is kept in an upright position with metal wires.

Finally, to avoid burning the excess of gun propellant completely, developing modular charges for the 105-mm caliber or the recycling of propellant would offer a solution with no excess bags to destroy by burning.

8.12 Nomenclature

2,4-DNT	2,4-Dinitrotoluene
CBI	Clean burning igniter
CFB	Canadian Forces Base
DRDC	Defence Research and Development Canada
EPA	U.S. Environmental Protection Agency
METC	Munitions Experimental Test Center
PCDD	Polychlorodibenzo-p-dioxins
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
PCDF	Polychlorodibenzo-furanes
TEF	Toxic equivalency factor
TEQ	Toxic equivalent quantity

8.13 References

1. Department of National Defence Canada. 2005. *Ammunition and explosives procedural manual: Destruction of duds and misfired ammunition on CF ranges and training areas*. C-09-008-002/FP-000.

2. Walsh, M.R., M.E. Walsh, and A.D. Hewitt. 2009. *Energetic residues from the expedient disposal of artillery propellants*. ERDC/CRREL TR-09-8. Hanover, NH: U.S. Army Engineer Research and Development Center.

3. Walsh, M.R., M.E. Walsh, and A.D. Hewitt. 2010. Energetic residues from field disposal of gun propellants. *Journal of Hazardous Materials*, doi:10.1016/ j.jhazmat.2009.08.056, 173(2010): 115-122.

4. Diaz, E., S. Brochu, I. Poulin, D. Faucher, A. Marois, and A. Gagnon. (in press). *Residual dinitrotoluenes from open burning of gun propellant*. DRDC Valcartier, DRDC TR 2009-xxx.

5. Brochu, S., E. Diaz, S. Thiboutot, G. Ampleman, A. Marois, A. Gagnon, A.D. Hewitt, S.R. Bigl, M.E. Walsh, M.R. Walsh, K. Bjella, C. Ramsey, S. Taylor, H. Wingfors, U. Qvarfort, R.-M. Karlsson, M. Ahlberg, A. Creemers, and N. van Ham. 2008. *Environmental assessment of 100 Years of military training at Canadian Force Base Petawawa phase 1 – Study of the presence of munitions-related residues in soils and biomass of main ranges and training areas*. DRDC TR 2008-118. Val-Bélair, QC: DRDC-Valcartier.

6. Brochu, S., R. Martel, G. Comeau, V. Varfalvy, and V. Boulianne. 2009. Characterization of old grenade range of CFB Petawawa and evaluation of potential remediation options. Oral presentation to National Defence Head Quarters (NDHQ), Ottawa, Canada.

7. Health Canada, web page consulted in January 2009. http://www.hc-sc.gc.ca/hl-vs/iyh-vsv/environ/dioxin-eng.php.

8. Kulkarni, P.S., J.G. Crespo, and C.A.M. Afonso. 2008. Dioxins sources and current remediation technologies – a review. *Environment International* 34: 139-153.

9. Canadian Council of Ministers of the Environment. 2002. Canadian soil quality guidelines for the protection of environmental and human health: Dioxins and furans. In: *Canadian environmental quality guidelines*. Winnipeg: Canadian Council of Ministers of the Environment.

10a. Ministère du Développement durable, Environnement et Parcs, Grille des critères applicables aux cas de contamination des eaux souterraines, Politique de protection des sols et de réhabilitation, webpage consulted in May 2009 http://www.mddep.gouv.qc.ca/sol/terrains/politique/annexe_2_grille_eaux.htm#dioxine.

10b. U.S. Environmental Protection Agency. 2006. National drinking water regulations. EPA 816-K-06-003. Washington, DC: Office of Water.

11. Department of National Defence Canada. 2004. *Ammunition and explosives technical information: Ammunition for 105-mm howitzer*. C-74-315-H00/TA-000.

12. Department of National Defence Canada. 2006. *Technical information – Ammunition and explosives: Ammunition for 155-mm howitzer*. C-74-320-BA0/TA-000.

13. Department of National Defence Canada. 1974. Canadian Forces Technical Order, Description and maintenance instruction, Fusee, Warning, Railroad, 5 min, C-74-370-GAA/TA-000.

14. CIL/Orion, Div. EVAN Inc. 2007. *Material safety data sheet, railway fusees*. Lachute, QC, Canada.

15. Thiboutot, S. 2009. Towards Sustainable ranges: Burning excess artillery propellants. Presented to stakeholders in NDHQ, Constitution Building.

16. Centre d'Expertise en Analyse Environmentale du Québec. 2006. *Détermination des dibenzo-para-dioxines polychlorés et dibenzofuranes polychlorés : Dosage par chromatographie en phase gazeuse couplée à un spectromètre de masse*. MA. 400 – D.F. 1.0, Rév. 4, Ministère du Développement Durable, de l'Environnement et des Parcs du Québec.

17. U.S. EPA. *Estimating exposure to dioxin-like compounds volume i: executive summary*. EPA/600/8-88/005Ca. Washington, DC: U.S. Environmental Protection Agency.

18. CANOSCOM, ADM (IE), ADM (Mat) and DCC/NOG Ottawa. 2009. *CF ammunition demilitarization capability: Options analysis*. Report on Project No. 00001101.

19. Van den Berg, M., L. Birnbaum, B.T.C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. van Leeuwen, A.K.D. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenck, D. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and for wildlife. *Environmental Health Perspectives* 106: 775.

Appendix 8-A: Toxic Equivalency Factors

Table 8-A1. Toxicity equivalency factors for polychlorinated dibenzodioxins and dibenzofurans as proposed by the World Health Organization [19].

Compounds	TEF
Chlorinated dibenzo-p-dioxins (CDD)	
2,3,7,8-Tetra CDD	1
1,2,3,7,8-Penta CDD	0.5
1,2,3,4,7,8-Hexa CDD	0.1
1,2,3,6,7,8-Hexa CDD	0.1
1,2,3,7,8,9-Hexa CDD	0.1
1,2,3,4,6,7,8-Hepta CDD	0.01
Octa CDD	0.001
Chlorinated dibenzofurans (CDF)	
2,3,7,8-Tetra CDF	0.1
1,2,3,7,8-Penta CDF	0.05
2,3,4,7,8-Penta CDF	0.5
1,2,3,4,7,8-Hexa CDF	0.1
1,2,3,6,7,8-Hexa CDF	0.1
2,3,4,6,7,8-Hexa CDF	0.1
1,2,3,7,8,9-Hexa CDF	0.1
1,2,3,4,6,7,8-Hepta CDF	0.01
1,2,3,4,7,8,9-Hepta CDF	0.01
Octa CDF	0.001

9 Energetic Residues from Blow-in-Place Detonation of 60-mm and 120-mm Fuzed High-Explosive Mortar Cartridges

Michael R. Walsh, Charles M. Collins, and Alan D. Hewitt[*]

9.1 Abstract

Military live-fire training missions frequently result in unexploded ordnance (UXO) on training ranges. Disposal of the rounds, often done in situ, is necessary in some cases for range safety or maintenance. In February 2008, the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) teamed with the 716th Explosive Ordnance Disposal detachment at Fort Richardson, AK, to detonate two series of seven 60-mm and 120-mm fuzed high-explosive (HE) rounds to determine the resulting energetic residues. Each round was detonated using a single block of C4 (91% RDX) as a donor charge. All rounds were separated to allow each detonation plume to be sampled as a distinct decision unit. Samples were collected from the snow surface using multi-increment sampling for residues analysis. The 60-mm plumes averaged 200 mg of HE or 0.022% of the original mass. The 120-mm plumes averaged 25 mg of HE or 7.1×10^{-4}% of the original mass. Quality assurance procedures were conducted both in the field and at the laboratory to ensure data fidelity.

9.2 Preface

This report was prepared by Michael R. Walsh, Engineering Resources Branch, and Alan D. Hewitt and Charles M. Collins, Environmental Sciences Branch, Cold Regions Research Engineering Laboratory (CRREL), U.S. Army Engineer Research and Development Center (ERDC). Manuscript review was provided by Dr. C.L. Grant, emeritus professor, University of New Hampshire, and Christopher R. Williams of CRREL. Funding was provided by the Soil and Water Monitoring Program of U.S. Army Garrison, Alaska (Gary Larson, coordinator).

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Field work of this nature is complex and requires the involvement and cooperation of many different people and entities. The authors thank L.D. Fleshman, Range Facility Manager of U.S. Army Alaska, for his support of this and the many tests we have conducted on his ranges over the years. We also thank SFC Jason Doty and the men of the 716th Explosive Ordnance Disposal detachment at Fort Richardson, AK, for taking time from their busy schedules to obtain the munitions required for these tests and then blowing them up. Jeff Bryant of Bering Sea Eccotech supported us as the Site Safety Officer and as our unexploded ordnance technician (UXO Tech III), helping us to avoid any encounters with UXOs. Our field crew included Jon Zufelt, Stephanie Saari, Anna Wagner, Jennifer Fadden, and Art Gelvin (CRREL) and Rebecca Terry (U.S. Army Corps of Engineers, Jacksonville, FL). Back at the lab, Nancy Perron and Marianne Walsh joined in the analysis of the samples. A lot had to happen right and on time to make these tests successful, and this crew made it happen—our thanks to all of them.

9.3 Unit conversion factors

Multiply	By	To Obtain
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
inches	0.0254	meters
pounds (mass)	0.45359237	kilograms

9.4 Introduction

Firing ranges provide soldiers the opportunity to train using a variety of munitions. However, live-fire training with high-explosive munitions will result in the generation of energetic residues on the range. The major sources include unexploded (non-functioning) ordnance, low-order detonations with a significant fraction of the high-explosive filler remaining unconsumed, and small quantities of explosive residues from fully functioning high-order detonations. These are potential and contributing sources of unconsumed energetic materials that can contaminate the soil and the groundwater and, in sufficient quantities, can threaten human health and the environment and result in the loss of use of the facility.

Hundreds of thousands of rounds are fired into military impact ranges each year (Foster 1998). The majority of these rounds detonate cleanly and efficiently and deposit very little explosive residue (Hewitt et al. 2003; Taylor et al. 2004; Walsh et al. 2005a, 2006b; Walsh 2007). However, a small percentage of the ordnance, estimated to be less than 2%, does not function properly, resulting in unexploded ordnance (UXO; Dauphin and Doyle 2000). UXO is a serious range safety hazard. Along with low-order detonations, where only part of the explosive filler is consumed, they are the most significant point source for HE contamination on an impact range. Range closures due to contamination have driven the military toward more thorough range maintenance, including clearance of UXO. Studies show that the disposal of these items in situ (blow-in-place [BIP]) is not as efficient as the live-fire detonation of munitions and may result in the deposition of significant quantities of explosives on the range (Hewitt et al. 2003; Walsh et al. 2005a, 2006a).

The data set for BIP residues is limited, due in part to the difficulty of quantifying residues from the detonation of a munition. The methods developed by Jenkins et al. (2000) and Walsh et al. (2005c, 2007) on snow-covered ice for both live-fire and BIP detonations allow the isolation of detonation residues from previous range activities, the effective demarcation of the residue plume, and the efficient collection of residues for analysis. This report addresses the major remaining data gap in range use of common U.S. Army high-explosive munitions, the BIP disposal of unexploded, fuzed 60-mm and 120-mm mortar cartridges.

In 2008, we conducted a series of BIP tests on fuzed 60-mm and 120-mm mortar cartridges. The study objective was to determine the explosives residues quantities on a per-round basis and to compare these results with those of previous results obtained under similar conditions.

9.5 Field tests

9.5.1 Field site

The tests were conducted on the Eagle River Impact Area, Fort Richardson, Alaska. Eagle River Flats (ERF) is an estuarine salt marsh along the upper Cook Inlet that periodically floods and freezes over the winter, building up layers of ice over the impact area (Figure 9-1). With a fresh layer of snow on the ice, this area is ideal in the winter for conducting tests of explosive residues because the detonations are segregated from past activity on the Flats and residue plumes are easily discerned on the snow surface. At the time of these tests in February 2008, temperatures ranged from -4 °C to near freezing. Winds were variable from the north at under 3 m/sec with partially overcast skies. Snow depth ranged from 10 to 30 cm, and ice thickness varied to up to 65-cm deep. The snow surface was consolidated by prior wind and sun exposure but was not crusted over. No snow fell and no drifting occurred during the tests. Little unfrozen water lay beneath the ice.

The tests were conducted in a location designated as Area C. The test area is underlain by a shallow ponded area—frozen to depth during testing—and an "upland" (mudflat) zone between the pond and the river levee. This area is easily accessible from an access road to the edge of the Flats. An ice road was cleared and plowed to the test site and parallel roads plowed perpendicular to the prevailing winds to provide access to the detonation points (Figure 9-2).

Figure 9-1. Eagle River Flats impact area in winter.

Figure 9-2. Ice road to BIP sites from ERF access road.

9.5.2 Munitions

Two munitions were detonated during our tests (Table 9-1). The 60-mm test munitions were M888 HE cartridges with an M935 point detonating (PD) fuze mounted in the nose (Figure 9-3a). For the 120-mm tests, the M933 HE cartridge with an M745 point detonating fuze (Figure 9-3b) was detonated. The donor charge for both munitions was a single block of C4. Appendix 9-A contains complete munitions data for these tests.

9.5.3 Tests

Our tests were conducted in association with the 716th Explosive Ordnance Disposal (EOD) detachment, Fort Richardson, AK. Coordinating with the mission command, we located detonation points for each set of seven rounds on either side of the access roads to enable testing with the wind blowing in either direction. The 716th EOD detachment was responsible for drawing the munitions, setting the charges, and detonating the rounds.

The 120-mm tests were run first. A background surface snow sample from the test area was collected before detonation activity. Clean ice blocks were cut for the tests from a nearby freshwater lake to be used to prevent penetration to ground when the rounds were detonated. These blocks were

Table 9-1. Explosives constituents for munitions used during firing point tests.

Munition	Component	Constituent	Weight (g)
M888	HE Filler	Comp B	358
		RDX[a]	215
		TNT	140
	M935 Fuze	—	13.1
		RDX[a]	12.7
	M702 Ign. Ctg.[b]	Prop M9	3.37
		NG	1.35
M933	HE Filler	Comp B	2,990
		RDX[a]	1,794
		TNT	1,166
	M745 Fuze	—	10.2
		RDX[a]	7.9
		HMX	0.13
	M981 Ign. Ctg.[b]	Prop M44	68
		NG	30
M112 (Donor)	C4	—	567
		RDX[a]	516

[a] RDX may contain up to 9% HMX in Composition B explosive.
[b] Ignition cartridge.

30- to 45-cm thick. Each fuzed M933 HE cartridge was placed 15 m from the access road and 40-m apart on an ice block approximately 1-m long by 0.5-m wide by 0.4-m thick. A block of C4 explosive (M112) was placed adjacent to the body of the horizontal cartridge near the nose end. A blasting cap initiator and time fuze were then attached to the donor charge. When the area was clear, the rounds were set off simultaneously. One donor initiator failed to function properly and was replaced within 20 min. The area was once again cleared and the round detonated. At the time of detonation, the temperature was -3.8 °C with a north wind of 0–3 m/sec. There was no precipitation and no drifting of snow.

Following clearance of the detonation points, the plumes were demarcated by walking the visible perimeter of the soot-discolored snow with a global positioning satellite (GPS) system (Trimble GPS Pathfinder Pro XR; ±1-m accuracy). The outline of the plume was recorded, as was the detonation point for each event. Triplicate 10- x 10- x 2.5-cm deep multi-increment (MI) surface snow samples were then taken within each plume, and duplicate MI samples were also taken from the 0- to 2-m annulus outside the visible plume. To obtain the MI samples within the plume, parallel lanes

a. M888 60-mm HE cartridge with M112 donor charge on ice surface.

b. M933 120-mm HE cartridge on ice block.

Figure 9-3. Munitions used in BIP tests.

2-m apart were walked throughout the plume, and increments systematically collected every 3 m from a randomly selected starting location at the beginning of the first lane. For outside-the-plume (OTP) samples, a similar procedure was used except there was only one lane through the middle of the annulus and samples were systematically collected from either side of the lane from a random starting point. On one plume, triplicate 20- x 20- x 2.5-cm MI surface samples were taken directly followed by 10- x 10- x 2.5-cm subsurface samples from the area just sampled. These quality assurance procedures were done to determine if we adequately delineated the plume and if we sampled deep enough to collect the majority of the residues at the sampled points. For a full description of energetics sampling on snow, see Walsh et al. (2007).

The following day, the procedure was repeated for the 60-mm mortar cartridges. In this case, however, the rounds were set directly on the ice at a distance of 42-m apart. All rounds detonated simultaneously and the sampling procedure repeated. One additional test was performed on one of the detonation plumes. The plume was divided into three zones based on perceived soot density. Each of these gradient zones was then sampled in duplicate to determine the difference in energetics concentrations. This test was performed to determine the effect of "gradient bias," or the tendency to sample only where the greatest evidence of contamination exists (Walsh et al. 2005c).

9.6 Sample processing and analysis

The multi-increment snow samples were transferred to a lab set up nearby on post for processing. The samples were melted, filtered (Figure 9-4), and the aqueous fraction concentrated using solid-phase extraction (Walsh and Ranney 1998; Walsh et al. 2007). When processing was completed, the solid-phase extraction (SPE) cartridges and the soot fraction filters were shipped to the analytical chemistry laboratory at CRREL's main office in Hanover, NH, for final processing and analysis.

The filters containing the soot fractions were extracted using acetonitrile. Each sample was shaken with the solvent for 18 hr. The acetonitrile extracts from the solid phase extraction of the melted snow and of the solid residue on the filters were analyzed by high-performance liquid chromatography (HPLC). Analyte concentrations were determined following the general procedures of SW 846 Method 8330 to determine nitroaromatics and nitramines by HPLC (USEPA 1994). The HPLC method has an analytical error that is very small, about 2% relative standard deviation (RSD) for replicate injections.

Before HPLC analysis, 1 mL of each acetonitrile extract was mixed with 3 mL of reagent-grade water. Determinations were made on a modular system from Thermo Electron Corporation (Waltham, MA) composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength ultraviolet/visible absorbance detector set

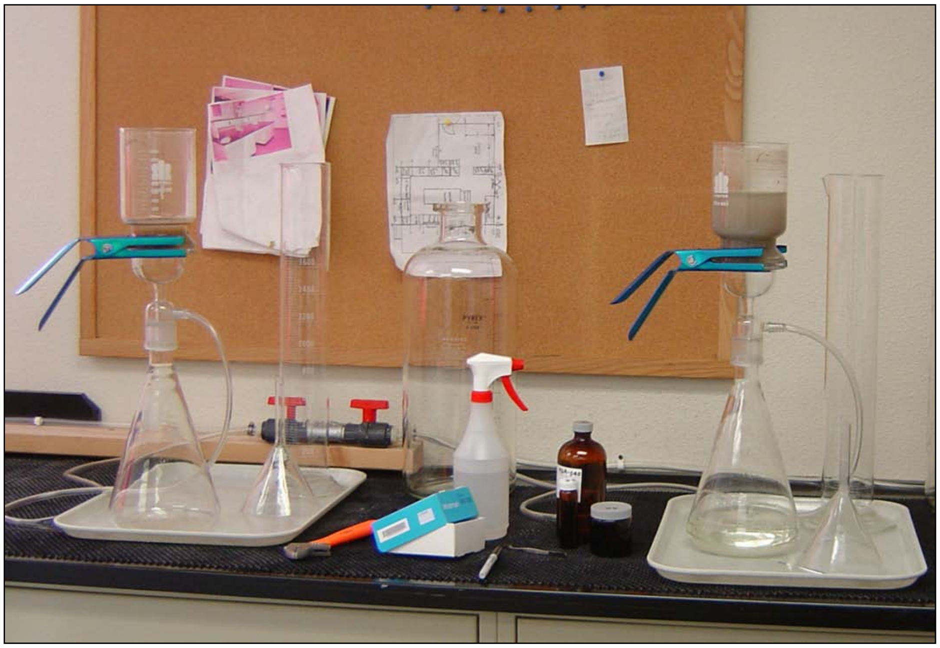

Figure 9-4. Sample filtration setup.

at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15-cm x 3.9-mm (4-µm) NovaPak C8 column (Waters Chromatography Division, Milford, MA) at 28 °C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference materials were 8095 Calibration Mix A (1 mg/mL) and a single-component solution of NG (1 mg/mL). A spike solution at 1,000 µg/L was prepared from 8095A Calibration Mix and the single-component solution of NG (10,000 µg/L). Spiked water samples at 2 µg/L were prepared by mixing 0.10 mL of the spike solution to 500 mL of water in a volumetric flask. Following SPE, the extract target concentration was 200 µg/L for each analyte.

To calculate the mass of unreacted energetics deposited on the snow, we multiplied the average concentration of each plume (mass/unit area basis) by the measured area of the plume (Jenkins et al. 2002; Hewitt et al. 2003). We used a detection limit of 0.02 mg/L for HMX, RDX, and TNT and 0.05 mg/L for NG. Values below these limits are labeled as ND in the data.

9.7 Quality assurance procedures

Quality assurance (QA) procedures were conducted both in the field and in the lab. Field QA, noted previously, included replicate sampling within the residue plumes, sampling outside the demarcated plumes, using multiple sampling designs, and sampling below previously sampled points.

We also conducted QA procedures in the processing lab. Blank samples consisting of filtered water (Barnstead E-Pure filtration system; 80 MΩ minimum) were periodically run through a filter assembly and pre-concentrated using SPE for later analysis at the lab. This procedure is designed to determine if cross-contamination from the sample filtering apparatus or glassware is occurring. SPE laboratory control samples (LCSs) were run to determine cartridge filter performance. These processes are described in greater detail in Walsh et al. (2005b).

9.8 Results

9.8.1 Baseline samples

The background sample collected from the firing points before the test was blank, indicating clean test areas. Results are given in Appendix 9-D.

9.8.2 BIP detonation plumes

A total of 88 MI samples composed of 7,811 increments were taken to characterize the BIP detonation plumes. The demarcated plume sizes ranged from approximately 400 m^2 for a 60-mm detonation to 2,000 m^2 for a 120-mm detonation, averaging 1,500 m^2 for the 120s and 500 m^2 for the 60s (Table 9-2). OTP areas varied from approximately 200 m^2 to 580 m^2, averaging about 30% of the plume area for the 120s and 46% of the plume area for the 60s. Areas were calculated with geographic information system software using the GPS field data points. In most cases, the 10-cm scoop was used to sample the plumes, OTP areas, and subsurface. On average, 0.08% of the plume areas and 0.2% of the OTP areas were sampled for the 120s, and 0.19% of the plume areas and 0.4% of the OTP areas were sampled for the 60s (Table 9-3). A map of the detonation plumes derived from the GPS data is given in Figure 9-5.

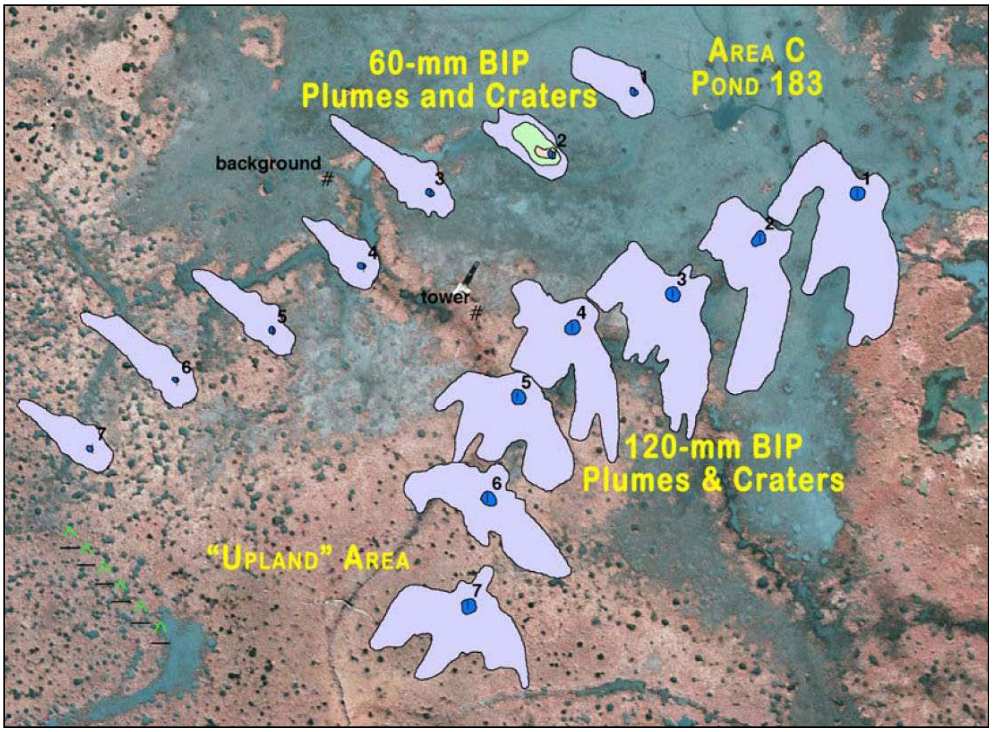

Figure 9-5. Plume shape and locations.

Table 9-2. Data for sampled areas—decision unit areas.

Detonation No.	Round Type	Plume		Plume+OTP		OTP Area (m²)
		Length (m)	Area (m²)	Length (m)	Area (m²)	
1	120 mm	280	2,000	290	2,600	580
2	120 mm	210	1,500	220	1,900	420
3	120 mm	270	1,800	240	2,300	520
4	120 mm	250	1,500	240	2,000	490
5	120 mm	220	1,400	210	1,800	440
6	120 mm	200	1,200	210	1,700	410
7	120 mm	230	1,400	240	1,900	470
	Averages	**240**	**1,500**	**240**	**2,000**	**480**
1	60 mm	94	480	110	680	200
2	60 mm	96	470	110	680	200
3	60 mm	140	620	150	910	290
4	60 mm	94	400	100	590	200
5	60 mm	120	500	130	740	240
6	60 mm	130	600	140	870	270
7	60 mm	100	430	110	650	220
	Averages	**110**	**500**	**120**	**730**	**230**
7-medium	60 mm	54	150	—	—	—
7-dark	60 mm	23	27	—	—	—

Table 9-3. Data for sampled areas—sampling statistics.

Munition	Decision Unit	Sampling Tool Size (cm)	Average No. of Increments	Average Area Sampled (m^2)	Average Area Sampled (%)
120 mm	Plume 1	10 x 10 x 2.5	137	1.37	0.07%
	OTP 1	10 x 10 x 2.5	100	1.00	0.17%
	Plume 2	10 x 10 x 2.5	142	1.42	0.07%
	OTP 2	10 x 10 x 2.5	100	1.00	0.24%
	Plume 3	10 x 10 x 2.5	97	0.97	0.05%
	OTP 3	10 x 10 x 2.5	100	1.00	0.19%
	Plume 4	10 x 10 x 2.5	148	1.48	0.10%
	OTP 4	10 x 10 x 2.5	100	1.00	0.20%
	Plume 5	10 x 10 x 2.5	102	1.02	0.07%
	OTP 5	10 x 10 x 2.5	101	1.01	0.23%
	Plume 6	10 x 10 x 2.5	105	1.05	0.08%
	OTP 6	10 x 10 x 2.5	100	1.00	0.24%
	Plume 7	10 x 10 x 2.5	123	1.23	0.09%
		20 x 20 x 2.5	30	1.20	0.08%
	Subsurface 7	10 x 10 x 2.5	30	0.30	0.02%
	OTP 7	10 x 10 x 2.5	63	0.63	0.14%
Averages	**Plume**		**122**	**1.22**	**0.08%**
	OTP		**95**	**0.95**	**0.20%**
60 mm	Plume 1	10 x 10 x 2.5	80	0.80	0.17%
	OTP 1	10 x 10 x 2.5	100	1.00	0.50%
	Plume 2	10 x 10 x 2.5	84	0.84	0.18%
	-Light	10 x 10 x 2.5	53	0.53	0.20%
	-Medium	10 x 10 x 2.5	87	0.87	0.49%
	-Dark	10 x 10 x 2.5	41	0.41	1.52%
	OTP 2	10 x 10 x 2.5	84	0.84	0.41%
	Plume 3	10 x 10 x 2.5	100	1.00	0.16%
	OTP 3	10 x 10 x 2.5	95	0.95	0.33%
	Plume 4	10 x 10 x 2.5	96	0.96	0.24%
	OTP 4	10 x 10 x 2.5	87	0.87	0.45%
	Plume 5	10 x 10 x 2.5	107	1.07	0.21%
	OTP 5	10 x 10 x 2.5	89	0.89	0.37%
	Plume 6	10 x 10 x 2.5	92	0.92	0.15%
	OTP 6	10 x 10 x 2.5	83	0.83	0.31%
	Plume 7	10 x 10 x 2.5	100	1.00	0.23%
		20 x 20 x 2.5	26	1.04	0.24%
	Subsurface 7	10 x 10 x 2.5	26	0.26	0.06%
	OTP 7	10 x 10 x 2.5	89	0.89	0.41%
Averages	**Plume**		**94**	**0.94**	**0.19%**
	OTP		**90**	**0.90**	**0.40%**

Analytical data averaged for the replicates are given in Table 9-4. Two significant digits are used for the data in this table and throughout this report. The samples were analyzed for a series of energetic compounds: RDX, HMX, TNT, and NG. The NG is contained in the ignition cartridge in the tail of the mortar cartridge. In combination with the nitrocellulose matrix in which it is embedded, it is less sensitive than the donor and filler charges (low explosive as opposed to high explosive). Its normal means of reaction is deflagration (rapid burning) rather than detonation. This, in combination with its distance from the donor charge, results in less material consumed during the BIP operation. The HMX is a byproduct in the manufacturing process for RDX and is found in quantities of 8% to 12% in the Type B RDX in the Comp B filler (U.S. Army 2004). It is also found in very small quantities in the fuze of the 120-mm cartridge. More complete data sets can be found in Appendixes 9-B and 9-C.

Table 9-4. Analytical data for energetics in plumes.

Munition	Detonation No.	Total Mass (mg)			For RDX		For HMX	
		HMX	RDX	NG	Range	RSD	Range	RSD
120 mm	1	<0.02	4.6	3,900	1.8	20%	—	0%
	2	4.4	13	4,400	2.5	10%	2.4	28%
	3	8.0	19	3,300	8.9	23%	4.0	25%
	4	4.3	46	3,900	31	34%	0.5	6%
	5[a]	<0.02	6.3	4,500	2.1	17%	—	0%
	6	4.4	37	7,600	9.9	14%	2	18%
	7 (100)	<0.02	17	3,500	3.7	13%	—	0%
	7 (20)[b]	<0.02	35	8,100	—	—	—	0%
	Averages	**3.0**	**22**	**4,800**	**11**	**22%**	**1.2**	**11%**
60 mm	1	4.2	32	200	8.8	16%	1.3	18%
	2	9.6	49	240	6.7	7.2%	3.7	19%
	3	50	400	240	99	13%	21	21%
	4	27	270	170	3.5	0.73%	7.8	17%
	5	36	220	290	150	35%	17	24%
	6	4.4	30	250	9.8	16%	2.2	28%
	7 (100)	20	220	230	27	6.4%	2.7	7.0%
	7 (20)	21	260	200	190	38%	5.5	13%
	Averages	**22**	**180**	**230**	**56**	**16%**	**8.2**	**19%**

Notes:

Range is the difference between the highest and lowest values for the analyte.

[a] RDX value includes the OTP mass (0.35 mg).

[b] Two of three values for RDX are below quantitation range; range and RSD not calculated.

Using the results presented in Table 9-4, we can derive the average efficiency of the BIP operations. For the 120s, 7.1 x 10^{-4} % of the cartridge and donor charge HE loads remained on average after detonation. If only HMX and RDX are considered, 1.1 x 10^{-3}% remained on average after detonation. The residues rate ranged from 1.3 x 10^{-4} % for BIP No. 1 to 1.4 x 10^{-3}% for BIP No. 4. NG residues averaged 16%. For the 60s, 2.3 x 10^{-2}% of the cartridge and donor charge HE loads remained on average after detonation. For the RDX and HMX alone, 2.7 x 10^{-2}% remained on average. The residues rates ranged from 3.9 x 10^{-3}% for BIP No. 6 to 5.1 x 10^{-2}% for BIP No. 3. NG residues averaged 17%, quite close to the value obtained for the 120s. The averaged HE residues deposition mass was 25 mg/round for the 120s and 200 mg/round for the 60s. Very little TNT was detected in the 60-mm residues and none was detected in the 120-mm residues. Table 9-5 summarizes these data and Table 9-8 (in Discussion section) compares them to other detonation tests.

The gradient test yielded the expected results. In the small, darkest zone, 42% of the residues mass was recovered from just 6% of the area. In the intermediate zone, 44% of the mass was recovered from 32% of the area. In the lightest zone, only 15% of the mass was recovered from an area encompassing 63% of the plume. Looking at the ratios of recovered energetics to percent of area sampled within the plume, the dark area contained seven times more residues per unit area than the plume as a whole. Table 9-6 summarizes the data from this test.

The field QA procedure results indicate that the majority of detectable energetic residues were within the sampled depth of the demarcated plume area and meet data quality objectives. Table 9-7 contains the results for both series of tests. The amount of HE residues found in the sampled area outside the demarcated plume (OTP) compared to inside the plume is expressed as a percentage of the plume mass under OTP:Plume. For the

Table 9-5. Summary for blow-in-place detonations.

Munition	No. of Rounds	Plume Area (m^2)	RDX (mg)	HMX (mg)	TNT (mg)	Total (mg)	Total (%)[a]
60-mm mortar (M374)	7	500	180	22	ND	200	2.3 x 10^{-2}
120-mm mortar (M1)	7	1,600	22	3.0	ND	25	7.7 x 10^{-4}

[a]Explosives load includes the contribution of the C4 donor charge.

ND, not detected (below detection limits of instrumentation).

Table 9-6. Gradient test results for HMX and RDX.

Zone	Total Mass (mg)				Area (m²)	% of Area	% of Mass	Ratio Mass/Area
	HMX		RDX					
Plume[a]	9.6	–	49	–	470	100%	100%	1.0
Light	0.0	0%	8.8	16%	300	63%	15%	0.23
Medium	2.7	44%	24	44%	150	32%	44%	1.4
Dark	3.4	56%	21	40%	27	6%	42%	7.2
Total	6.1	64%	54	110%	470	–	–	–

[a]Averaged results for total plume from Table 9-4, 60-mm Plume 2.

OTP sampling, the target value is <5% of the plume mass. Only one of the 14 OTP samples exceeded 5%, 5.5% for plume 5. The OTP residue mass for plume 5 was thus added to the plume mass in Table 9-4. The target value for the subsurface mass to plume mass (SS:Plume) is <1% of the plume mass. Neither of the subsurface samples exceeded the target value. Values for the RSDs of the triplicate plume samples, found in Table 9-4, were also very good. The target value is < 30% RSD. Only 3 of the 32 sets of data for the HE residues exceeded 30%, and all were less than 40%. Average RSD for the 32 sets of data is 17% (0%–38%).

Finally, the QA results from the lab are also very good. All filtration blanks were clean with the exception of one that had trace amounts of NG on the filter. The source of the NG could not be determined but did not adversely affect other data. The SPE glassware test blanks had no detectable energetics, and the LCS runs returned values from 90%–105% on average (0.18–0.21 mg/L). Data can be found in Appendix 9-D.

Table 9-7. Field quality assurance test results.

	60-mm BIPs				120-mm BIPs			
	RDX		HMX		RDX		HMX	
Plume No.	OTP:Plume	SS:Plume	OTP:Plume	SS:Plume	OTP:Plume	SS:Plume	OTP:Plume	SS:Plume
1	0.0%	–	0.00%	–	0.0%	–	0.00%	–
2	0.0%	–	0.00%	–	0.0%	–	0.00%	–
3	0.2%	–	0.00%	–	0.0%	–	0.00%	–
4	0.6%	–	0.00%	–	1.7%	–	0.00%	–
5	0.8%	–	0.00%	–	5.5%	–	0.00%	–
6	0.0%	–	0.00%	–	0.9%	–	0.00%	–
7 (100)	1.6%	0.59%	3.20%	0.09%	0.0%	0.0%	0.00%	0.00%
7 (20)	1.3%	0.50%	3.06%	0.11%	0.0%	0.0%	0.00%	0.00%
Averages	**0.42%**	**0.54%**	**0.45%**	**0.10%**	**1.2%**	**0.00%**	**0.00%**	**0.00%**

9.9 Discussion

Working with energetics residues is a difficult proposition. This is especially true with an unconfined charge, such as the block of C4 used as a donor charge (Brochu et al. 2004). Residues are particulate in form and quite heterogeneously distributed. The quantity of residues also tends to be quite low, especially for the larger munitions that are more efficient when detonated. These low quantities result in many analyte concentrations at or near the analytical detection limits. Another confounding factor we came up against was the high quantity of NG in the samples. Because the rounds had not been fired, the ignition cartridges in the tails of the mortars were not expended, and the full load of propellant was present in these cartridges. Because the propellant is designed to burn rather than detonate, the BIP process is inefficient in the disposal of the material. Relatively large quantities of NG in the field samples made analysis of the samples difficult.

Configuration of the donor charge on the test munitions was according to standard EOD practice. The use of a complete block of C4, containing 516 g of RDX, to initiate a 60-mm mortar cartridge, containing less than 370 g of high explosives, may seem excessive, but it is standard practice. Part of the reason why the BIP of the 60-mm cartridge was so much “dirtier” than the BIP of the 120-mm cartridge was the presence of such a large amount of unconfined explosive during the operation. Detonation tests of blocks of C4 alone indicate relatively high residues rates, 2.6 x 10^{-3}% (n = 11), compared to residue rates from fully functioning rounds (<2 x 10^{-4}%) and BIP operations with the larger projectiles (< 8 x 10^{-4}%) (Walsh 2007). With the 120s, the resulting detonation of the cartridge assists in the consumption of the donor charge, making the overall process much more efficient. Work needs to be done to refine the protocol for configuring a BIP operation.

Overall, the data fit in well with other BIP and live-fire data. Table 9-8 summarizes these data for tests conducted on snow by CRREL since early 2002. The trend has been that BIPs are not as clean as live-fire detonations, larger rounds consume the HE more efficiently than the smaller rounds, and mortar cartridges are less efficient than howitzer rounds. With the exception of the live-fire 60-mm HE cartridges, this trend is demonstrated by the results shown in the table.

Table 9-8. HE munitions BIP and live-fire detonation energetics residues data.

Weapon System	BIP[a] (TNT, HMX, RDX)	Live-Fire Detonation (TNT, HMX, RDX)
Mortars		
60 mm (Comp B)	200 mg / 2.3 x 10^{-2}%	0.076 mg / 2.0 x 10^{-5}%
81 mm (Comp B)	150 mg / 1.0 x 10^{-2}%	9.4 mg / 1.0 x 10^{-3}%
120 mm (Comp B)	25 mg / 7.7 x 10^{-4}%	21 mg / 4.8 x 10^{-4}%
Howitzers		
105 mm (Comp B)	50 mg / 1.9 x 10^{-3}%	0.27 mg / 1.3 x 10^{-5}%
155 mm (Comp B)	17 mg / 2.2 x 10^{-4}%	0.31 mg / 4.4 x 10^{-6}%
155 mm (TNT)	15 mg / 2.1 x 10^{-4}%	0.00 mg / 0.0 x 10^{-6}%

[a] Includes donor charge mass.

9.10 Conclusions

Two tests were conducted on the ice-covered Eagle River Flats impact area of Fort, Richardson, AK, to determine the quantity and percent levels of energetics residues remaining after standard blow-in-place detonation of fuzed 60-mm and 120-mm mortar cartridges using a single block of C4 as a donor charge. Seven rounds of each high-explosive munition were detonated and the resultant plumes sampled in triplicate. Quality assurance procedures were conducted in the field to ensure the detonation plumes were correctly demarcated and the sampling was valid. Multi-increment sampling on the snow surface was used to characterize the decision units. The averaged result for the 60-mm test was 200 mg of RDX and HMX residues per round, giving a residues rate of 0.022% of the original analyte load (fuze plus filler plus donor charge). Residues found in a 2-m band outside the demarcated plume averaged 0.43% of the plume load, and subsurface sampling below previously sampled points yielded less than 0.32% of the surface sample mass. The averaged result for the 120-mm test was 27 mg of RDX and HMX residues per round, giving a residues rate of 0.00077% of the original analyte load (fuze plus filler plus donor charge). Residues found in a 2-m band outside the demarcated plume averaged 0.58% of the plume load, and subsurface sampling below previously sampled points contained undetectable amounts of high explosives. The results of these tests fit well with deposition data for other munitions.

9.11 Nomenclature

AcN	acetonitrile
HMX	octahydro-1,35,7-tetranitro-1,3,5,7-tetrazocine

NG	nitroglycerine
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	2,4,6-trinitroluene

9.12 References

Brochu, S., S. Thiboutot, J. Lewis, G. Ampleman, and P. Brousseau. 2004. *Estimation of the quantity of explosive residues resulting from the detonation of unconfined explosives charges*, Chapter 7. *In* Distribution and fate of energetics on DoD test and training ranges: Interim Report 4. ERDC TR-04-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dauphin, L., and C. Doyle. 2000. *Study of ammunition dud and low order detonation rates*. U.S. Army Defense Ammunition Center-Technical Center for Explosives Safety. Technical Report. Aberdeen Proving Ground, MD: U.S. Army Environmental Center.

Foster, J. 1998. Report of the Defense Science Board Task Force on Unexploded Ordnance (UXO) Clearance, Active Range UXO Clearance, and Explosive Ordnance Disposal Programs. Washington, DC: Department of Defense.

Hewitt, A. D., T. F. Jenkins, T. A. Ranney, J. A. Stark, M. E. Walsh, S. Taylor, M. R. Walsh, D. J. Lambert, N. M. Perron, N. H. Collins, and R. Kern. 2003. *Estimates for explosives residues from the detonation of army munitions*. ERDC/CRREL Technical Report 03-16. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Jenkins, T. J., T. A. Ranney, P. H. Miyares, N. H. Collins, and A. D. Hewitt. 2000. *Use of surface snow sampling to estimate the quantity of explosive residues resulting from land mine detonations*. ERDC/CRREL Technical Report TR-00-12. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Jenkins, T. F., M. E. Walsh, P. H. Miyares, A. D. Hewitt, N. H. Collins, and T. A. Ranney. 2002. Use of snow-covered ranges to estimate explosives residues from high-order detonations of army munitions. *Thermochimica Acta*, 384:173-185.

Taylor S., J. H. Lever, B. Bostick, M. R. Walsh, M. E. Walsh, and B. Packer. 2004. *Underground UXO: are they a significant source of explosives in soil compared to low- and high-order detonations?* ERDC/CRREL Technical Report TR-04-23. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

U.S. Army. 1994. *Military explosives*. Department of the Army Technical Manual 9-1300-214. Washington, DC: Headquarters, Department of the Army.

USEPA. 1994. *Nitroaromatics and nitramines by high performance liquid chromatography (HPLC)*. Method 8330A. Washington, DC: U.S. Environmental Protection Agency.

Walsh, M. E., and T. A. Ranney. 1998. *Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and GC-ECD*. Special Report 98-2. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh M. R, S. Taylor, M. E. Walsh, S. R. Bigl, K. Bjella, T. A. Douglas, A. B. Gelvin, D. J. Lambert, N. M. Perron, and S. P. Saari. 2005a. *Residues from live fire detonations of 155-mm howitzer rounds*. ERDC/CRREL Technical Report TR-05-14. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh M. R, M. E. Walsh, C. M. Collins, S. P. Saari, J. E. Zufelt, A. B. Gelvin, and J. W. Hug. 2005b. *Energetic residues from live-fire detonations of 120-mm mortar rounds*. ERDC/CRREL Technical Report TR-05-15. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh M. R., M. E. Walsh, C. A. Ramsey, and T. F. Jenkins. 2005c. *An examination of protocols for the collection of munitions-derived explosives residues on snow-covered ice*. ERDC/CRREL Technical Report TR-05-08. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M. R., M. E. Walsh, G. Ampleman, S. Thiboutot, and D. D. Walker. 2006a. *Comparison of explosive residues from blow-in-place detonation of 155-mm high-explosive projectiles*. ERDC/CRREL Technical Report TR-06-13. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M. R., M. E. Walsh, C. A. Ramsey, R. J. Rachow, J. E. Zufelt, C. M. Collins, A. B. Gelvin, N. M. Perron, and S. P. Saari. 2006b. *Energetic residue deposition from 60-mm and 81-mm mortars*. ERDC/CRREL Technical Report TR-06-10. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M. R. 2007. *Explosives residues resulting from the detonation of common military munitions: 2002—2007*. ERDC/CRREL Technical Report TR-07-02. Hanover, NH: U.S. ArmyEngineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Walsh, M. R., M. E. Walsh, and C. A. Ramsey. 2007. *Measuring energetics residues on snow*. ERDC/CRREL Technical Report TR-07-019. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

Appendix 9-A: Munitions Data

Table 9-A1 contains information relevant to the munitions used during the tests covered in this report. Table 9-A2 contains data on the explosive load of the test components. Propellant charges are given in Table 9-1. The amount of propellant used per round can and did vary throughout the tests.

Table 9-A1. Munitions data.

NSN	DODIC	Nomenclature	Lot No.	Drawn for Tests
1310011493185	B643	Cartridge, 60 MM HE, M888, W/Fuze, PD, M935	MA-99A057-001	8
1315013431941	C623	Cartridge, 120 MM HE, M933, W/Fuze, PD, M745	MM-97K025-002	8
1375007247040	M023	Charge, Demolition, M112	—	20

Note: Drawn from Fort Richardson Ammo Supply Point, 11 February 2008.

Table 9-A2. Energetics loads before detonation.

Munition	Energetics Quantities (g)			
	TNT	RDX	HMX	NG
Cartridge, 60 mm, M888	140	215	0	0
Fuze, Point detonating, M935	0	15	0	0
Cartridge, Ignition, M702	0	0	0	1.35
Cartridge, 120 mm, M933	1,166	1,793	0	0
Fuze, Point detonating, M745	0	43	0	0
Cartridge, Ignition, M981	0	0	0	30
Charge, Demolition, M112	0	516	0	0

Note: HMX may compose up to 9% of the mass of RDX.

Appendix 9-B: 120-mm Data

Table 9-B1 contains sampling data, analytical data, and final results for the 120-mm BIP test. Detection limits are 0.02 mg/L for RDX, HMX, and TNT and 0.05 mg/L for NG.

Table 9-B1. 120-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)			Filters Analyte Mass (µg)			No. of Increment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)		
			HMX	RDX	NG	HMX	RDX	NG				HMX	RDX	NG
FRA-001	1-1	OTP 0–2 m	ND	ND	7.5	ND	ND	ND	100	1.00	575	0.00	0.00	4.3
FRA-002	1-2	OTP 0–2 m	ND	ND	6.0	ND	ND	ND	100	1.00	575	0.00	0.00	3.5
FRA-003	1-1	Plume-1	ND	4.3	3,800	BQL	BQL	606	162	1.62	2,000	0.0	5.4	5,439
FRA-004	1-2	Plume-1	ND	3.1	2,319	BQL	BQL	218	125	1.25	2,000	0.0	4.9	4,058
FRA-005	1-3	Plume-1	ND	2.2	890	BQL	BQL	531	125	1.25	2,000	0.0	3.6	2,274
Plume Averages			—	**3.2**	**2,336**	—	—	**452**	—	—	—	**0.0**	**4.6**	**3,923**
FRA-006	2-1	OTP 0–2 m	ND	ND	11.94	ND	ND	5.8	100	1.00	423	0.00	0.00	7.5
FRA-007	2-2	OTP 0–2 m	ND	ND	15.07	ND	BQL	5.8	100	1.00	423	0.00	0.00	8.8
FRA-008	2-1	Plume-2	ND	8.0	2,475	5.8	4.9	1,936	150	1.50	1,500	5.8	12.9	4,411
FRA-009	2-2	Plume-2	ND	8.0	3,659	3.8	3.6	1,710	143	1.43	1,500	4.0	12.1	5,632
FRA-010	2-3	Plume-2	ND	9.0	2,481	*3*	4.0	324	133	1.33	1,500	3.4	14.6	3,164
Plume Averages			—	**8.3**	**2,872**	**4.2**	**4.2**	**1,323**	—	—	—	**4.4**	**13.2**	**4,403**
FRA-011	3-1	OTP 0–2 m	ND	—	10	ND	ND	6.7	100	1.00	519	0.00	0.00	8.9
FRA-012	3-2	OTP 0–2 m	ND	—	7.9	BQL	ND	4.9	100	1.00	519	0.00	0.00	6.7
FRA-013	3-1	Plume-3	ND	6.0	1,638	4.6	*2*	ND	97	0.97	1,770	8.4	14.5	2,989
FRA-014	3-2	Plume-3	ND	9.0	1,358	5.4	3.8	519	97	0.97	1,770	9.9	23.5	3,426
FRA-015	3-3	Plume-3	ND	7.7	1,566	3.2	3.2	321	97	0.97	1,770	5.9	19.9	3,444
Plume Averages			—	**7.6**	**1,521**	**4.4**	**3.0**	**420**	—	—	—	**8.0**	**19.3**	**3,286**

Table 9-B1 (cont'd). 120-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)			Filters Analyte Mass (µg)			No. of Increment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)		
			HMX	RDX	NG	HMX	RDX	NG				HMX	RDX	NG
FRA-016	4-1	OTP 0–2 m	ND	2.3	11	BQL	BQL	3.2	100	1.00	490	0.00	1.1	6.9
FRA-017	4-2	OTP 0–2 m	ND	0.90	12	ND	ND	5.6	100	1.00	490	0.00	0.44	8.8
FRA-021	4-1	Plume-4	1.5	35	2,836	*3*	8.6	78	148	1.48	1,510	4.6	44.4	2,972
FRA-022	4-2	Plume-4	1.2	36	2,988	3.0	25	2,415	148	1.48	1,510	4	61.5	5,513
FRA-023	4-3	Plume-4	0.97	26	2,944	*3*	4.5	96	148	1.48	1,510	4.1	31.0	3102
Plume Averages			**1.2**	**32**	**2,923**	**3.0**	**13**	**863**	—	—	—	**4.3**	**45.6**	**3,862**
FRA-025	5-1	OTP 0–2 m	ND	0.81	7.6	ND	BQL	4.5	103	1.03	435	0.00	0.34	5.12
FRA-026	5-2	OTP 0–2 m	ND	0.82	8.2	BQL	BQL	5.4	100	1.00	435	0.00	0.36	5.87
FRA-024	5-1	Plume-5	ND	3.9	1,809	ND	BQL	1,014	100	1.00	1,400	0.0	5.5	3,952
FRA-027	5-2	Plume-5	ND	5.5	2,740	ND	BQL	660	103	1.03	1,400	0.0	7.5	4,621
FRA-028	5-3	Plume-5	ND	4.4	2,321	ND	BQL	1,266	103	1.03	1,400	0.0	5.9	4,875
Plume Averages			—	**4.6**	**2,290**	—	—	**980**	—	—	—	**0.0**	**6.3**	**4,483**
FRA-029	6-1	OTP 0–2 m	ND	0.88	12	BQL	BQL	5.1	100	1.00	411	0.00	0.36	6.9
FRA-030	6-2	OTP 0–2 m	ND	0.80	17	BQL	ND	8.2	100	1.00	411	0.00	0.33	10
FRA-031	6-1	Plume	ND	18	2,851	3	10	8,610	105	1.05	1,240	3.5	33.3	13,535
FRA-032	6-2	Plume	ND	21	2,394	4.3	8.4	1,062	105	1.05	1,240	5.1	34.7	4,081
FRA-033	6-3	Plume	0.79	23	3,062	*3*	14	1,347	105	1.05	1,240	4.5	43.2	5,207
Plume Averages			—	**20.7**	**2,769**	**3.4**	**11**	**3,673**	—	—	—	**4.4**	**37.1**	**7,608**
FRA-034	7-1	OTP 0–2 m	ND	BQL	13	ND	ND	2.4	63	0.63	465	0.00	0.00	11
FRA-035	7-2	OTP 0–2 m	ND	BQL	184	ND	ND	2.4	63	0.63	465	0.00	0.00	138
FRA-042	7-1	Plume	ND	6.4	2,140	BQL	8.8	355	123	1.23	1,440	0.0	17.7	2,921
FRA-043	7-2	Plume	ND	7.2	2,822	BQL	8.0	1,290	123	1.23	1,440	0.0	17.8	4,815
FRA-044	7-3	Plume	ND	6.0	2,156	BQL	*6*	323	123	1.23	1,440	0.0	14.0	2,902
Plume Averages			—	**6.5**	**2,373**	—	**7.6**	**656**	—	—	—	**0.0**	**16.5**	**3,546**
FRA-045	7-1	Surf Plume	ND	15	4,508	BQL	29	3,680	37	1.48	1,440	0.0	60.8	11,338
FRA-046	7-2	Surf Plume	ND	10	4,193	ND	*9*	3,438	26	1.04	1,440	0.0	26.6	10,566

Table 9-B1 (cont'd). 120-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)			Filters Analyte Mass (µg)			No. of Increment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)		
			HMX	RDX	NG	HMX	RDX	NG				HMX	RDX	NG
FRA-048	7-3	Surf Plume	ND	10	1,726	ND	*4*	96	26	1.04	1,440	0.0	19.0	2,524
Plume Averages			—	**11.6**	**3,476**	ND	**14.0**	**2,405**	—	—	—	**0.0**	**35.5**	**8,143**
FRA-036	7-1	SS Plume	ND	ND	14	ND	ND	30	37	0.37	1,440	0.0	0.0	169
FRA-037	7-2	SS Plume	ND	ND	7.7	ND	ND	1.1	26	0.26	1,440	0.0	0.0	49
FRA-041	7-3	SS Plume	ND	ND	11	ND	ND	4.5	26	0.26	1,440	0.0	0.0	85

Notes:

41 samples; 4,059 increments.

Italicized numbers are values at or near quantitation value limits (reported as value limit).

Underlined bold numbers represent high NG value that may be affecting HMX and RDX values.

ND, not detected (below detection limits of instrumentation); BQL, below quantitative limits (reported as zero).

Rep, repetition.

The minimum mass reported (mg) is computed by multiplying 5x the detection limit in the AcN extract (mg/L) times the volume of AcN used to extract the sample (quantitation mass limit).

Appendix 9-C: 60-mm Data

Table 9-C1 contains sampling data, analytical data, and final results for the 60-mm BIP test. Detection limits are 0.02 mg/L for RDX, HMX, and TNT and 0.05 mg/L for NG.

Table 9-C1. 60-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)				Filters Analyte Mass (µg)			No. of Increment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)			
			HMX	RDX	TNT	NG	HMX	RDX	NG				HMX	RDX	TNT	NG
FRA-049	1-1	OTP 0–2 m	ND	BQL	ND	ND	ND	BQL	ND	100	1.00	199	0.0	0.0	0.0	0.0
FRA-050	1-2	OTP 0–2 m	ND	BQL	ND	ND	ND	ND	BQL	100	1.00	199	0.0	0.0	0.0	0.0
FRA-051	1-1	Plume-1	BQL	26	ND	132	7.8	37	166	80	0.80	480	4.7	38	0.0	180
FRA-052	1-2	Plume-1	BQL	22	ND	140	7.7	27	234	80	0.80	480	4.6	29	0.0	220
FRA-053	1-3	Plume-1	BQL	20	ND	112	5.6	29	214	80	0.80	480	3.3	29	0.0	190
Plume Averages			**—**	**23**	**—**	**128**	**7.0**	**31**	**205**	**—**	**—**	**—**	**4.2**	**32**	**0**	**200**
FRA-054	2-1	OTP 0–2 m	ND	BQL	ND	BQL	ND	ND	BQL	84	0.84	205	0.0	0.0	0.0	0.0
FRA-055	2-2	OTP 0–2 m	ND	BQL	ND	BQL	ND	BQL	ND	84	0.84	205	0.0	0.0	0.0	0.0
FRA-056	Light-1	Plume-2-Light	ND	8.2	ND	19.3	ND	6.7	29	53	0.53	290	0.0	8.1	0.0	26
FRA-057	Light-2	Plume-2-Light	ND	10	ND	10.0	ND	6.7	9.8	53	0.53	290	0.0	9.4	0.0	11
FRA-061	Med-1	Pl.-2-Med	ND	60	ND	382	14	92	735	87	0.87	150	2.3	26	0.0	190
FRA-062	Med-2	Pl.-2-Med	ND	56	ND	379	18	65	813	87	0.87	150	3.1	21	0.0	210
FRA-063	Dark-1	Plume-2-Dark	4.8	121	ND	563	50	224	1008	41	0.41	27	3.6	23	0.0	100
FRA-064	Dark-2	Plume-2-Dark	4.5	127	ND	549	44	179	976	41	0.41	27	3.2	20	0.0	100
FRA-067	2-1	Plume-2	3.2	50	ND	143	11	31	240	85	0.85	470	7.6	45	0.0	210
FRA-068	2-2	Plume-2	4.3	63	ND	207	13	31	270	85	0.85	470	9.8	52	0.0	260
FRA-069	2-3	Plume-2	3.9	62	ND	205	16	27	223	83	0.83	470	11	50	0.0	240
Plume Averages			**3.8**	**58**		**185**	**13**	**29**	**244**	**—**	**—**	**—**	**9.6**	**49**	**—**	**240**
FRA-070	3-1	OTP 0–2 m	BQL	1.4	ND	ND	ND	ND	ND	95	0.95	291	0.0	0.43	0.0	0.0

Table 9-C1 (cont'd). 60-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)				Filters Analyte Mass (µg)			No. of Incre-ment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)			
			HMX	RDX	TNT	NG	HMX	RDX	NG				HMX	RDX	TNT	NG
FRA-071	3-2	OTP 0–2 m	BQL	2.7	ND	ND	ND	ND	ND	95	0.95	291	0.0	0.82	0.0	0.0
FRA-072	3-1	Plume-3	8.1	245	(8.2)	138	73	424	272	100	1.00	620	50	410	5.1	260
FRA-073	3-2	Plume-3	9.2	254	(3.3)	157	54	298	191	100	1.00	620	39	340	2.0	220
FRA-074	3-3	Plume-3	5.4	196	(2.8)	134	92	516	272	100	1.00	620	60	440	1.7	250
Plume Averages			**7.6**	**231**	**4.8**	**143**	**73**	**413**	**245**	**—**	**—**	**—**	**50**	**400**	**3.0**	**240**
FRA-075	4-1	OTP 0–2 m	BQL	3.9	BQL	BQL	BQL	5.0	BQL	87	0.87	196	0.0	2.0	0.0	0.0
FRA-076	4-2	OTP 0–2 m	BQL	3.2	BQL	BQL	BQL	2		87	0.87	196	0.0	1.2	0.0	0.0
FRA-077	4-1	Plume-4	8.4	415	(1.9)	297	50	228	152	96	0.96	400	25	270	0.8	190
FRA-081	4-2	Plume-4	9.9	434	(1.3)	237	49	216	126	96	0.96	400	24	270	0.6	150
FRA-082	4-3	Plume-4	5.0	286	(1.3)	187	72	365	228	96	0.96	400	32	270	0.5	170
Plume Averages			**7.8**	**378**	**1.5**	**240**	**57**	**270**	**169**	**—**	**—**	**—**	**27**	**270**	**0.6**	**170**
FRA-083	5-1	OTP 0–2 m	BQL	2.8	BQL	BQL	ND	3.3	ND	89	0.89	243	0.0	1.65	0.0	0.0
FRA-084	5-2	OTP 0–2 m	BQL	3.3	BQL	ND	BQL	3.0	ND	89	0.89	243	0.0	1.70	0.0	0.0
FRA-085	5-1	Plume-5	22	413	(11)	358	76	241	567	107	1.07	500	46	300	5.1	430
FRA-086	5-2	Plume-5	13	233	(9.2)	352	48	89	83	107	1.07	500	28	150	4.3	200
FRA-087	5-3	Plume-5	16	311	(9.1)	366	59	137	149	107	1.07	500	35	210	4.2	240
Plume Averages			**17**	**319**	**10**	**359**	**61**	**156**	**266**	**—**	**—**	**—**	**36**	**220**	**4.5**	**290**
FRA-088	6-1	OTP 0–2 m	ND	BQL	ND	ND	ND	ND	BQL	83	0.83	271	0.0	0.0	0.0	0.0
FRA-089	6-2	OTP 0–2 m	ND	BQL	ND	ND	ND	BQL	BQL	83	0.83	271	0.0	0.0	0.0	0.0
FRA-090	6-1	Plume-6	BQL	22	ND	160	4.9	19	174	98	0.98	600	3.0	25	0.0	200
FRA-091	6-2	Plume-6	BQL	20	ND	161	8.3	29	290	98	0.98	600	5.1	30	0.0	280
FRA-093	6-3	Plume-6	BQL	22	ND	165	6.9	25	192	80	0.80	600	5.2	35	0.0	270
Plume Averages			**—**	**21**	**—**	**162**	**6.7**	**24**	**219**	**—**	**—**	**—**	**4.4**	**30**	**—**	**250**
FRA-092	7-1	OTP 0–2 m	ND	4.5	(1.6)	ND	2	7.2	BQL	98	0.98	216	0.44	2.6	0.35	0.0
FRA-094	7-2	OTP 0–2 m	ND	4.9	(1.0)	ND	3.0	11	BQL	80	0.80	216	0.81	4.2	0.27	0.0
FRA-101	7-1	Plume-7	4.3	166	(3.2)	191	45	330	360	100	1.00	430	21	210	1.4	240

Table 9-C1 (cont'd). 60-mm mortar BIP test data.

Sample ID	Plume No. and Rep	Type	Snow Melt Analyte Mass (µg)				Filters Analyte Mass (µg)			No. of Incre-ment	Area (m^2) Sampled	DU Area (m^2)	Total Mass (mg)			
			HMX	RDX	TNT	NG	HMX	RDX	NG				HMX	RDX	TNT	NG
FRA-102	7-2	Plume-7	4.6	177	(2.0)	183	38	302	290	100	1.00	430	18	210	0.8	200
FRA-103	7-3	Plume-7	4.1	167	(3.4)	225	41	375	354	100	1.00	430	19	230	1.5	250
		Plume Averages	**4.3**	**170**	**2.8**	**199**	**41**	**336**	**335**	—	—	—	**20**	**220**	**1.2**	**230**
FRA-104	7-1	Surf P-7	9.4	260	(5.1)	267	43	636	354	27	1.08	430	21	360	2.0	250
FRA-105	7-2	Surf P-7	4.7	184	(2.3)	170	51	429	309	26	1.04	430	23	250	1.0	200
FRA-106	7-3	Surf P-7	3.3	138	(1.4)	142	39	250	227	26	1.04	430	18	160	0.6	150
		Plume Averages	**5.8**	**194**	**2.9**	**193**	**45**	**438**	**297**	—	—	—	**21**	**260**	**1.2**	**200**
FRA-095	7-1	SS Plume-7	ND	1.4	ND	ND	ND	ND	ND	27	0.27	430	0.0	2.2	0.0	0.0
FRA-096	7-2	SS Plume-7	BQL	*0.5*	ND	0.4	ND	ND	ND	26	0.26	430	0.0	0.8	0.0	0.6
FRA-097	7-3	SS Plume-7	BQL	*0.5*	ND	ND	ND	ND	ND	26	0.26	430	0.0	0.8	0.0	0.0
		Plume Averages	—	**1**	—	**0.4**	—	—	—	—	—	—	—	**1.3**	—	**0.21**

Notes:
47 samples; 3,752 increments.
Rep, repetition.
ND, not detected (below detection limits of instrumentation); BQL, below quantitation limits (values reported as zero).
Values in parentheses are estimated TNT concentrations.
Italicized numbers are values at or near quantitation value limits (reported as value limit).
Underlined bold numbers represent abnormal NG value that may be affecting HMX and RDX values.
The minimum mass reported (mg) is computed by multiplying 5x the detection limit in the AcN extract (mg/L) times the volume of AcN used to extract the sample (quantitation mass limit).

Appendix 9-D: Laboratory QA Data

Table 9-D1 contains data derived from laboratory quality assurance runs. Detection limits are 0.02 mg/L for RDX, HMX, and TNT and 0.05 mg/L for NG. The background sample had no detectable (ND) quantities of explosives in it. A small amount of NG was recovered from the filter of Water Blank-2. The source of this contamination was not traceable.

Table 9-D1. Quality assurance data.

		Water Concentrations mg/L				Filter Concentrations mg/L				Target Concentrations (mg/L)			
Sample ID	Description	HMX	RDX	TNT	NG	HMX	RDX	TNT	NG	HMX	RDX	TNT	NG
FRA-018	Water Blank-1	<0.02	<0.02	–	<0.050	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.050
FRA-019	SPE Blank-1	<0.02	<0.02	–	<0.050	–	–	–	–	<0.02	<0.02	<0.02	<0.050
FRA-020	**SPE LCS-1**	0.216	0.204	–	0.197	–	–	–	–	0.20	0.20	0.20	0.20
FRA-038	Water Blank-2	<0.02	<0.02	–	<0.050	<0.02	<0.02	<0.02	**0.51**	<0.02	<0.02	<0.02	<0.050
FRA-039	SPE Blank-2	<0.02	<0.02	–	<0.050	–	–	–	–	<0.02	<0.02	<0.02	<0.050
FRA-040	**SPE LCS-2**	0.210	0.201	–	0.176	–	–	–	–	0.20	0.20	0.20	0.20
FRA-058	Water Blank-3	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.050
FRA-059	SPE Blank-3	<0.02	<0.02	<0.02	<0.05	–	–	–	–	<0.02	<0.02	<0.02	<0.050
FRA-060	**SPE LCS-3**	0.202	0.202	0.174	0.177	–	–	–	–	0.20	0.20	0.20	0.20
FRA-078	Water Blank-4	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.050
FRA-079	SPE Blank-4	<0.02	<0.02	<0.02	<0.05	–	–	–	–	<0.02	<0.02	<0.02	<0.050
FRA-080	**SPE LCS-4**	0.206	0.205	0.183	0.187	–	–	–	–	0.20	0.20	0.20	0.20
FRA-098	Water Blank-5	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02	<0.050
FRA-099	SPE Blank-5	<0.02	<0.02	<0.02	<0.05	–	–	–	–	<0.02	<0.02	<0.02	<0.050
FRA-100	**SPE LCS-5**	0.216	0.195	0.182	0.204	–	–	–	–	0.20	0.20	0.20	0.20
FRA-047	Background	ND	ND	ND	ND	ND	ND	ND	ND	0	0	0	0
Averages for LCS runs		**0.21**	**0.20**	**0.18**	**0.19**	**–**	**–**	**–**	**–**	**0.20**	**0.20**	**0.20**	**0.20**

10 Summary

Michael R. Walsh

10.1 Introduction

Important gaps in our previous understanding of environmental impacts on military training ranges have been filled through the research conducted under the Strategic Environmental Research and Development Program (SERDP) ER-1481 continuation that was initiated in 2008. We now have a better understanding of deposition rates for major weapon systems in common use in the United States and Canada. The results of the characterization of a legacy shoulder-fired rocket range at Carpiquet, Canada, are very insightful. They indicate that, after many years, accumulated energetic surface residues will still be an issue, although the presence of energetics in the vadose zone may not be. The column studies conducted at *Institut National de la Recherche Scientifique* (INRS) were successful in determining fate and transport of energetic residues from spent propellants on rocket ranges, and were a good tie-in with the rocket residues deposition rate and the legacy range studies. The propellant burn study proved quite informative, with results indicating the importance of disposing of propellant in a controlled manner. This study is already having a major impact in Canada and should have the same in the United States. We are already in the midst of developing both a static and mobile burn pan to solve the problem of residues resulting from expedient field disposal of excess propellant. With the completion of the mortar projectiles blow-in-place (BIP) study, we have a concluded an examination of energetic residues produced by the detonation and BIP of a common representative of high-explosive (HE) munitions for the most common weapon systems utilized during live-fire training missions.

We have a few irons in the fire, with the triple-base firing point and burn point tests completed, but the results are yet to be written up. We are also ready to proceed with firing point tests for the 40-mm grenade machine guns and the close-proximity detonation tests on adjacent 81-mm HE projectiles. INRS is preparing for a final set of column studies.

We have summarized below the significant findings from the various tasks completed through 2009 for the ER-1481 extension. A summary of related publications follows.

10.2 Characterization of residues deposition and accumulation

10.2.1 Deposition rate studies

Two shoulder-fired rocket firing point tests were completed. The first was conducted by DRDC (Thiboutot) at the Liri Antitank Range at Canadian Forces Base (CFB) Valcartier, QC, in June of 2008. The weapon system tested was a 66-mm M72 A5-C1 Light Antitank Weapon System, a frequently-used weapon system for Canadian forces. The A5 rocket motor burns 122 g of M7 Type I double-base propellant (54.6% nitrocellulose [NC], 35.5% nitroglycerine [NG]). A maximum of 8.5% of the propellant consists of potassium perchlorate (KP), a strong oxidizer. The propellant is in the form of long (142–147 mm) cylinders with a 6-mm outside diameter and a 4-mm inside diameter. A total of 98 rockets were fired in two events over 3 days; 65 the first day, 33 the third.

Residues were collected from an area 10-m downrange and 30 m behind the firing positions. Particle traps consisting of lightweight aluminum rectangular pans (47 × 36 cm) with <3-cm ethanol inside were used to collect residues uprange and downrange. The traps were periodically replenished with ethanol over the course of the firings. A total of 35 traps were employed; one 5 m downrange, four 10 m downrange spaced 2 m apart except at the center (4 m) and the remainder spaced 2 m apart along six transects spaced 5 m apart behind the firing position. The total area covered by the transects was 400 m^2, with about 2% of that area covered by the traps.

Results from this test are as follows. A total of 4.1 g of NG was estimated to occur in the sampled areas from the residues recovered for the 2 days. This is equivalent to approximately 42 mg of NG per round or 0.1% of the original NG load per round. Of the NG recovered, 92% was found behind the firing position. Of that amount, over 90% was within the first 20 m behind the position.

The second test was conducted in March 2009 by the Cold Regions Reserach Engineering Laboratory (CRREL; Walsh) with assistance from Defence Research and Development Canada (DRDC) at the 40/90 Range at Fort Richardson, AK. The weapons system tested was the 84-mm M136

AT4 Rocket and Launcher, a common U.S. Army antitank weapon. The rocket motor burns 355 g of AKB204 double-base propellant (61% NC, 37.5% NG). No KP is used in the propellant, which is in the form of long thin strips. A total of six rockets were fired over the course of 2 hours. In May, a second round of sampling was conducted in the backblast area behind the original firing position.

Residues in March were collected from an area up to 50-m downrange and 36 m behind the firing positions. Residues were collected from the surface and below the surface of the snow surrounding the firing position. The demarcated backplume and adjacent concentric areas (OTPs) were 940 m^2, the downrange plume and adjacent concentric areas were 890 m^2, and the two downrange transects had areas of 27 m^2 (40-m downrange) and 25 m^2 (50-m downrange). A total of 21 multi-increment samples comprising a total of 1,035 increments were taken over all the decision units. The total samples area was 4.6 m^2, about 0.45% of the total area covered by the decision units. In May, 2-cm deep soil samples were collected from a 30- x 30-m area that encompassed the entire back plume and most of the adjacent winter OTPs. Three ≈100-increment samples were taken.

Results from this test are as follows. A total of 570 g of NG was estimated to occur within the decision units sampled in March. This is equivalent to an estimated 95 g of NG per round or 73% of the original NG load per round. Of the NG recovered, 93% was found behind the firing position. Of that amount, over 99% was within the demarcated backblast plume. As a confirmation, we examined the solid residues on four filters from the backblast plume samples and, assuming ≈80% 0f the residues were propellant residues, the agreement between the theoretical mass of NG in the solid residues and the analytical results is within 5%. The March results indicated that around 50% of the NG had leached out of the propellant residues during the spring "flush", with an estimated mean mass for the area of 250 g of NG or 42 g/round.

The third test was conducted in February 2009 by DRDC (Ampleman) with assistance from CRREL at the tank firing range at CFB Valcartier in Quebec, Canada. The weapons system tested was the Canadian Leopard C2 Main Battle Tank, armed with a 105-mm gun. For our test, 90 rounds of C109 A1 squash head/practice-tracer (SH/P-T) were fired from a single gun position. Propellant for the cartridges was M1 single-base (NC with 2,4-dinitrotoluene [DNT]) propellant in a 3-kg charge. The composition of the propellant is nominally 85% NC and 10% DNT, DNT being the target compound in this test. Firing was begun in the afternoon, with the last rounds fired around 2300 hours that night.

Residues were collected using two methods. As with previous tests conducted by DRDC, particle traps were set out along transects in front of the firing position. The traps were heavy-duty stainless steel roasting pans measuring 53 × 48 × 7.6 cm with a thickness of 0.25 cm. They were weighted down and held in place with specially designed holders. A total of 57 particle traps were installed 3 (3 traps), 5 (5 traps), 10 (7 traps), 15 (7 traps), 20 (7 traps), 25 (7 traps), 30 (7 traps), 40 (7 traps), and 45 m (7 traps) in front of the tank. Following cessation of firing, the traps were collected and residues were removed by rinsing with acetone. Snow sampling was also conducted. After demarcating the residue plume, both surface and subsurface replicate samples were taken over the 430-m^2 main plume area (extending 27 m downrange) and replicate surface samples were taken over the 170 m^2 of the adjacent areas to the main plume (OTP) and the 490-m^2 area downrange plume (27- to 46-m downrange). A single peripheral sample was taken over a 210-m^2 OTP area surrounding the downrange plume. A total of 10 samples, comprising 299 increments and 4.04 m^2 of surface area, were taken in the four decision units. This represents 0.31% of the total area of the decision units.

The two sets of results are in close agreement. A total of 710 mg of DNT was estimated to occur within the decision units sampled based on the results of the particle trap collection method. This is equivalent to an estimated 7.9 mg of DNT per round or 0.0026% of the original DNT load per round. Of the DNT recovered, the highest concentrations were found immediately in front of the gun (3 m) and in the 20- and 25-m transects. Migration of the traps because of the muzzle blast makes a clear determination of the residues densities difficult. For the snow samples, the surface sample in the main plume was estimated to contain a little over 390 mg of DNT with an additional 120 mg recovered from the subsurface sample, a result that was expected because of the violence of the tank's muzzle blast. The OTP for the main plume contained an estimated 9.1 mg of DNT. For the downrange decision units, the main plume contained an estimated 36 mg of DNT while its OTP held approximately 1.0 mg. Totaling all the DUs, we ended up with an estimated 590 mg of DNT, or 6.5 mg DNT per round. This is equivalent to 0.0022% of the original DNT load. The agreement between the two sampling methods is within 15%.

10.2.2 Characterization study

A characterization study of a legacy antitank rocket range was completed by DRDC. The Carpiquet range is located on CFB Valcartier in Quebec, Canada. The range was closed in 1975 and has not been used since. The characterization of the site was quite thorough, with surface and subsurface soil samples taken as well as subsurface water samples.

Surface samples were taken over several decision units using the multi-increment (MI) sampling protocol. Twelve decision units were set up parallel to the former firing position wall, one 5 x 16-m, two 2 x 8-m, and nine 2 x 16-m long. A total of 91 MI samples composed of 100 increments each were taken to a depth of 2 cm in the decision units, including seven replicate samples. Four soil profile pits were dug, three behind one of the former firing positions (6, 9, and 12 m behind the position) and one behind the other firing position at 9 m. For the first three pits, soil samples were collected at each 5-cm interval down to 50 cm and then at a 10-cm interval from 50- to 60-cm deep. For the fourth pit, a 100-cm profile was taken at 10-cm intervals. Each interval was examined separately to obtain the analyte profile. Following the soil sampling, four vadose zone lysimeter arrays were installed by INRS-ETE to obtain percolated groundwater below the surface. Three lysimeters were installed 6.1 m from the firing wall at depths of 10-, 30-, and 60-cm below ground surface and a fourth was installed 45 m southeast of the firing wall at a depth of 40 cm as a background well. Finally, three groundwater monitoring wells were installed at the site to allow sampling of water from the saturated zone. Two wells were located 8.5-m behind the right-hand side firing position and the third was 35.4-m behind the center of the firing wall. The depth to the bottom of the 1-m screen for each well was 4 m and 5 m for the right-hand wells, and 5 m for the other well.

Results from this study indicated that highly contaminated firing points will need to be monitored for many years after closure. Surface concentrations of 4,700 mg/kg NG were found near the firing positions, with concentrations over 4,000 mg/kg NG as far out as 12 m. The profile sample results showed that most of the NG resides in the near-surface zone of the soil. With surface concentrations in the 2,700 to 4,800 mg/kg range in the top 5 cm, concentrations rapidly fell to the 3–380 mg/kg range at 15 cm. Little NG was detected below 20 cm. Sieve analyses indicated that the majority of the NG occurred in the soil fraction 0.125 to 2 mm. Microscopic examination of some of the soil samples revealed recognizable propellant fibers that, through Expray analysis, contained NG within the NC matrix. Some NG has moved in the soil profile as colloidal solid particles. None of the water samples that were collected from the lysimeters and groundwater monitoring wells contained detectable amounts of NG or its degradation products. In all cases, the detection limit was equal to or below 3 µg/L.

10.2.3 Fate and transport – large column studies

A set of six large-diameter, stainless steel, soil column test fixtures were designed and constructed at the National Science Research Institute (INRS-ETE), Quebec City, Quebec, Canada, with the objective of determining the fate and transport of NG from spent shoulder-fired rocket propellant recovered from firing points on military ranges. Soils were collected from active firing points for surface application to the columns. A 2-year time period, representative of the two sites from which the soils were collected, was to be simulated for the columns. Analytes of interest included NG, NG breakdown products, and perchlorates.

The columns were constructed of a base layer (60 cm) of clean soil (<8 mm) collected from the vicinity of the firing points at each of the two sites topped with a 2-cm layer of sieved (<5 mm) soil containing propellant debris from two firing positions at each site. The base layer was assembled in compacted 1.6-cm lifts. The contaminated soil was then added as a 2-cm layer to two of the three columns for each experiment; the third column was used as a control. This column had sodium bromide applied to it to determine transport pore volume, the retardation factor, and (from inference) the adsorption coefficient. Time-domain reflectometry (TDR) probes at 10-, 30-, and 50-cm from the top were used to determine pore volume in this and the other two columns for each experiment. Simulated rain (pH 6-7) was applied to the top in a regime that simulated the rainfall at the two sites. Water effluent from the percolated simulated rainfall was collected through seven holes in the base of the column. Temperature in the test room was controlled to simulate the accelerated seasons.

All but one column performed well enough to obtain reliable data. Breakthrough curves for bromide and perchlorate were comparable, indicating that perchlorates are not adsorped, transformed, or biodegraded under aerobic transport conditions. Maximum perchlorate concentrations exceeded drinking water standards during the simulated spring “flush” or thaw. Peaks also occurred for nitrates in the “spring,” indicating transformation of NG and nitrites in the aerobic soil conditions. Examinations of the surface soil layer indicated that the nitrites and perchlorates were almost completely absent, perchlorates by flushing and nitrites by transformation and flushing. Nitrate levels were reduced to half their original values, although there was some make up from nitrite and NG transformation. The loss of NG was small, l6% for one column, negligible for the other, which is an indication of the tight binding within the NC matrix of the propellant. Of the 16% that leached from the propellant in one of the columns, one-fourth was not recovered in the effluent and was transformed to nitrates as none was found in the soil column below the 5-cm surface mixed soil zone. The organic content of the top soil had a degradation effect on the dissolved NG and especially the nitrites.

10.3 Characterization and optimization of open burning of excess propellants

10.3.1 Characterization of propellant burns

A study examining the effects of weather and climate on the efficiency of the open burning of propellants was completed by CRREL researchers. In this study, the open burning of excess propellants was conducted under winter and summer conditions. Winter condition tests were conducted at the Eagle River Flats impact range at Fort Richardson, Alaska, in February 2008. The summer tests were conducted at Observation Point 7 at Donnelly Training Area, Fort Wainwright, Alaska, in July 2008.

For the winter tests, double-base M45 mortar propellant (86% NC, 10% NG) was burned on snow, frozen ground, and in a stainless steel container. Ten to 11 M230 propellant charges containing 130 g of M45 propellant each were used in the tests. For the snow test, 11 charges were placed on the surface of the 40-cm deep snow and ignited with time fuze. The propellant burned through the snow to the frozen ground surface, with some evidence of unburned propellant grains evident. For the second test, 11 charges were placed on frozen ground that had been cleared of snow and ignited with time fuze. Again, the presence of propellant grains was noted. For the third test, 10 charges were burned in a 30-cm diameter stainless steel bowl. The bowl and its associated debris were collected for later analysis and the snow surface sampled for propellant residues. In June and July following the test, the first two sites were relocated, and surface and soil samples were taken for residues analyses.

For the summer test, M1 propellant (85% NC, 10% DNT) charge bags excess to a 105-mm howitzer training mission were burned on clean wet and dry sand. Five charges 6 and 7 containing a combined total of 3.27 Kg of propellant were used for each test. Both burns were started using a butane initiator. Following the burn, all soil that was visually affected by the burn was collected for analyses.

The winter tests resulted in very definite differences in burn efficiencies. For the burn in the pan, 0.21% of the original NG was estimated to remain. For the burn occurring on frozen soil, 5.2% of the NG was estimated to remain. The snow surface burn resulted in the greatest amount of residues, 18%. Extensive sampling of the latter two burn locations included soil profile sampling below clusters of unburned grains. Soil concentrations of NG rapidly dropped off with depth but were as high as 180 µg/g. Analysis of the recovered unburned grains indicated a loss of up to 44% of NG from the small grains over the course of the spring thaw. The results of the summer burns were not so dramatic, with less than 1% of the original mass of DNT recovered in the post-burn samples.

10.3.2 Investigation of the presence of dioxins and furans in post-burn propellant residue

While conducting a propellant burn characterization test, researchers at DRDC found dioxins and furans in the post-burn residues. This discovery was worrisome for two reasons. There was nothing in the tested propellant mixtures that would seem to generate dioxins or furans, and these two compounds are quite dangerous in the environment. During a joint project meeting with CRREL and INRS, it was suggested that the initiation device used by Canadian Forces, a railroad flare or fuze, might be the source of the compounds. With that in mind, DRDC conducted a series of experiments at CFB Valcartier starting in September 2008. The objective was to find out if the fuze was the source of the compounds.

Tests were conducted using propellants that do not contain perchlorates. The propellants were burned on snow, soils, and in a stainless steel burn pan. Flares were used to ignite the propellant for most tests, and care was taken to sample burned propellant, burned propellants with flare residues, and locations with mostly just flare residues. Tests were also conducted with just an initiation flare. Samples were analyzed for the presence of dioxins and furans.

Test results showed that the use of the railroad flare to initiate propellant burns resulted in the generation of significant quantities of dioxins and furans. Contaminant levels were highest where the flare was in contact with the propellant, indicating that the potassium perchlorate in the flare is reacting with the organic compounds in the propellants. DRDC has recommended to the Canadian Forces that the initiation procedure for burning propellants be altered to eliminate the use of railroad flares. As a result of this research, a change in protocol for propellant burns has now been initiated in Canada.

10.4 Simulation of live-fire breaching of UXO

No reportable results of testing for this task have been generated to date. An initiator adapter has been designed and built for the 81-mm HE mortar cartridges obtained for the tests. Arrangements have been made for the testing of these initiators in February and equipment, range access, and support are in place for the first round of tests in March 2011.

10.5 Explosives residues deposition rate tests

Over the course of three SERDP projects, a series of tests have been conducted to derive the deposition rates of energetic residues resulting from live-fire and BIP detonation of commonly used HE military munitions used for training. The final rounds to be tested were 60-mm and 120-mm mortar rounds. Tests were conducted by CRREL in early 2008 at the Eagle River Flats impact area on Fort Richardson, Alaska.

Tests were conducted on the ice-covered surface of the impact area. For the tests, complete rounds were set on the ice (60 mm) or 30- to 45-cm thick blocks of ice placed on the ice surface of the Flats (120 mm). Each round included a live fuze in the nose and a propellant ignition cartridge in the tail assembly. External propellant charges were removed. For each test, seven rounds spaced 40-m apart were detonated. Following detonation, residue plumes were visually demarcated, triplicate surface samples obtained, two adjacent 3-m wide annuluses were sampled, and one sample was taken below previously sampled locations within the main plume. A surface gradient sampling test was also conducted, comparing mass of energetic residues for three areas demarcated by the darkness of the residues on the snow surface.

The results from these tests were consistent with previous BIP tests. Residue rates for the HE component of the round were low for both munitions, averaging an estimated 2.3 x 10^{-2} % for the 60-mm rounds and 7.7 x 10^{-4} % for the 120-mm rounds. This is equivalent to 200 mg and 25 mg of HE per round, respectively. Nitroglycerine from the ignition cartridges remained at high levels follow detonation, with 4.8 g (16%) remaining per 120-mm round and 0.23 g (17%) remaining per 60-mm round. The propellant is not as shock sensitive as the HE filler and thus survives the detonation in greater quantity.

10.6 Dissemination, promotion, and demonstration of the multi-increment sampling strategy and EPA Method 8330B

The multi-increment sampling (MIS) strategy has been used for many years, especially by the geology community, to characterize areas for non-homogeneously distributed materials. CRREL and Envirostat have adapted and refined this strategy for the characterization of sites for the presence of energetic materials such as white phosphorus, HEs, and propellants. Development of the MIS protocol culminated in the publication of EPA Method 8330B, “Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC).” This method contains an appendix titled “Collecting and Processing of Representative Samples for Energetic Residues in Solid Matrices from Military Training Ranges,” the MI sampling strategy developed with funding from SERDP. Resistance to the change from discrete or grab sampling to MI sampling was strong when this Method was first published in late 2006, and SERDP tasked CRREL to help overcome this resistance through participation on various committees, presentations at meetings and conferences, and demonstrations through classes and workshops.

Since the inception of the SERDP ER-1481 extension, Alan Hewitt of CRREL tirelessly served as the chief spokesman for MIS. By the end of December 2009, Mr. Hewitt and his colleagues at CRREL and DRDC have given two field demonstrations, 21 presentations at conferences and meetings, and six workshops. One publication of MIS tools has been published (Walsh 2009). CRREL has worked with the states of Hawaii and Alaska on the development of their regulatory documents that incorporate MIS. In addition, input has been provided to guidance documents for the Corps of Engineers and the U.S. Army Environmental Center (USAEC). Four members of the NATO AVT-ET-108, Munitions Related Contamination–Source Characterization, Fate, and Transport are investigators on SERDP ER-1481, giving the project an international reach. Acceptance of MIS is widespread among our allies in Europe and is almost complete in the United States and Canada. Mr. Hewitt has also participated in the Interstate Technical Research Council (ITRC) and the EPA Federal Facilities Forum, both of which are in the process of implementing MIS into their guidance documents. This has been and continues to be a highly successful task for the project.

10.7 Current status

Work continues on all aspects of the project. We were greatly saddened upon the notification of team member Alan Hewitt's passing in January of 2010. We are working hard to cover the many venues in which he was involved in this project.

The winter field season is lining up to be a busy one, with several tests scheduled. Additional column studies utilizing different propellants are in the planning stages. We continue to write up results from last year's work, including new results from the firing and field expedient disposal of triple-base propellants.

The interest and relevance of our SERDP work has enabled us to leverage funding with several entities. In the United States, the Army Environmental Center; U.S. Army Garrison Alaska, and the U.S. Army have all provided support for tasks within ER-1481. In Canada, significant leveraging comes through the Canadian Department of National Defence. Inter-project leveraging also has been utilized.

Data gaps have been identified in the current work, and a proposal has been submitted to SERDP for another 3-year continuation of the project. Areas of interest include clean BIP of UXO, characterization of a demolitions training range, fate and transformation of trinitrotoluene, diffusion of energetic compounds from cracked or breached UXO, holding times for energetics in ground soils, presence of lead decoppering agent in burned propellants, continuation of the large-column propellant study, and continuation of MIS dissemination. We hope to continue the highly productive collaboration SERDP has enabled between CRREL and DRDC.

10.8 Bibliography

The following is a bibliography of published work on the project that has been compiled since the beginning of the SERDP ER-1481 Extension in January 2008. All publications are unclassified.

Ampleman, G., S. Thibout, A. Marois, A. Gagnon, and D. Gilbert. 2008. *Evaluation of the propellant residues emitted during 105-mm Leopard tank live firing and sampling of demolition ranges at CFB Gagetown, Canada*. Defence Research and Development, Canada, Valcartier, QC, Canada. DRDC Valcartier TR 2007-515.

Ampleman, G., S. Thiboutot, A. Marois, A. Gagnon, M.R. Walsh, and M.E. Walsh. 2009. Study of the propellant residues deposited by the live firing of 105-mm Leopard tank. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Brochu, S., I. Poulin, D. Faucher, and M.R. Walsh. 2008. Assessment of gaseous and particulate propellant residues resulting from small arms live firing. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 2-4, 2008.

Brochu, S., I. Poulin, D. Faucher, E. Diaz, and M.R. Walsh. 2009. Environmental assessment of small arms live firing: Study of gaseous and particulate residues. Poster: 237th ACS National Meeting, Salt Lake City, Utah, March 2009

Diaz, E., D. Gilbert, D. Faucher, A Marois, and A. Gagnon. 2008. *Gun propellant residues dispersed from static artillery firings of LG1 Mark II and C3 105-mm howitzers*. Defence Research and Development, Canada, Valcartier, QC, Canada. DRDC Valcartier TR 2007-282.

Diaz, E., I. Poulin, S. Brochu, A. Marois, and A. Gagnon. 2009. Residues from the open burning of gun propellant. Poster: 237th ACS National Meeting, Salt Lake City, Utah March 2009

Hewitt, A.D., M.E. Walsh, M.R. Walsh, S. Bigl, and M Chappell. 2009. Assessing sample processing uncertainty for energetic residues on military training ranges: Method 8330B. Poster: 237th ACS National Meeting, Salt Lake City, Utah, March 2009.

Hewitt, A.D., M.E. Walsh, M.R. Walsh, S.R. Bigl, S. Brochu, M.A. Chappell, and C.A. Ramsey. 2009. Method 8330B and multi-increment sampling (2009 Project of the Year Award). Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Hewitt, A.D. 2009. Estimating the surface loading of munitions constituents on military training ranges. Invited Speaker: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Session 3A, held in Washington DC, USA, December 1-3, 2009.

Jenkins, T.F., G. Ampleman, S. Thiboutot, S.R. Bigl, S. Taylor, M.R. Walsh, D. Faucher, R. Martel, I. Poulin, K.M. Dontsova, M.E. Walsh, S. Brochu, A.D. Hewitt, G. Comeau, E. Diaz, M.A. Chappell, J.L. Fadden, A.Marois, R. Fifield, B. Quemerais, J. Simunek, N.M. Perron, A. Gagnon, T. Gamache, J.C. Pennington, V. Moors, D.J. Lambert, D. Gilbert, R.N. Bailey, V. Tanguay, C.A. Ramsey, L. Melanson, and M.-C. Lapointe. 2008. Characterization and fate of gun and rocket propellant residues on testing and training ranges: Final report. ERDC TR-08-1. Hanover, NH, USA : U.S. Army Engineer Research and Development Center, Cold Regions Research and Development Laboratory.

Martel, R., A. Bellavance-Godin, G. Ampleman, S. Thiboutot, and L. Trépanier. 2009. Fate and behavior of propellant residues in water of the unsaturated zone under an anti-tank firing position. Presentation: 8th ISICP, Cape Town, South Africa, November 2-6, 2009.

Martel, R., A. Bellavance-Godin, S. Thiboutot, and G. Ampleman. 2009. Behavior of nitroglycerine and its metabolites in the unsaturated zone under an antitank firing position: Sand column test. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington D.C., USA, December 1-3, 2009.

Martle, R., A. Bellavance-Godin, R. Levesque, and S. Cote. (In press). Determination of nitroglycerin and its metabolites by solid-phase extraction and HPLC-UV. *Chromatographia*.

Poulin, I., S. Thiboutot, and S. Brochu. 2009. Production of dioxins and furans from the burning of excess gun propellant. Defence Research and Development, Canada, Valcartier, QC, Canada. DRDC Valcartier TR-2009-365.

Poulin, I., S. Thiboutot, and S. Brochu. 2009. Open burning of excess gun propellant: Investigation of the production of dioxins and furans as combustion by-products. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, and D. Gilbert. 2008. Deposition of nitroglycerine from the live firing of M72 A5 66-mm rockets. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington D.C., USA, December 2-4, 2008.

Thiboutot, S., G. Ampleman, S. Brochu, E. Diaz, I. Poulin, T.F. Jenkins, M.R. Walsh, M.E. Walsh, S. Taylor, A.H. Hewitt, R. Martel, J. Hawari, G. Sunahara, P.-Y. Robidoux. F. Monteil-Rivera, B. Lachance, S. Rocheleau, R.G. Kuperman, R.T. Checkai, M. Simini, R. Lajoie, and K. Legault. 2009. Canadian perspectives on risk-based contaminant management on active army training ranges. Invited Speaker, Session 3A: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA. December 1-3, 2009.

Thiboutot, S., G. Ampleman, A. Marois, M.R. Gagnon, and G. Bordeleau. 2009. Long-term fate of propellant residues in the soil surface and subsurface. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Thiboutot, S., G. Ampleman, I. Poulin, M. Kervarec, A. Gagnon, A. Marois, and F. Boucher. 2009. Prototype table for the burning of excess artillery propellant bags. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Walsh, M.E., S. Taylor, A.D. Hewitt, M.R. Walsh, C.A. Ramsey, and C.M. Collins. 2010. Field observations of the persistence of Comp B explosives residues in a salt marsh impact area. *Chemosphere* 78(2010) 467-473.

Walsh, M.R., M.E. Walsh, and A.D. Hewitt. 2008. *Energetic residues from blow-in-place detonation of 60-mm and 120-mm fuzed high-explosive mortar cartridges*. ERDC/CRREL TR-08-19. Hanover, NH, USA: U.S. Army Engineer Research and Development Center, Cold Regions Research and Development Laboratory,.

Walsh, M.R., M.E. Walsh, A.D. Hewitt, and C.M. Collins. 2008. Field-expedient disposal of excess artillery propellants. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 2-4, 2008.

Walsh, M.R., M.E. Walsh, and A.D. Hewitt. 2009. E*nergetic residues from the expedient disposal of propellants*. ERDC/CRREL TR-09-8. Hanover, NH, USA: U.S. Army Engineer Research and Development Center, Cold Regions Research and Development Laboratory.

Walsh, M.R. 2009. *User's manual for the CRREL multi-increment sampling tool*. ERDC/CRREL SR-09-2. Hanover, NH, USA: U.S. Army Engineer Research and Development Center, Cold Regions Research and Development Laboratory.

Walsh, M.R., M.E. Walsh, S. Thiboutot, G. Ampleman, and J.N. Bryant. 2009. *Propellant residues deposition from firing of AT4 rockets*. ERDC/CRREL TR-09-13. Hanover, NH, USA: U.S. Army Engineer Research and Development Center, Cold Regions Research and Development Laboratory.

Walsh, M.R., M.E. Walsh, S. Thiboutot, and G. Ampleman. 2009. Propellant residues resulting from training with shoulder-fired rockets. Poster: SERDP & ESTCP's Partners in Environmental Technology Technical Symposium & Workshop, Washington DC, USA, December 1-3, 2009.

Walsh, M.R., M.E. Walsh, and A.D. Hewitt. 2010. Energetic residues from the field disposal of gun propellants. *Journal of Hazardous Materials* 173(2010) 115-122.

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Michael R. Walsh, Guy Ampleman, Sonia Thiboutot, Marianne E. Walsh, Isabelle Poulin, Aurélie Bellavance-Godin, Richard Martel, Geneviève Bordeleau, Sylvie Brochu, Alan D. Hewitt, André Marois, Annie Gagnon, Charles M. Collins, Denis Gilbert, Peter Woods, Jeffrey N. Bryant, Susan R. Bigl, and Kelsey Gagnon

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14. ABSTRACT

The Cold Regions Research and Engineering Laboratory and Defence Research and Development Canada–Valcartier have partnered to improve the understanding of the distribution and fate of propellant residues on military training ranges. Field studies were conducted to estimate the propellant residue mass deposited per round fired from various munitions as well as residues from the field disposal of excess training propellants. Experiments were conducted to measure the rate of release of nitroglycerin and dinitrotoluenes after deposition. United States and Canadian installations were examined to determine the mass and distribution of residue accumulation. Profile sampling was conducted to document the depth to which these residues had penetrated the ground. Column studies were conducted with nitroglycerin, nitroguanidine, potassium perchlorate, and diphenylamine from intact and expended propellants to document transport rates for solution-phase propellant constituents and to develop process descriptors for use in models to enable prediction of fate and transport for these constituents. Gaps were filled in other areas of energetics residues deposition, rounding out a holistic overview of training impacts on military ranges. Testing of propellant burn structures was begun, and we continue to promote multi-increment sampling for energetics. Major accomplishments are presented for Environmental Restoration Project 1481, Phase II.

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