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*Strategic Environmental Research and Development Program*

# Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report

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# Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report

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Final report

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**Abstract:** Access to live-fire training ranges is vital in maintaining the readiness of our Armed Forces. Understanding the nature of residue deposition and fate is critical to ensuring sound management of ranges. The objective of this project was to characterize residues of high explosives on training ranges. Residues were evaluated by sampling on various types of ranges across the U.S. and Canada. Deposition from high-order and low-order detonations, demolition, including blow-in-place, was characterized. Environmental transport parameters were developed to support estimates of site-specific source terms for risk assessment and groundwater models. Protocols were developed for characterizing soils containing the highly distributed solid formulations typical of ranges. Results demonstrated that residues are specific to range activities. Demolition areas, low-order detonations sites, and firing positions have great potential for accumulation of residues. Demolition typically generates small areas of relatively high concentrations. Low-order detonations generate primarily large solid particles reflecting the predetonation composition. Artillery impact areas tend to have widely distributed, low concentrations. Firing positions may exhibit high concentrations of propellants. This project defines the characteristics, distribution, and potential environment transport of explosives residues on training ranges and provides a scientific basis for development of reasonable control measures.

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# Preface

This report was prepared by the U.S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS, and the Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, in partnership with Defence Research and Development Canada - Valcartier (DRDC-Val), Quebec, Canada. The research was sponsored by the Strategic Environmental Research and Development Program (SERDP), Arlington, VA, Bradley P. Smith, Executive Director, and Dr. Jeff Marqusee, Technical Director, under Compliance Project Number CP-1155, now Environmental Restoration Project Number ER-1155. The principal investigator was Dr. Judith C. Pennington, Environmental Processes and Engineering Division (EPED), ERDC-EL. Co-principal investigators were Dr. Thomas F. Jenkins, Environmental Sciences Branch (ESB), CRREL; Drs. Guy Ampleman and Sonia Thiboutot, DRDC-Val, Dr. James M. Brannon, EPED, and Jay Clausen, AMEC Earth and Environment, now with CRREL-ESB.

Various chapters of this report were reviewed by Dr. Jeff Davis and Dr. Mansour Zakikhani, ERDC-EL, Marianne Walsh, ERDC-CRREL, and Dr. Clarence L. Grant, Professor Emeritus, University of New Hampshire, Durham, NH. The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED, and Dr. Beth Fleming, Director, ERDC-EL.

COL Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

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

Whole report:

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Chapter 1:

Pennington, J. C. 2006. Introduction, Chapter 1. In *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.

Chapter 2:

Jenkins, T. F., S. Thiboutot, G. Ampleman, A. D. Hewitt, M. E. Walsh, S. Taylor, J. Clausen, T. A. Ranney, C. A. Ramsey, C. L. Grant, C. M. Collins, S. Brochu, E. Diaz, S. R. Bigl, and J. C. Pennington. 2006. Identity and distribution of residues of energetic compounds at military live-fire training ranges, Chapter 2. In *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.

Chapter 3:

Pennington, J. C., J. M. Brannon, J. C. Lynch, J. Lewis, K. Dontsova, S. L. Yost, and C. A. Hayes. 2006. Transport parameters for firing range residues, Chapter 3. In *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.

Chapter 4:

Hewitt, A. D., J. Lewis, and J. C. Pennington. 2006. Residues in groundwater, surface waters, and sediments, Chapter 4. In *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.

Chapter 5:

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Chapter 6:

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# Notation

| | |
|---|---|
| AcN | Acetonitrile |
| ADNTs | Aminodinitrotoluenes |
| 2ADNT | 2-amino-4,6-dinitrotoluene |
| 4ADNT | 4-amino-2,6-dinitrotoluene |
| 2A4NT | 2-amino-4-nitrotoluene |
| 4A2NT | 4-amino-2-nitrotoluene |
| AEC | Army Environmental Center |
| AFB | Air Force Base |
| ARAMS | Adaptive Risk Assessment Modeling System |
| bgs | Below ground surface |
| BIP | Blow-in-place |
| CAS | Chemical Abstracts Services |
| CCME | Canadian Council of Ministers of Environment |
| CEC | Cation exchange capacity |
| CFAD | Canadian Forces Ammunition Depot |
| CFB | Canadian Forces Base |
| CHPPM | Center for Health Promotion and Preventive Medicine |
| CIA | Central Impact Area |
| CLAWR | Cold Water Air Weapons Range |
| COC | Contaminants of Concern |
| CRREL | Cold Regions Research and Engineering Laboratory |

| | |
|---|---|
| 2,4DANT | 2,4-diamino-6-nitrotoluene |
| 3,5DNA | 3,5-dinitroaniline |
| 1,3DNB | 1,3-dinitrobenzene |
| 2,4DNT | 2,4-dinitrotoluene |
| 2,6DNT | 2,6-dinitrotoluene |
| DGE | Director General Environment, Canadian Department of National Defence |
| DLE | Director Land Environment, Canadian Department of National Defence |
| DND | Department of National Defence |
| DNT | 2,4-dinitrotoluene |
| DNX | Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine |
| DoD | Department of Defense |
| DOE | Department of Energy |
| DPA | Diphenylamine |
| DRDC | Defence Research and Development Canada |
| DRDC-Val | Defence Research and Development Canada – Valcartier |
| ECL | ethyl centralite |
| EIS | Environmental Impact Statement |
| EL | Environmental Laboratory |
| EOD | Explosives ordnance disposal |
| ER | Environmental Restoration |
| ERDC | Engineer Research and Development Center |
| FP | Firing Position |

| | |
|---|---|
| FY | Fiscal Year |
| GAC | Granular Activated Carbon |
| GC-ECD | Gas chromatography-electron capture detection |
| GC/MS | Gas chromatography/mass spectrometry |
| GIS | Geographic information system |
| GPS | Global positioning system |
| GMS | Groundwater Modeling System |
| HAFB | Holloman Air Force Base |
| HE | High explosive |
| HEP | High explosive plastic |
| HMX | 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine, or High Melting Explosive |
| IAGWSP | Impact Area Groundwater Study Program |
| ICP-MS | Inductively Coupled Plasma - Mass Spectrometry |
| IR | Infrared |
| IX | Ion Exchange |
| KBr | Potassium bromide |
| LAW | Light anti-tank weapon |
| LITR | Low-Cost Infantry Training Rounds |
| MADEP | Massachusetts Department of Environmental Protection |
| MC | Munitions Constituents |
| MCD | Main Charge Disruptor |
| mm/yr | Millimeters per year |
| MMR | Massachusetts Military Reservation |

| | |
|---|---|
| MNX | Hexahydro-1-mononitroso-3,5-dinitro-1,3,5-triazine |
| 3NA | 3-Nitroaniline |
| NB | Nitrobenzene |
| NG | Nitroglycerin |
| NNDPA | N-nitrosodiphenylamine |
| NQ | Nitroguanidine |
| 2NT | 2-nitrotoluene |
| 3NT | 3-nitrotoluene |
| 4NT | 4-nitrotoluene |
| NT | Nitrotoluene |
| OB/OD | Open Burning/Open Detonation |
| OC | Organic carbon |
| OE | Ordnance and Explosives |
| OM | Organic matter |
| PAH | Polycyclic aromatic hydrocarbons |
| PCB | Polychlorinated biphenols |
| PETN | Pentaerythritol tetranitrate |
| QA/QC | Quality assurance/quality control |
| R&D | Research and development |
| RRA | Rapid Response Action |
| RDX | 1,3,5-hexahydrotrinitrotriazine, or Research Development Explosive |
| RP-HPLC-UV | Reversed-phase high performance liquid chromatography with ultraviolet detection |

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|---|---|
| RPD | Relative Percent Difference |
| RSQG | CCME Residential Soil Quality Guideline |
| SARM | Standard Analytical Reference Materials |
| SERDP | Strategic Environmental Research and Development Program |
| SPE | Solid phase extraction |
| SVOC | Semi-Volatile Organic Compounds |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TES | Threatened and endangered species |
| Tetryl | n-Methyl-n-2,4,6-tetranitroaniline |
| TNB | 1,3,5-trinitrobenzene |
| TNT | 2,4,6-trinitrotoluene |
| TNX | Hexahydro-1,3,5-trinitroso-1,3,5-triazine |
| TOC | Total organic carbons |
| TOW | Tube-launched optically tracked wire-guided (missle) |
| USACE | United States Army Corps of Engineers |
| USEPA | U.S. Environmental Protection Agency |
| UXO | Unexploded ordnance |
| VOC | Volatile Organic Compounds |
| WATC | Western Area Training Center |
| WP | White phosphorous |
| w/w | Weight to weight |
| XRT | Experimental Rubbery TNT |

# 1 Introduction

## Background

### Rationale

The readiness of the Armed Forces of the United States and Canada is predicated on well-trained troops and continuous enhancements of their munitions arsenal. Sustained use of live-fire training ranges is especially critical to U.S. missions abroad, which currently demand rapid and effective mobilization. Concern that training activities potentially generate environmental contamination in the form of residual munitions constituents has threatened range sustainment. At the inception of Environmental Restoration (ER) Project ER-1155 (formerly Project CP-1155) in 2000, the state of knowledge concerning the nature, extent, and fate of residual munitions constituents was inadequate to ensure environmental sustainability on testing and training ranges. Improving the scientific understanding of munitions residues is critical to managing training ranges in support of military readiness, while simultaneously protecting the environment. Project ER-1155 was designed to characterize the distribution and fate of energetic residuals from various uses of live-fire munitions during testing and training.

### Regulatory issues

In April 1997 the U.S. Environmental Protection Agency (USEPA) issued Administrative Order No. 2 to the National Guard Bureau and the Massachusetts National Guard requiring that certain training activities (artillery and mortar firing) cease, pending the completion of environmental investigations at the Training Range and Impact Area at the Massachusetts Military Reservation (MMR) (USEPA 1997). In January 2000 USEPA Region I issued an Administrative Order for Response Action in the matter of "Training Range and Impact Area, Massachusetts Military Reservation" to the National Guard Bureau and the Massachusetts National Guard under authority of Section 1431(a) of the Safe Drinking Water Act, 42, U.S.C. § 300i(a) (USEPA 2000). The order required the respondents to "undertake Rapid Response Actions and Feasibility Studies, Design and Remedial Actions to abate the threat to public health presented by the contamination from past and present activities and sources at and emanating from the MMR Training Range and Impact Area." This order set an important precedent for suspension of military training due to environmental contamination of soils and groundwater. The environmental monitoring and remedial actions at MMR have been reviewed each year during execution of ER-1155. Hundreds of soil and groundwater samples are collected and analyzed for this site each year starting in 2001. Results of detections have been summarized in ER-1155 Interim Reports each year starting with the 2002 report.

## Scope of ER-1155

The overall purpose of Project ER-1155 was to develop techniques for assessing the potential for environmental contamination from energetic materials on testing and training ranges. Techniques were developed to define the physical and chemical properties, concentrations, and distribution of energetics and residues of energetics in soils, and the potential for transport of these materials to groundwater. Other issues, such as off-site transport in surface runoff or as a component of airborne dust, are also important but are beyond the scope of the project.

Four major substudies were conducted during Project ER-1155.

- Surface soils associated with impact craters, target areas, and firing points have been characterized on U.S. and Canadian ranges. Special protocols were developed to optimize sample representativeness and to define the complex distribution of explosives residues on the soil surface. Experiments were conducted on 27 military installations in the United States and Canada. Results created a working concept for the distribution of explosives associated with specific types of live-fire training. Chapter 2 summarizes the results.
- The potential for explosive residue movement is described by empirically determined parameters such as dissolution rates, adsorption coefficients, and transformation/degradation rates. These parameters are required for adequately simulating transport by numerical modeling of vadose zone and groundwater systems. Transport parameters are also useful in environmental risk assessments to define the exposure potential for contaminant receptors. During the execution of ER-1155, these transport parameters were determined for an extensive list of explosives components. The behavior of several formulations of explosives and selected propellants were included. Chapter 3 summarizes the results.

- A concerted effort was made to characterize surface, groundwater, and sediments on all of the Canadian ranges included in SERDP ER-1155. These efforts were funded directly to DRDC by elements of the Canadian government. Occasionally during the execution of ER-1155, samples of surface water, groundwater, and sediments were collected from artillery, anti-tank, and demolition ranges in the United States. These sampling events were often characterized by the collection of one-time “grab” samples; therefore, the samples were not necessarily representative. However, the Canadian data and U.S. detections suggest that both surface and groundwater transport of explosive residues are possible on specific types of ranges. Chapter 4 summarizes the results.
- During the execution of ER-1155, several studies were conducted to determine the mass and distribution of energetic residues resulting from blow-in-place (BIP) of unexploded ordnance. These tests were conducted on snow at Canadian Forces Base Valcartier, Quebec, Fort Richardson, AK, Fort Drum, NY, and Camp Ethan Allen, VT. Tests were also conducted on a tarp at Redstone Arsenal, AL. On several occasions, opportunities arose to sample immediately after a BIP exercise on the range. Munitions ranged from artillery projectiles and mortars to hand grenades, mines, and torpedoes. Chapter 5 summarizes the results.

## Objectives

The primary objective of the study was to provide the U.S. Department of Defense (DoD) with techniques to assess the potential for groundwater contamination from residues of energetic compounds (TNT, PETN, RDX, NG, 2,4DNT, and HMX) at testing and training ranges. Results of the project facilitate informed decision-making, help to minimize environmental impacts of testing and training, and contribute to continued operation of ranges.

Specific objectives include the following:

1. To develop sampling protocols that can be used to determine the nature and extent of surface soil contamination around impact areas and firing points. The protocol includes sampling strategies and analytical methods best suited to this application.

2. To provide source-term estimates of post-blast residues based on the extent of surface soil contamination, dissolution rates, and fate and transport process descriptors.
3. To provide data describing the relevant environmental processes controlling the fate and transport of residues of energetic compounds on ranges.

## Leveraged studies

To meet the challenge of sustained training while protecting groundwater and other environmental resources, the U.S. Department of Defense is funding a broad spectrum of research and development (R&D) efforts. These efforts are funded under multiple programs and through many installations and address various aspects of range sustainability. Examples of programs funding R&D efforts related to range sustainment and environmental stewardship are the following. Collaboration and leveraging of these projects are indicated where appropriate.

1. **Strategic Environmental Research and Development Program (SERDP)** identifies, develops, and transitions environmental technologies that relate directly to defense mission accomplishment. The SERDP is the DoD's corporate environmental R&D program, planned and executed in full partnership with the Department of Energy (DOE) and the USEPA, with participation by numerous other Federal and non-Federal organizations. The DoD's environmental concerns may be viewed in terms of operational and/or cost impacts to its primary mission of maintaining military readiness for national defense. SERDP strives to minimize or remove major negative environmental impacts on DoD's ability to conduct this mission. SERDP has supported an extensive program of research related to range sustainment. SERDP projects with which were collaborated and/or coordinated are described below.
    a. *Compliance Project (CP)-1197,* "A Field Program to Identify Toxic Release Inventory Chemicals and Determine Emission Factors from DoD Munitions Activities" (Chet Spicer, Battelle Columbus). The objective of the project was to demonstrate a methodology for measuring emissions of toxic release inventory chemicals from DoD munitions activities and to apply the method to determine emission factors from munitions activities at DoD facilities. This study was completed in 2005.
    b. *CP-1305,* "Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges" (Eric Foote/Jeff Morse, Battelle Columbus). When this project

was granted access to an Eglin Air Force Base (AFB) range, the ER-1155 team was invited to conduct the initial soil characterization and share the data with both projects. Therefore, protocols developed in ER-1155 to sample surface soils on the range were used.

c. *CP-1330,* "On-Range Treatment of Ordnance Debris and Bulk Energetics Resulting from Low-Order Detonations" (Phil Thorne, Applied Research Associates, Inc.). The objective of this project was to develop a low-cost, fieldable process for the rapid decontamination of energetic material from range scrap. Debris was provided from low-order detonation tests at Blossom Point, MD, to facilitate trials of the techniques under development. This project was completed in 2004.

d. *CP-1159,* "A Predictive Capability for the Source Terms of Residual Energetic Materials from Burning and/or Detonation Activities" (Charles Kolb, Aerodyne). The objectives of this project were to define and model gaseous and particulate species formed by detonations. Range residue data was shared with this project. Results reported at the 2004 SERDP Symposium indicated that propellant residues and their combustion products predominate in the particulate emissions and that ablated metal alloys from the munition casing were also detected. This project was completed in 2004.

e. *CS-1395,* "Development and Application of a Physiological-Based Framework for Assessing the Biological Significance of Military Activities on Threatened and Endangered Animal Species" (Marshall Adams, Oak Ridge National Laboratory). The objective of this project is to develop and apply a bioassessment tool that can be used by natural resource managers to assess the fitness of threatened and endangered species (TES) populations by measuring a suite of sensitive and rapidly responding physiological indicators, which are related to reproductive and population-level fitness. For this project, a range characterization protocol was developed and applied that provided concentrations of energetic compounds at distance scales appropriate to the home range of two TES, one at Camp Shelby, MS, and the other at Eglin AFB, FL.

2. **Army Environmental Quality Technology Program.** Three studies conducted at the Environmental Laboratory, Vicksburg, MS concerned fate and transport processes for explosives. The first two work units were focused on explosives from unexploded ordnance (UXO) rather than from the more diffuse and diverse explosives residues that exist at firing ranges. The third work unit focused on propellants, smokes, and illuminants. Data contributed to the comprehensive database of process descriptors for ER-1155.

a. A835/301X/UX001 “Characterization and Mobilization of Unexploded Ordnance” to quantify chemical signatures emanating from UXOs under various environmental and geophysical conditions. The study was designed to provide the technical basis for chemical sensor development, for discrimination between UXOs and innocuous clutter, and for refinement in classification of detected UXO.
b. A835/309E/RE004 “Fate and Transport of Explosives Contaminants” to develop screening level and comprehensive fate and transport models and process descriptors for UXOs in soil, aquifer, and aquatic environments for use in the exposure phase of risk assessments.
c. AF25/309F/HF201 “Fate and Transport of Propellants, Smokes, and Illuminants,” to determine the state of the science concerning process descriptors for representatives of these classes of compounds.
d. Large-scale characterization of major contamination sources on military training ranges (Tom Jenkins, ERDC-CRREL). The objective of this work unit was to develop methods at the landscape scale for determining the types, numbers, physical dimensions, and distribution of large distributed sources of energetic compounds at various types of ranges.
e. Minimization of explosive residues in blow-in-place procedures (Judy Pennington, ERDC-EL). The objective of this work unit is to optimize BIP procedures while minimizing constituent contamination without compromising effectiveness and implementation ease. This project conducted in coordination with the CE Huntsville and conducted at Redstone Arsenal is heavily leveraged with ER-1155. This project will be completed in 2006.
f. Range and landscape level characterization methodology (Rose Kress, ERDC-EL). The objective of this work unit was to develop geospatial methods for predicting patterns of contaminant distribution at the landscape level.
g. Surface runoff of distributed source contaminants from soils: A laboratory simulation study (Cynthia Price, ERDC-EL). The objectives of this work unit were to describe movement of residues into the overland flow plane during rainfall/runoff events, to define stream routing relationships in surface runoff, and to develop soil infiltration and runoff extraction coefficients for modeling mass loading to surface and groundwater.
h. Development of a distributed source contaminant transport model for the Army Risk Assessment Model (ARAMS, Billy Johnson, ERDC-EL). The objective of this work unit was to develop a model to simulate

transport in the watersheds, rivers, streams, and groundwater linking a geographic information system (GIS) interface and best management plans to ARAMS.

i. Transport of explosives residues through the vadose zone (Judy Pennington, ERDC-EL). The objective of this work unit is to describe transport of RDX from solid explosives compositions on the soil surface through dissolution, degradation, and transport by developing process descriptors suitable for use in groundwater and transport models. This project will be completed in 2006.

3. **Defence Research and Development Canada – Valcartier (DRDC-Val).** The Director Land Environment (DLE) from the Canadian Head Quarters has tasked DRDC-Val scientists to perform research characterization of their main army training areas, to assess the impacts of live-fire training. Part of the work conducted within ER-1155 is strongly linked with this objective. ER-1155 includes partial funding for CFB Shilo and Gagetown and for Cold Lake Air Weapons Range for surface characterization while the hydrogeological portion of these studies is supported by DLE. Moreover, the DLE mandate includes the analysis of other types of range contaminants such as heavy metals, petroleum products, and radioactive compounds when appropriate. Just as data generated on U.S. ranges under ER-1155 are shared with DRDC-Val, so also are all of the data generated for Canadian studies shared with the United States. The DLE mandate included other training areas such as the one at Canadian Forces Base (CFB) Valcartier and results obtained at this training area will be added to the ER-1155 database. Future work at other Canadian training areas, such as Petawawa, Wainwright, or Suffield, will still be supported partly by DLE. On a yearly basis, approximately 30 percent of the funding has been contributed by the SERDP project. Finally, the Director General Environment (DGE), sponsors DRDC-Val for a small-scale UXO corrosion study. The scientific leader of this study has liaised with the Principal Investigator of SERDP CP-1226 to discuss the data that will be acquired and link the studies. DGE also sponsors work on the ecotoxicological properties of explosives, work that is closely linked with ER-1155. Finally, a new Sustain Research thrust was established in 2004 and projects were approved on the development of greener weapons, on the corrosion of munition casings, and on the study of the gaseous emissions from gun firing. These projects are led by DRDC scientists involved in ER-1155 and results will be shared with SERDP through the follow-on project ER-1481 "Characterization and fate of gun and rocket propellant residues on testing and training ranges."

4. **U.S. Army Alaska Directorate of Public Works.** The U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) has worked for several years for the U.S. Army Alaska Directorate of Public Works at Fort Richardson, the Donnelly Training Area (formerly Fort Greely), and Fort Wainwright. Some of this work was an outcome of the environmental impact statement (EIS) in support of the renewal of the lease of land from the public domain under the Military Lands Withdrawal Act (Public Law 106-65). As a portion of this EIS, the Army has pledged to implement a program to identify possible munitions contamination and evaluate the potential for surface water and groundwater contamination. In FY02 methods to collect representative samples at firing points were evaluated at the Donnelly Training Area ranges, including sampling at firing points. In FY03 sampling experiments were conducted at firing points within the Donnelly Training Area to evaluate various options for collection of representative samples in areas where 105-mm howitzers were fired using single-based propellants. These samples were also utilized to compare various subsampling methods to maintain representativeness though the subsampling step of analysis.
5. **U.S. Army Environmental Center (AEC) Range Sustainment Program.** The AEC (John Buck) and the Center for Health Promotion and Preventive Medicine (CHPPM, Barrett Borry) have also conducted a "Range Sustainment Program" to proactively ensure sustained training on ranges and to protect drinking water sources on active ranges. Project ER-1155 coordinated with this project and has shared site access with it whenever possible to benefit both efforts.
6. **UXO in marine environments.** The Naval Facilities Engineering Service Center, Port Hueneme, CA, and the Space and Naval Warfare Systems Center, San Diego, CA, are conducting a study in conjunction with ERDC Environmental Laboratory (EL) to determine toxicological and geochemical interactions of ordnance and explosives in marine environments. Geochemical studies have determined dissolution, adsorption, and transformation rates of explosives in saline systems. Process descriptors determined in freshwater were compared with those determined in salt water to determine what descriptors are affected by salinity. The toxicology studies will focus on bioavailability, toxicity, bioaccumulation, trophic transfer, and tissue concentrations of explosives in marine organisms, and the toxic effects of mixtures of explosives. This project will be completed in 2006.

7. **Range characterization at a missile demolition range.** Hill AFB, UT, destroys out-of-date missiles from the various services using either open burning or open detonation. Environmental personnel at Hill AFB requested assistance from ERDC to develop a range characterization protocol appropriate to the scale of these activities. ERDC applied the technology developed in ER-1155 to the problem and provided Hill AFB with the sample collection protocol and the analytical processing and analysis techniques to allow collection and analysis of representative soil samples to assess energetic residues concentrations within this range.
8. **Previous Main Charge Disruptor (MCD) testing.** Creation of low-order detonations has special application where disposal of munitions by BIP demolition requires consideration of the safety of personnel or of the integrity of nearby property. A previous Naval Explosive Ordnance Disposal Technology Division (NAVEOD) program, "Developmental Testing of the Main Charge Disruptor (MCD)," was designed to reduce the hazard of removing such munitions by developing methods to detonate the munitions without releasing maximum energy. Testing was performed with the MCD against pipe bombs and projectile munitions (Baker et al. 1997). Phase A involved testing of the MCD tool against Mk 80 series and penetrator bombs (Blankenbiller 1999). Additional testing (Phase B) was performed in November 1999 with the MCD tool against more Mk 80 series bombs (Gill 1999). In May 2000 three MCD candidates were tested against a variety of simulated UXOs containing Tritonal, PBXN-109, Composition H-6, and Composition B (Baker et al. 2000). Included in the list of simulated UXOs was the 155-mm, 105-mm, and 8-in. projectile. The MCD tool chosen from the May 2000 testing demonstrated the ability to achieve various yields based on placement and explosive loading of the tool. Application of the MCD tool for studying residues from low-order detonations of artillery projectiles for project CP-1155 was based on these previous tests.

## Additional information and reports

A bibliography of journal articles, technical reports, and presentations generated during execution of project ER-1155 is included at Appendix A. Web sites where reports may be available include the following:

ER-1155 (http://el.erdc.usace.army.mil/el/serdp/)

ERDC CRREL (http://www.crrel.usace.army.mil/products/products.html)

DRDC-Val (http://www.valcartier.drdc-rddc.gc.ca)

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# 2 Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges

## Introduction

Over the past few years a series of field experiments has been conducted at 27 military installations in the United States and Canada (Figure 2-1). The objectives of these studies have been to identify the types of energetic residues present in the surface soils at various types of military live-fire training ranges and to estimate concentrations and distributions of these residues. The concern is that these surface residues could serve as sources for off-site migration of various compounds in groundwater or surface water. Until now most of the results from these studies have been available only in U.S. and Canadian government reports for individual (occasionally several) installations. It is the objective of this report to summarize and synthesize the huge body of knowledge that has been gained from these studies. Also, research to develop approaches to remediate ranges is underway, often with an incomplete understanding of the nature of the problems to be addressed.

For the purposes of this discussion energetic compounds are defined as those chemicals used in military explosives and propellants. These include 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine (HMX), which are used as high explosives (HEs), and nitrocellulose (NC), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), and nitroguanidine (NQ), which are used in gun and rocket propellants. Residues of these compounds are deposited onto surface soils, generally as particles (HEs and propellants) or fibers and slivers (propellants) as troops conduct live-fire training.

A number of different types of live-fire and demolition ranges have been studied at U.S. and Canadian military bases. These include hand grenade, rifle grenade, anti-tank rocket, demolition, tank firing, mortar, artillery, C-130 gunship, and bombing ranges. Training at these ranges is conducted with different types of munitions that contain a variety of energetic formulations. At many ranges, the area where the weapon is fired is separate from the impact area where detonations occur. Generally, energetic

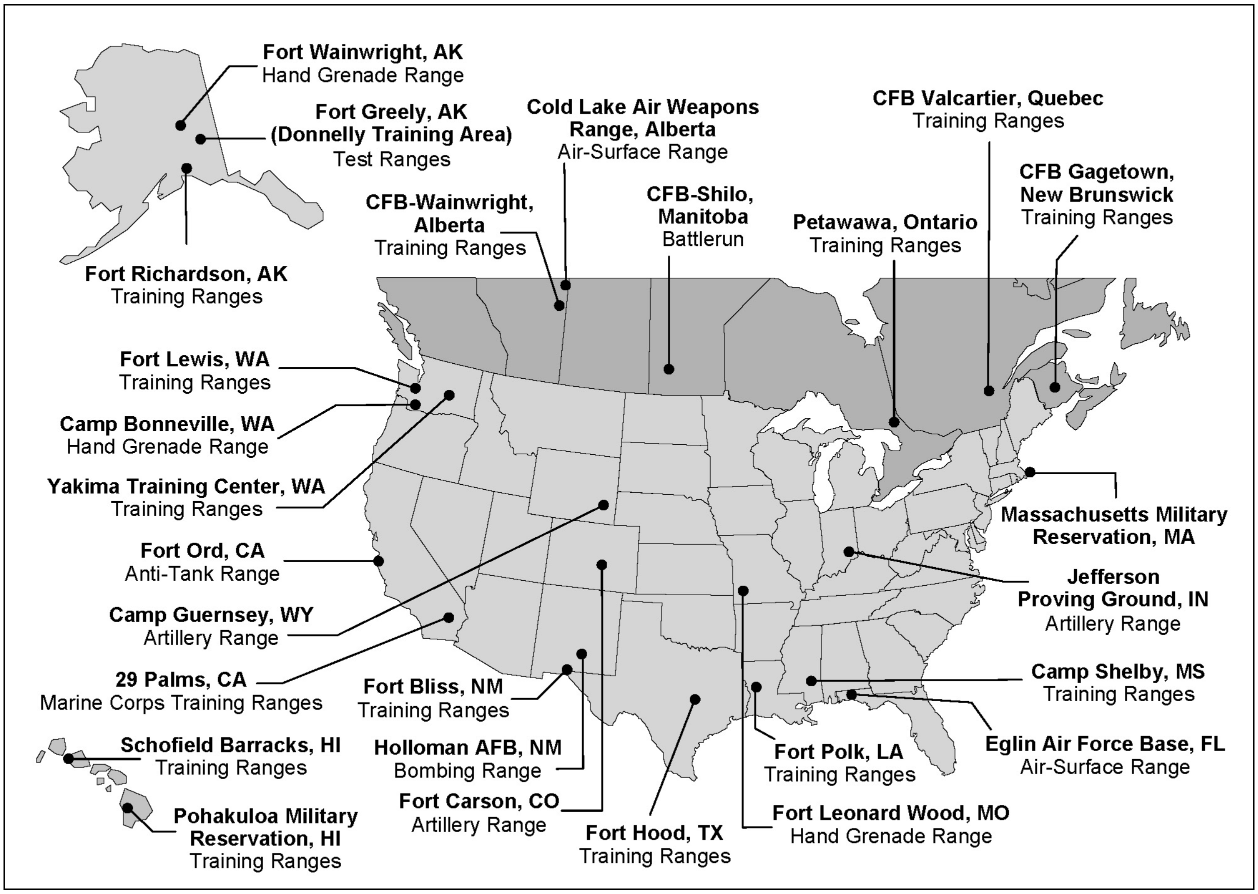


Figure 2-1. U.S. and Canadian installations where field experiments were conducted.

residues at the firing points are composed of compounds used in propellant formulations, whereas residues at the impact areas are compounds used as HEs in the munition warheads, or white phosphorus (WP) from smoke rounds.

## Methods

### Soil sampling

Soil sampling methods for the various types of ranges have evolved as the understanding of the nature of deposition and distribution of energetic compounds has improved. Generally, stainless steel scoops were used to sample noncohesive soils such as sands and gravels, and specially designed corers were used in more cohesive soils such as silts and clays, and where vegetation is present (M. R. Walsh 2004). Because of the presence of UXOs at many of these ranges, soil sampling often was limited to surface and near-surface depths. Because deposition of residues occurs as particles and fibers at the surface, this was not considered a serious limitation; furthermore, soil-profiling data indicate that the major residue concentrations are nearly always in the top few centimeters of soil.

When soil sampling was conducted to estimate the mean concentration of a compound for a given area, multi-increment composite samples were found to be essential for obtaining representative samples. This was necessitated by the high degree of spatial heterogeneity found for residues of all types of energetic compounds (M. E. Walsh et al. 1997, 2004; Jenkins et al. 1999, 2004a, 2004b, 2005; Hewitt et al. 2005) and the excessive cost associated with analyzing very large numbers of discrete samples. The numbers of increments or mass in the sample needed to provide a reliable estimate of the mean concentration for various ranges differs depending on the nature of the residue deposition (Jenkins et al. 2004a, 2004b, 2005; Hewitt et al. 2005; M. E. Walsh et al. 2005) and the size of the area being characterized. Generally 30 to 50 increments were found to be adequate for 10-m × 10-m (100-$m^2$) areas, and 50 to 100 increments were adequate for 100-m × 100-m (10,000-$m^2$) areas. Discrete samples were used to characterize residues near ruptured items and in areas where solid explosives were observed on the surface, or when doing near-surface depth profiling near high-concentration sources.

### Sample processing and subsampling

As with sample collection, various methods of sample processing and subsampling were used during these studies as more knowledge was gained of the nature of these residue-containing soils. Because of the particulate nature of the residues, compositional heterogeneity can be a significant component of overall uncertainty (Pitard 1993). Compositional heterogeneity has been defined by Pitard (1993) as the heterogeneity that is inherent to the composition of each particle making up the sample. As a result, the sample processing methodology specified in SW846 Method 8330 (USEPA 1994) was found to be inadequate in several respects for quantitative analysis of energetic compounds in soils from training ranges. Two major changes proved necessary. The first change was to increase the sieve size used during sample processing from #30 (0.595 mm) to #10 (2 mm). For example, it was found that in soils from the Fort Lewis hand grenade range, about half of the RDX mass and more than half of the TNT mass was in the size fraction greater than 0.595 mm and less than 2 mm (Table 2-1). Hewitt et al. (2004) and M. E. Walsh et al. (2005) reported

Table 2-1. Comparison of energetic residues in various particle size ranges for soil samples from the Fort Lewis, WA, hand grenade range.

| Sample | TNT Concentration, mg/kg | | | RDX Concentration, mg/kg | | |
|---|---|---|---|---|---|---|
| | >2 mm | <2 to >0.595 mm | <0.595 mm | >2 mm | <2 to >0.595 mm | <0.595 mm |
| 1 | 0.19 | 1.36 | 0.81 | 0.02 | 0.05 | 0.13 |
| 2 | 0.21 | 21.0 | 2.71 | 0.02 | 6.36 | 1.11 |
| 3 | 0.36 | 3.28 | 0.55 | 0.02 | 0.71 | 0.29 |
| 4 | 0.18 | 0.42 | 2.41 | 0.01 | 0.71 | 0.29 |
| 5 | 0.30 | 5.72 | 1.65 | 0.02 | 0.04 | 0.35 |
| 6 | 0.03 | 16.0 | 0.04 | 0.03 | 0.07 | 0.38 |
| 7 | 0.11 | 3.25 | 0.34 | 0.03 | 6.73 | 1.86 |
| 8 | 0.10 | 0.05 | 0.08 | 0.02 | 0.05 | 0.15 |
| 9 | 0.29 | 3.08 | 0.06 | 0.03 | 6.62 | 0.68 |
| 10 | 0.05 | 0.05 | 0.03 | 0.02 | 0.07 | 0.13 |
| Sample | Mass of TNT, mg[1] | | | Mass of RDX, mg[1] | | |
| | >2 mm | <2 to >0.595 mm | <0.595 mm | >2 mm | <2 to >0.595 mm | <0.595 mm |
| 1 | 0.05 | 0.31 | 0.65 | 0.01 | 0.01 | 0.01 |
| 2 | 0.05 | 5.11 | 1.94 | 0.01 | 1.54 | 0.79 |
| 3 | 0.07 | 0.70 | 0.39 | 0.004 | 0.15 | 0.20 |
| 4 | 0.04 | 0.10 | 1.53 | 0.003 | 0.01 | 0.18 |
| 5 | 0.05 | 1.23 | 1.19 | 0.004 | 0.01 | 0.26 |
| 6 | 0.01 | 4.03 | 0.03 | 0.01 | 0.02 | 0.27 |
| 7 | 0.03 | 0.98 | 0.04 | 0.01 | 2.03 | 2.20 |
| 8 | 0.03 | 0.01 | 0.078 | 0.005 | 0.01 | 0.13 |
| 9 | 0.06 | 0.77 | 0.06 | 0.01 | 1.65 | 0.59 |
| 10 | 0.02 | 0.02 | 0.03 | 0.01 | 0.03 | 0.13 |

[1] Calculated from the concentrations of TNT and RDX times the mass of soil in the various particle size ranges.

similar findings for soils containing propellant residues. Thus, in the most recent work, 2-mm (10-mesh) sieves were used to separate oversized material from the air-dried soil (Jenkins et al. 2004a, 2004b).

Secondly, Walsh et al. (2002) demonstrated that mechanical grinding prior to subsampling was effective at significantly reducing the subsampling relative standard deviation, sometimes by as much as two orders of magnitude. After sieving, soils from impact areas were ground for 60 sec on a Labtech Essa LM2 (Labtech Essa Pty. Ltd., Bassendean, WA, Australia) puck mill grinder. For soils from firing points where the residues are often present as fibers, it was necessary to grind for 5 minutes in

1-minute increments, allowing a short cooling period between grinds (M. E. Walsh et al. 2005). After grinding, samples were mixed thoroughly and spread to form a 1-cm-thick layer, and subsamples were obtained by collecting at least 30 increments randomly from the ground material to obtain a subsample mass of about 10 g (Jenkins et al. 2005).

### Sample analysis

The 10-g portions of soil were extracted with 20 mL of acetonitrile using either an ultrasonic bath or shaker table for 18 hours. The extracts were then analyzed using either reversed-phase high-pressure liquid chromatography (RP-HPLC) Method 8330 (USEPA 1994) or gas chromatography with electron capture detection (GC-ECD) Method 8095 (USEPA 1999). Many samples were analyzed using both methods to provide increased confidence in the identity of detected analytes and to provide analytical results for various energetic compounds that can differ in concentration by several orders of magnitude within the same sample.

A few samples were analyzed by other methods such as gas chromotometry/mass spectrometry (GC/MS) to identify the presence of other organics, but the main objective of this work was to determine concentrations of the energetic compounds and their major environmental transformation products. Thus, the suite of target analytes included the major nitroaromatic and nitramine HEs used by the Army (TNT, RDX, HMX, tetryl, pentaerythritol tetranitrate [PETN]), the major monomeric propellant-related compounds (NG, 2,4DNT, 2,6DNT), and the major environmental transformation products that are known to form in aerobic surface and near-surface soils (1,3,5-trinitrobenzene [TNB], 2-amino-4,6-dinitrotolene [2ADNT], and 4-amino-2,6-dinitrotoluene [4ADNT]). The mono nitro compounds (nitrobenzene [NB], 2-nitrotoluene [2NT], 3-nitrotoluene [3NT], and 4-nitrotoluene [4NT]) are target analytes of Method 8330 and Method 8095 and would have been detected if present, but none were detected in soils from these ranges. In samples containing percent levels of TNT, unsymmetrical isomers of trinitrotoluene and other isomers of DNT are detectable, but no attempt was made to quantify these trace manufacturing impurities. In a recent study by Clausen et al. (2004), in which more than 15,000 soil samples from the MMR were analyzed, these target analytes constituted the major detectable organic compounds.

## Results and discussion

The types of ranges studied for each installation where field experiments were conducted are discussed in the following sections and are organized by range type. This organization was used because different munitions containing different energetic compounds are used at the various types of ranges, and the nature of the deposition and the resulting distribution patterns differ as well.

### Hand grenade ranges

Hand grenade ranges are generally only a few hectares in size and, because of the large number of individual detonations in a small area, are poorly vegetated. These ranges often have several training bays from which soldiers threw grenades. Most of the detonation craters lie at distances between 15 and 35 m from the throwing pits. The surfaces of these ranges vary from gravels and sands to clays depending on the location. The management practices used at the various installations also vary significantly. At some ranges, craters are filled in and the surface is leveled frequently; at others, the craters are left intact.

The majority of training at hand grenade ranges in the United States is with M67 fragmentation grenades, in which the explosive charge is 185 g of Composition B. In Canada, training is generally with C-13 fragmentation grenades that have the same specifications as the M67. Composition B is 60 percent military-grade RDX, 39 percent military-grade TNT, and 1 percent wax. Military-grade RDX contains about 90 percent RDX and 10 percent HMX. Military-grade TNT contains about 99 percent 2,4,6-TNT and a few tenths of a percent of other isomers of TNT and DNT (Leggett et al. 1977).

Because discrete samples in close proximity from these ranges varied by several orders of magnitude (Jenkins et al. 2001), two types of studies were conducted to improve reproducibility. First the use of multi-increment samples as a means of overcoming the contribution of distributional heterogeneity was studied. Distributional heterogeneity has been defined by Pitard (1993) as the heterogeneity that is inherent in the manner in which the particles are scattered. A study at the Fort Wainwright hand grenade range was conducted where five discrete samples and five sets of replicate multi-increment samples of 5, 10, 20, and 40 increments each were collected within a 10-m × 10-m area. The results for RDX, HMX, TNT, and TNB are presented in Table 2-2.

Table 2-2. Concentrations of energetic residues for discrete and multi-increment surface soil samples at Fort Wainwright, AK, hand grenade range.

| | | Concentration Range, mg/kg | | | |
|---|---|---|---|---|---|
| Sample Type | N | HMX | RDX | TNT | TNB |
| Discrete | 5 | 0.38–3.5 | 0.78–24 | 0.02–3.7 | 0.02–0.41 |
| 5-increment | 5 | 1.3–2.1 | 6.0–14 | 0.80–1.8 | 0.09–0.21 |
| 10-increment | 5 | 2.0–4.5 | 11–28 | 0.68–2.7 | 0.14–0.29 |
| 20-increment | 5 | 1.7–2.3 | 7.1–14 | 0.54–2.5 | 0.10–0.19 |
| 40-increment | 5 | 1.5–2.1 | 6.5–13 | 0.35–1.9 | 0.09–0.18 |

RDX concentrations for the five discrete RDX values ranged from 0.78 to 24 mg/kg whereas concentration for the 5, 10, 20, and 40 multi-increment samples ranged from 6.0 to 14, 10 to 28, 7.1 to 14, and 6.5 to 13 mg/kg, respectively. This reduction in the range of values as the number of increments increased was observed for the three other analytes as well. Subsequent sampling at hand grenade ranges utilized multi-increment samples with increments ranging from 20 to 100, and this approach resulted in a great improvement in reproducibility of replicate samples compared with characterization using discrete samples. At CFB Petawawa, triplicate replicate 100-increment samples of the entire range resulted in mean concentrations of RDX, HMX, and TNT of 0.63 ± 0.25, 0.22 ± 0.07, and 0.14 ± 0.08 mg/kg, respectively. For purposes of estimating the mass of residues present at hand grenade ranges, these multi-increment sample estimates should be adequate in most cases.

A total of 11 active and 2 closed hand grenade ranges was sampled (Table 2-3). The old Castle range at CFB Gagetown was active when it was first sampled in 1998 (Dube et al. 1999), but was inactive when sampled in 2002 and 2003 (Thiboutot et al. 2003). The target analytes detected at these ranges include RDX, TNT, HMX, TNB, 2ADNT, and 4ADNT. Of the analytes found, RDX usually is present at the highest concentration, with mean surface concentrations ranging from < 0.01 to 51 mg/kg.

The hand grenade ranges appear to fall into two groups; one group of six ranges had concentrations of RDX less than 0.12 mg/kg and the other group of seven ranges had concentrations between 0.45 and 51 mg/kg

(Table 2-3). Studies conducted by Hewitt et al. (2003) have estimated that about 25 µg of RDX and less than 1 µg of TNT are deposited on the soil surface when a hand grenade detonates as designed.

Table 2-3. Summary of results for energetic compounds detected in surface soils at hand grenade ranges.

| Installation | Year Sampled | Samples Analyzed | Mean Concentration, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HMX | RDX | TNT | TNB | 4ADNT | 2ADNT |
| Fort Lewis, WA[1,3] | 2000 | 23[1] | 1.8 | 7.5 | 9.3 | 0.05 | 0.15 | 0.13 |
| | 2001 | 5[2] (50) | 1.0 | 4.4 | 1.5 | ND[3] | ND | ND |
| Fort Richardson, AK[1,3] | 2000 | 27[1] | 0.02 | 0.08 | 0.03 | ND | 0.01 | 0.01 |
| Camp Bonneville, WA[2] | 2000 | 48[1] | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fort Leonard Wood, MO[1] | 2001 | 18[2] (30) | 0.19 | 0.45 | <0.01 | <0.01 | <0.01 | <0.01 |
| CFB Shilo, MB[4,7] | 2001 | 15[2] (20) | 0.05 | 0.71 | 0.06 | <0.01 | 0.02 | 0.02 |
| Fort Wainwright, AK[4] | 2002 | 25[2] (1, 5, 10, 20, 40) | 2 | 11 | 1.2 | 0.15 | ND | ND |
| Schofield Barracks, HI[4] | 2002 | 3[2] (30) | 9.1 | 51 | 36 | 0.28 | 0.40 | 0.03 |
| Pohakuloa Training Center, HI[4] | 2002 | 7[2] (30) | 0.53 | 5.6 | 0.78 | <0.01 | <0.01 | <0.01 |
| CFB Gagetown, New Brunswick | | | | | | | | |
| Old Castle Range[5,8] | 2002 | 5[2] (30) | 0.02 | 0.12 | 0.12 | <0.01 | <0.01 | <0.01 |
| New Castle Range[4,9] | 2002 | 5[2] (30) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| New Castle Range[4,10] | 2003 | 15[2] (25) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Fort Polk, LA[4] | 2003 | 2[2] (30) | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| CFB Petawawa, ON[4] | 2004 | 9[2] (25, 100) | 0.18 | 0.65 | 0.16 | <0.01 | <0.01 | <0.01 |

[1] Discrete samples.

[2] Multi-increment samples with (n) increments per sample.

[3] Not determined.

[4] Active ranges.

[5] Closed ranges.

[6] Jenkins et al. 2001.

[7] Ampleman et al. 2003b.

[8] Dube et al. 1999.

[9] Thiboutot et al. 2003.

[10] Thiboutot et al. 2004.

The relatively high concentrations of RDX, HMX, and TNT in the surface soils at Fort Lewis, Fort Wainwright, Schofield Barracks, and Pohakuloa (and probably those at Fort Leonard Wood, CFB Shilo and CFB Petawawa as well) cannot be explained by fragmentation grenades that detonated as designed. At all of these locations, partially detonated carcasses of M67 (or C13) grenades (Figure 2-2) were found. In several instances, chunks of the HE fill were observed next to these carcasses, and the inside surfaces of these grenades were coated with HE. It is not certain whether these partial detonations occurred when the rounds were thrown or occurred when duds (grenades that did not detonate due to malfunction) were blown in place by explosives ordnance disposal (EOD) technicians using C4 explosive (91 percent RDX). In either case, the high concentrations of residues observed at these seven ranges are believed to be due to these partial detonation events.

a. Low-order hand grenade carcass.

b. Pieces from a low-order grenade.

Figure 2-2. Partially detonated grenade carcass and pieces from a low-order grenade found at Fort Lewis hand grenade range.

Once a partial detonation takes place, the multitude of normal high order detonations tends to disperse these residues across the range as usage continues. These partial detonations must be rare because about half of the ranges studied had mean surface concentrations of less than 0.12 mg/kg; residue concentrations in this concentration range could have originated from the thousands of high-order detonations that occur annually at these ranges.

It is interesting that the mean concentration of RDX at the old Castle range at CFB Gagetown was 5.6 mg/kg when it was sampled as an active range in 1998 (Dube et al. 1999), but the mean concentration was only 0.12 mg/kg after it had been closed and was resampled in 2002 (Thiboutot et al. 2003).

In most cases, the highest concentrations of energetic compounds reside in the top few centimeters of soil. For example, at Fort Lewis where the surface is left undisturbed, 16 discrete sample pairs of surface soil and soil from a 10-cm depth were collected in July 2001 at locations ranging from 15 to 25 m from the throwing pit (Jenkins et al. 2001). The mean concentrations were 10.8 and 12.5 times greater in surface soils than at the 10-cm depth for RDX and HMX, respectively, and about 49 times greater for TNT in the surface relative to the 10-cm depth (Table 2-4). Depending on the management practices for a given range, however, residues can be deeper in the soil profile. For example at Fort Leonard Wood, the surface of the range is disked periodically and the concentrations of RDX, TNT, and HMX were similar from the surface to a depth of 11 cm (Table 2–4). Soil samples were not collected at greater depths at these sites because of the fear of encountering live, undetonated hand grenades that had become buried by subsequent detonations.

Table 2-4. Concentrations of energetic residues at various depths at the Fort Lewis and Fort Leonard Wood hand grenade ranges.

| Soil Depth, cm | Mean Concentration, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | TNB | 4ADNT | 2ADNT |
| Fort Lewis, WA | | | | | | |
| 0–1.5 | 1.8 | 7.5 | 9.3 | 0.05 | 0.15 | 0.13 |
| 10.0–12.5 | 0.14 | 0.69 | 0.19 | 0.02 | 0.06 | 0.08 |
| Fort Leonard Wood, MO | | | | | | |
| 0–1.5 | 0.52 | 0.31 | <0.01 | 0.02 | <0.01 | <0.01 |
| 1.5–3.0 | 0.83 | 0.81 | <0.01 | 0.04 | <0.01 | <0.01 |
| 3.0–5.0 | 1.0 | 0.42 | <0.01 | 0.03 | <0.01 | <0.01 |
| 5.0–7.0 | 0.54 | 0.57 | <0.01 | 0.02 | <0.01 | <0.01 |
| 7.0–11.0 | 0.29 | 0.36 | 0.05 | 0.02 | <0.01 | <0.01 |

### Anti-tank rocket range impact areas

Anti-tank rocket ranges are several hundred hectares in size and covered with low growing vegetation due to the necessity of maintaining a line-of-sight for training. Targets are usually derelict armored vehicles that are placed downrange at distances of 100 m or more from the firing points. The weapon most often fired at these ranges is the 66-mm M72 light anti-tank weapon (LAW). This item (Figure 2-3) contains M7 double-base propellant and the warhead contains 0.3 kg of the melt-cast explosive octol with either a tetryl or RDX booster, depending on the date of manufacture. M7 propellant for the LAW rocket contains 54.6 percent NC, 35.5 percent NG, 7.8 percent potassium perchlorate, 0.9 percent ethyl centralite, and 1.2 percent carbon black. Octol is composed of 70 percent HMX and 30 percent TNT.

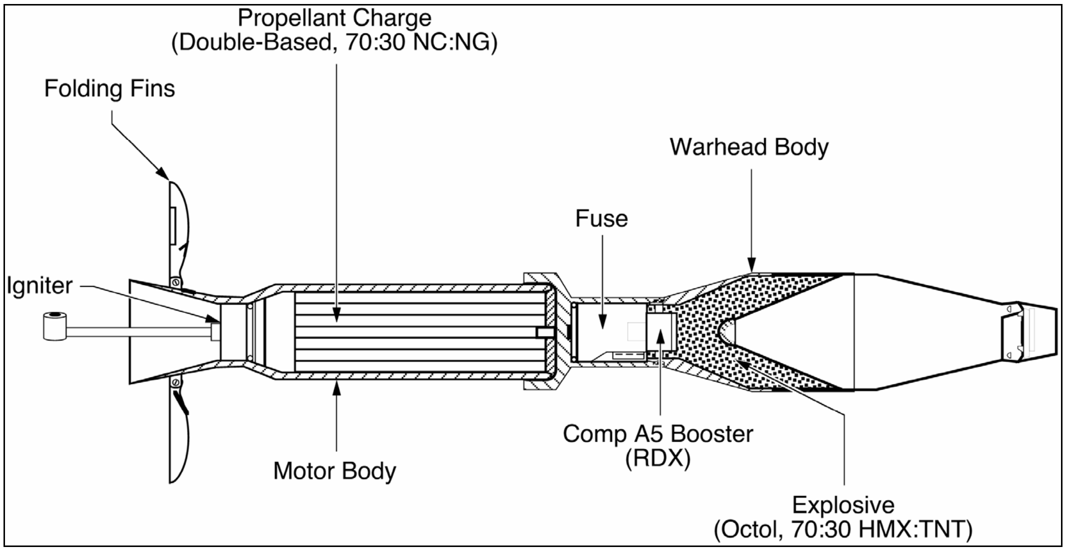


Figure 2-3. Diagram of 66-mm M72 LAW rocket.

At some ranges, practice rounds are fired that contain propellant but do not contain octol. Field experiments were conducted at one closed and seven active anti-tank rocket ranges, including Fort Ord, CA; CFB Valcartier, Quebec; Yakima Training Center, WA; Western Area Training Center (WATC) Wainwright, Alberta; Fort Bliss, NM; CFB Gagetown, New Brunswick; Pohakuloa Training Center, HI; and CFB Petawawa, Ontario (Table 2-5).

Table 2-5. Concentrations of energetic compounds detected in surface soils adjacent to targets at anti-tank rocket ranges.

| Installation[1] | Year Sampled | Samples Analyzed | Mean Concentration, mg/kg | | | | |
|---|---|---|---|---|---|---|---|
| | | | HMX | RDX | TNT | 4ADNT | 2ADNT |
| CFB Valcartier, QC[2,3,4] | 1995 | 16[5] | 803 | 4.6 | 24 | <0.1 | <0.1 |
| | 1995 | 5[5] | 399 | 0.76 | 3 | <0.1 | <0.1 |
| | 1996 | 20[5] | 662 | <0.1 | 4 | <0.1 | <0.1 |
| | 2003 | 4[6] (30) | 898 | 2.8 | 7 | <0.1 | <0.1 |
| WATC Wainwright, BC[2,3] | 1997 | 11[5] | 987 | 5.3 | 126 | <0.1 | <0.1 |
| Fort Ord, CA[7,8] | 1997 | 8[9] | 307 | 0.25 | 0.2 | 0.69 | 0.55 |
| CFB Gagetown, New Brunswick[2,4] | 1998 | 10 | 680 | <1 | 4 | <0.1 | <0.1 |
| | 2002 | 5[6] | 874 | 0.5 | 6 | 0.8 | 0.7 |
| | 2003 | 8[6] | 489 | 0.5 | 2 | 0.4 | 0.5 |
| Yakima Training Center, WA[2,10] | 2001 | 6[6] (30) | 23 | 0.8 | 0.04 | 0.05 | 0.12 |
| CFB Petawawa, Ontario[2] | 2004 | 3[6] (50) | 745 | 0.32 | 73 | <0.1 | <0.1 |

[1] Impact areas at Pohakuloa and Fort Bliss anti-tank ranges were not sampled.
[2] Active ranges.
[3] Thiboutot et al. 1998.
[4] Jenkins et al. 2004a.
[5] Composite samples.
[6] Multi-increment samples with (n) increments per sample.
[7] Closed range.
[8] Jenkins et al. 1998.
[9] Discrete samples.
[10] Pennington et al. 2002.

The primary residue detected at anti-tank rocket range impact areas is HMX with concentrations in surface soils adjacent to targets generally in the hundreds of mg/kg (Table 2-5). TNT, RDX, 4ADNT, and 2ADNT are often detectable as well, but the concentrations are at least several orders of magnitude lower. HMX concentrations decline as the distance from the target increases (Figure 2-4).

Observations from site inspections indicate that LAW rockets frequently rupture upon impact without detonating, thereby depositing crystalline explosive over the soil surface. This deposition is thought to be the major source of explosives residues at the impact areas of these ranges. For example, soil samples were collected next to a ruptured M72 rocket at 0- to 0.5-cm, 2- to 6-cm, and 6- to 10-cm depths at Yakima Training Center, WA. The concentration of HMX, TNT, and RDX declined from 10400, 358, and 46 mg/kg at the 0- to 0.5-cm depth, respectively, to 49, 1.7, and 1.5 mg/kg at 6- to 10-cm depth (Pennington et al. 2002).

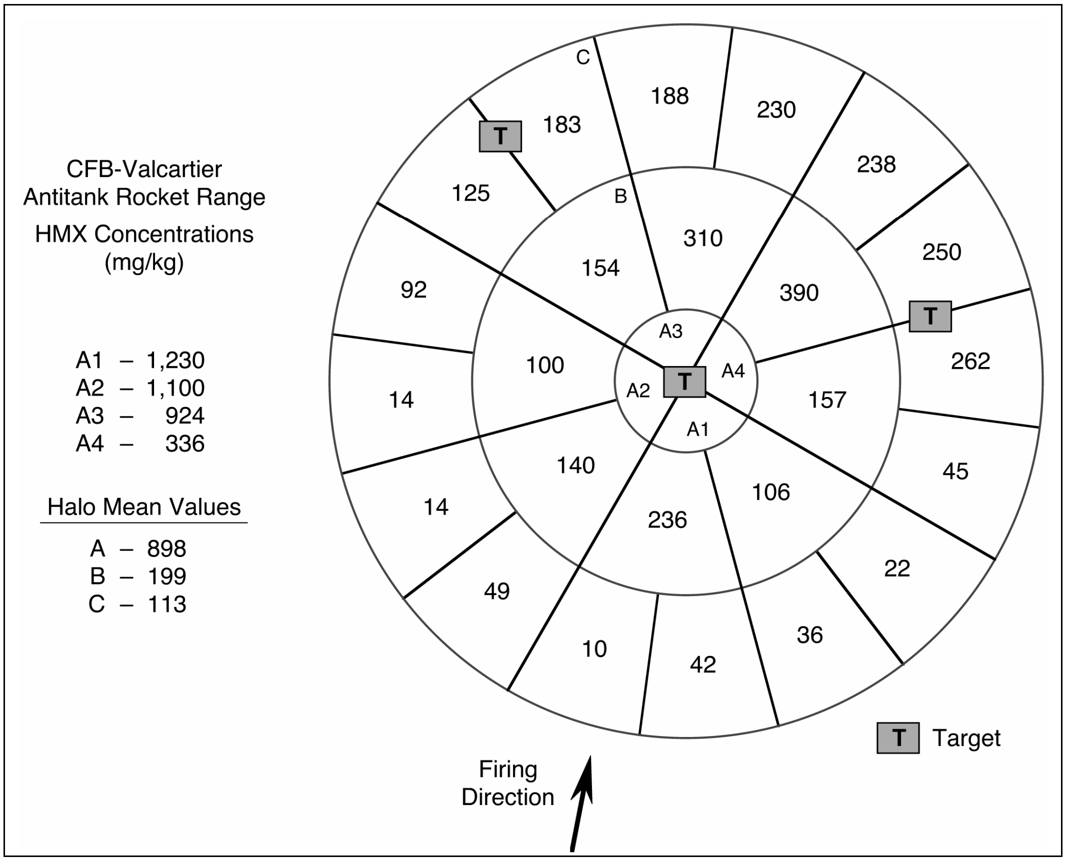
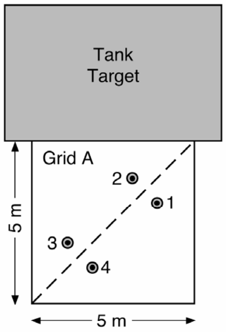


Figure 2-4. HMX concentrations at the target area of CFB Valcartier anti-tank rocket range. (The position of the target is shown with a T.)

Because the aqueous solubility of HMX is small (about 4–5 mg/L at 25 °C), HMX tends to accumulate on the surface while the more soluble TNT (about 150 mg/L) dissolves, becomes associated with soil cation exchange sites, and undergoes environmental transformations (McCormick et al. 1976). The amino transformation products of TNT can covalently bind to soil organic matter, thereby becoming immobilized (Thorn et al. 2002). The HMX that slowly dissolves does not strongly interact with soils and can be carried through the vadose zone to underlying groundwater aquifers. In most cases concern over the possible presence of buried UXOs has limited the collection of deep soil cores; however, soil samples were collected at the Fort Ord, CA, anti-tank rocket range to a depth of 120 cm (Figure 2-5). In this case, HMX was detectable at concentrations generally < 1 mg/kg as deep as 120 cm whereas TNT, RDX, and amino transformation products of TNT were not detected at depths below 15 cm (Jenkins et al. 1998). Similar results were obtained for depth samples at other sites, although samples usually were not collected at depths below 15 cm.



**Sample 3**

| Sample Depth | Concentrations (mg/kg) HMX | RDX | TNT | 4ADNT | 2ADNT |
|---|---|---|---|---|---|
| 0 – 15 cm: | 479 | 0.2 | 0.2 | 0.4 | 0.2 |
| 15 – 30 cm: | 4.3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 30 – 45 cm: | 1.3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 45 – 60 cm: | 0.2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 105 –120 cm: | 2.0 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |

**Sample 2**

| Sample Depth | Concentrations (mg/kg) HMX | RDX | TNT | 4ADNT | 2ADNT |
|---|---|---|---|---|---|
| 0 – 15 cm: | 302 | 0.6 | 0.1 | 1.2 | 1.0 |
| 15 – 30 cm: | 1.0 | 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 30 – 45 cm: | 0.4 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 45 – 60 cm: | 0.2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 105 –120 cm: | 0.4 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |

**Sample 4**

| Sample Depth | Concentrations (mg/kg) HMX | RDX | TNT | 4ADNT | 2ADNT |
|---|---|---|---|---|---|
| 0 – 15 cm: | 136 | 0.1 | 0.1 | 0.7 | 0.6 |
| 15 – 30 cm: | 0.6 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 30 – 45 cm: | 0.4 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 45 – 60 cm: | 0.3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 105 –120 cm: | 0.7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |

**Sample 1**

| Sample Depth | Concentrations (mg/kg) HMX | RDX | TNT | 4ADNT | 2ADNT |
|---|---|---|---|---|---|
| 0 – 15 cm: | 273 | 0.5 | 0.1 | 1.1 | 0.9 |
| 15 – 30 cm: | 0.7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 30 – 45 cm: | 0.7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 45 – 60 cm: | 0.7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| 105 –120 cm: | 7.0 | < 0.1 | < 0.1 | 0.1 | 0.1 |

Figure 2-5. Concentrations of energetic compounds with depth at Fort Ord anti-tank rocket range impact area.

Because anti-tank rockets are propelled all the way to the target, propellants can still be present when these rockets detonate upon impact. Small pieces of propellant are thereby spread over the soil surface in the area around the targets. These residues can be seen visually and NG has been detected at the impact areas at concentrations as high as 23 mg/kg.

As with hand grenade ranges, collection of reproducible samples at anti-tank ranges has been problematic (Jenkins et al. 1999). At CFB Valcartier, a 10-m × 10-m area just in front of a target was divided into one hundred 1-m × 1-m cells and a discrete sample was collected from the top 1.5 cm in each. The concentrations of HMX in these samples varied from 8 to 1,520 mg/kg, demonstrating the futility in trying to represent the mean concentration for decision units using discrete samples (Jenkins et al. 2004a, 2005). Multi-increment samples have been shown to provide more representative samples for characterizing the impact areas at these ranges (Jenkins et al. 2005). Here again, the use of machine grinding to reduce the soil particle size and an increase in sample size to 10 g were effective at minimizing the error due to compositional heterogeneity for samples collected at anti-tank range impact areas where HMX is the major contaminant (Walsh et al. 2002).

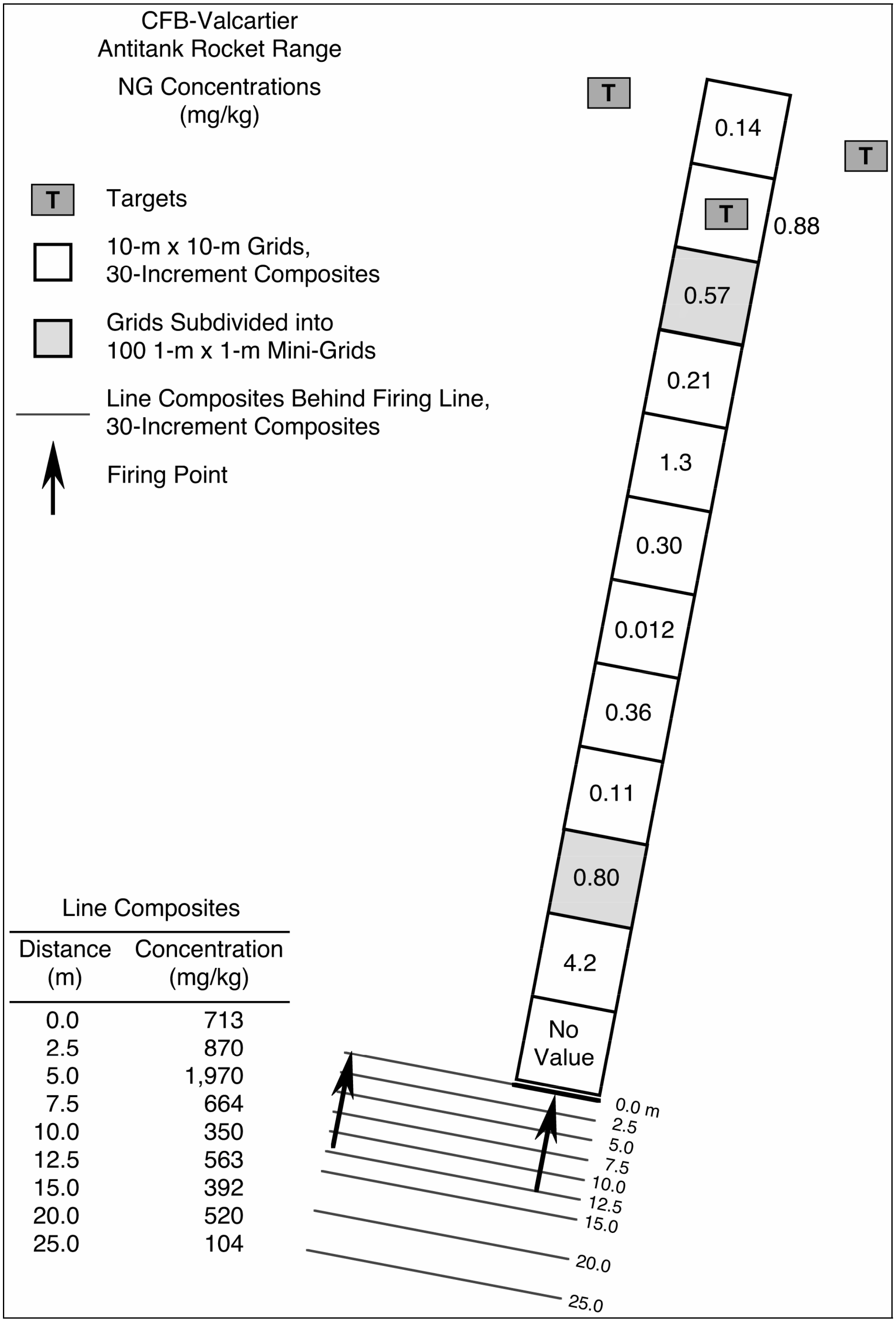
### Anti-tank range firing points

Sampling has been conducted at six anti-tank rocket range firing points (Table 2-6). In all cases, NG was the primary energetic compound detected, although only a few samples were analyzed for perchlorate. NG concentrations in surface soil samples from 0 to 25 m behind the firing line at CFB Valcartier were generally in the hundreds of mg/kg, whereas concentrations between the firing line and the target were generally much lower (Figure 2-6). Often a gravelly parking area is located behind the firing line at anti-tank rocket ranges and the soil was sampled at depths as great as 63 cm in this area at CFB Gagetown in 2003 (Thiboutot et al. 2004). In one soil profile, NG concentrations declined from 20 mg/kg in the surface 0- to 5-cm depth to 6.4 mg/kg at the 20- to 27-cm depth, and to a concentration of about 0.2 mg/kg from the 40-cm depth to as deep as 60 cm (Table 2-7). Surface concentrations as high as 11,300 mg/kg were found at this site (Thiboutot et al. 2003).

Table 2-6. Summary of results for nitroglycerin near firing points at active anti-tank rocket ranges.

| Installation | Year Sampled | Samples Analyzed | Mean NG Concentration, mg/kg | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | In Front | | | | | Behind | | | |
| | | | 0–10 m | 10–20 m | 20–30 m | 30–40 m | 40–50 m | 0–10 m | 10–20 m | 20–30 m | 30–40 m |
| Yakima Training Center, WA[1] | 2001 | 2 (30)[2] | 3 | NS[3] | NS | NS | NS | NS | NS | NS | NS |
| Schofield Barracks, HI[4] | 2002 | 4 (30)[2] | NS | NS | NS | NS | NS | 1,200 | 9.4 | NS | NS |
| CFB Gagetown, NB[5,6] | 2002 | 4 (30)[2] | 176 | 65 | NS | NS | 14 | 1,130 | NS | NS | NS |
| | 2003 | 15 (30)[2] | 160 | 160 | 87 | 55 | 12 | 4,700 | 2320 | 380 | 84 |
| Fort Bliss, NM[7] | 2002 | 10 (30)[2] | 1 | 0.5 | <0.1 | NS | NS | 1 | NS | NS | NS |
| CFB Valcartier, QC[8] | 2003 | 13 (30)[2] | NS | 4.2 | 0.8 | 0.1 | 0.4 | 910 | 490 | 104 | NS |
| CFB Petawawa, ON | 2004 | 8 (40)[2] | NS | NS | NS | NS | NS | 2240 | 380 | NS | NS |

[1] Pennington et al. 2002.
[2] Multi-increment samples with (n) increments.
[3] No sample collected.
[4] Hewitt et al. 2004.
[5] Thiboutot et al. 2003.
[6] Thiboutot et al. 2004.
[7] Pennington et al. 2003.
[8] Jenkins et al. 2004a.



Line Composites

| Distance (m) | Concentration (mg/kg) |
|---|---|
| 0.0 | 713 |
| 2.5 | 870 |
| 5.0 | 1,970 |
| 7.5 | 664 |
| 10.0 | 350 |
| 12.5 | 563 |
| 15.0 | 392 |
| 20.0 | 520 |
| 25.0 | 104 |

Figure 2-6. Concentrations of nitroglycerin in multi-increment soil samples in front of and behind the rocket firing line at CFB Valcartier anti-tank rocket range.

Table 2-7. Nitroglycerin concentrations in depth profile samples collected in front of and behind the firing point at Wellington Anti-tank Range at CFB Gagetown in 2003.

| Location | Soil Concentration, mg/kg |
|---|---|
| Front, Center of Firing Point, 10 m | NG |
| 0–5 cm | 11[1] |
| 5–7 cm | 15 |
| 7–11.5 cm | 6.5 |
| 11.5–13 cm | 0.06 |
| 13–18 cm | <d |
| 18–22 cm | 0.01 |
| 22–27 cm | <d |
| 27–31 cm | 0.02 |
| 31–35 cm | 0.02 |
| 35–39 cm | 0.01 |
| 39–42 cm | 0.00 |
| 42–47 cm | 0.00 |
| 47–52 cm | 0.01 |
| 52–57 cm | 0.01 |
| Behind, center of firing point, 10 m | |
| 0–5 cm | 20 |
| 5–10 cm | 14 |
| 10–20 cm | 0.50 |
| 20–27 cm | 6.4 |
| 27–35 cm | 5.8 |
| 35–39 cm | 0.32 |
| 39–42 cm | 0.23 |
| 42–47 cm | 0.15 |
| 47–50 cm | <d |
| 50–56 cm | 0.03 |
| 56–59 cm | 0.22 |
| 59–63 cm | 0.34 |

[1] Analysis by RP-HPLC (unshaded) and GC-ECD (shaded).

At CFB Valcartier, a 10-m × 10-m area 20–30 m in front of the firing line was subdivided into one-hundred 1-m × 1-m cells from which were collected a discrete surface sample (0–2.5 cm). NG concentrations ranged from 0.02 to 3.4 mg/kg, indicating once again that discrete samples should not be used to estimate energetic concentrations for areas (decision units) near firing points (Jenkins et al. 2004a). A set of 50 30-increment samples was simulated using random numbers from this set of 100 discrete samples. The values obtained ranged from 0.34 to 0.93 mg/kg (Jenkins et al. 2004a). The value for the 30-increment sample actually collected within this 10-m × 10-m area was 0.80 mg/kg, well within the range simulated. Clearly the use of a 30-increment sample to estimate the mean concentration within this area provides a much more reproducible estimate than one or a small set of discrete samples.

### Artillery ranges

Artillery ranges are the largest training ranges in the army inventory, covering an area of hundreds of square kilometers. Firing positions are often arranged around the circumference of the range with firing fans leading into the impact areas, generally positioned near the center of the range (Figure 2-7). In the past, fixed firing points were established, but with more modern mobile artillery, firing activities have become more diffuse as training has evolved to support a “shoot and scoot” strategy. Once fired, artillery and mortar rounds travel several kilometers before impacting in the general vicinity of targets. The flight path takes these rounds over an area referred to as the firing safety fan, where only a very few defective rounds impact. Often, this is the largest area of the range. Once the rounds arrive near targets, most rounds are set to detonate upon impact.

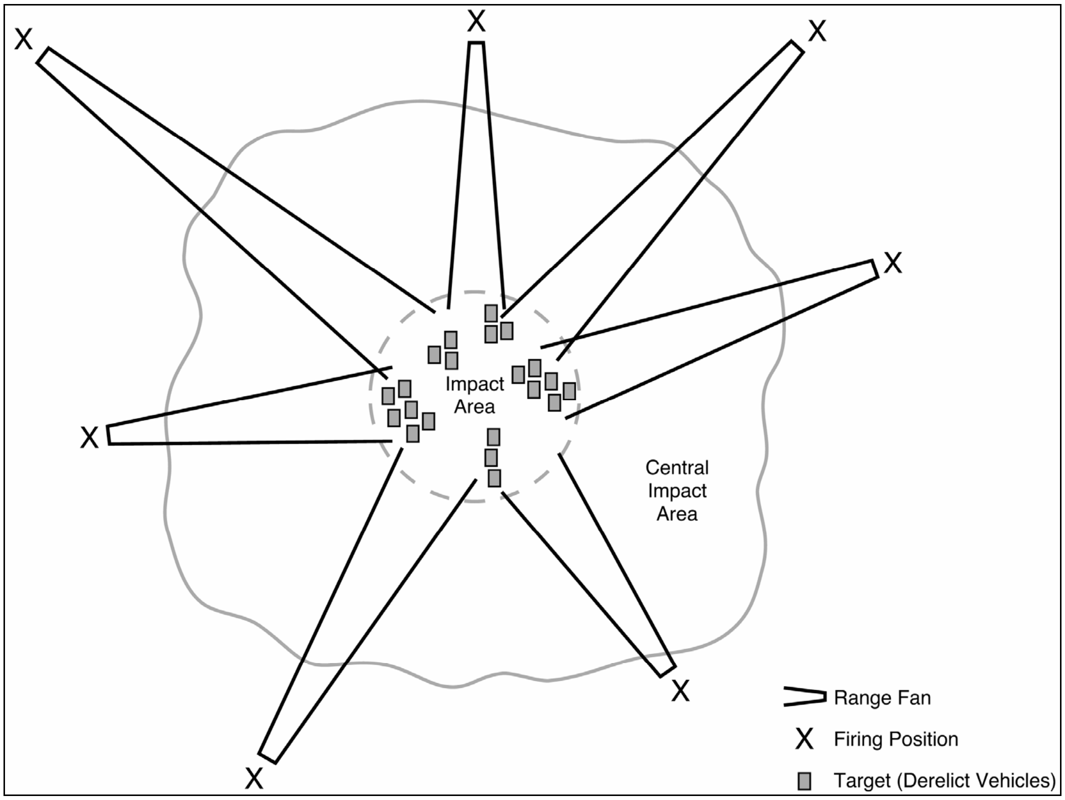


Figure 2-7. Schematic diagram of an artillery range showing firing points, range safety fan, and impact areas.

When the rounds perform as designed, these detonations result in the formation of a crater in the soil; the size is based on the type of round and the physical properties of the soil. Occasionally a round will impact without detonating, resulting in either a surface or subsurface UXO. For ranges where the soil is rocky or very hard, many of these UXO items can be seen on the surface. In a relatively small number of cases, a round will partially detonate upon impact, resulting in what is called a low-order detonation. In this case, only a portion of the explosive fill is consumed, sometimes leaving a substantial fraction of the explosive fill in or near the ruptured casing. Sometimes a high-order detonation will occur near enough to a surface UXO item that the item will be ruptured without detonation or with a low-order detonation. Here again, a substantial portion of the explosive fill will remain.

Climatic conditions and vegetative cover varies widely for the artillery ranges sampled in different parts of North America. For example, samples were taken from ranges located in hot arid portions of the western United States (Pennington et al. 2003; Hewitt et al. 2005), ranges in subarctic Alaska and Canada (Walsh et al. 2001, 2004; Ampleman et al. 2003a), a range located in a salt marsh in coastal Alaska (Walsh et al. 1995), ranges in moist southeastern United States (Jenkins et al. 2004b; Hewitt et al. 2005), ranges in a tropical setting in Hawaii (Hewitt et al. 2004), and ranges in cool, moist areas of eastern Canada (Thiboutot et al. 2003, 2004). Some ranges are sparsely vegetated, some heavily forested, some are open plains, and others are located in wetlands.

Many of the artillery ranges have been used for training for many decades. The munitions that have been fired include ordnance currently in the inventory as well as ordnance that was used pre- and post World War II, the Korean Conflict, and Vietnam. Because there has been no uniform management strategy in the past, UXOs of a wide array of munitions are present on these ranges, and many of these items are still live. For this reason, access is tightly controlled and the length of time permitted for accessing the various ranges varied considerably.

The munitions fired to the greatest extent into these ranges are artillery and mortars, although various rockets, missiles, and Air Force and Navy bombs have been used as well. Currently the major munition systems being fired into these ranges include 155-mm howitzers, 105-mm howitzers, 120-mm main tank guns, 81-mm mortars, 60-mm mortars, and

120-mm mortars. Munitions including 90-mm recoilless rifle rounds, 4.2-in. mortar rounds, 8-in. artillery rounds, bombs of various sizes, 40-mm grenades, 106-mm high-explosive plastic (HEP) rounds, 2.75-in. LAW rockets, and TOW missiles also have been fired into some of these ranges. These munitions are delivered using single-, double-, triple-based gun propellants and rocket and missile propellants. Single-based propellant is composed of NC and 2,4DNT, double-based propellant is composed of NC and NG, and triple-based propellant is composed of NC, NG, and nitroguanidine (NQ). The HEs used in artillery and mortar warheads are generally either TNT or Composition B, although some older rounds also contained tetryl (methyl-2,4,6-trinitrophenyl nitramines). Some smoke-generating munitions contain WP. Bombs that have been dropped in some of these ranges contain TNT or tritonal (TNT and aluminum), 40-mm grenades contain Composition A5 (RDX), and LAW rockets contain octol (HMX and TNT).

A listing of the 16 artillery ranges where samples were collected is shown in Table 2-8. After each installation, the types of areas sampled are identified. At the beginning of this work, very little information about energetic residues on these ranges was available, so a variety of areas were sampled, including firing points, target areas, areas in and near detonation craters, areas adjacent to UXO items, areas where chunks of explosive were observed on the surface, areas where a round had undergone a low-order detonation, and areas that were away from the firing points or targets but were within the firing safety fans.

### Artillery range firing points

A number of firing point areas have been sampled at various artillery ranges (Table 2-8). These included areas where 105-mm and 155-mm howitzers have been fired, an area where various mortars were fired, and an area where 120-mm tank guns were fired (Table 2-9). The largest amount of sampling was conducted in areas where 105-mm howitzers were fired. The propellant used for these guns is single-based and 2,4DNT was found to be the residue present at the highest concentration in all cases. No attempt was made to determine the concentration of NC because it is polymeric and does not present a problem for off-site migration, which is the major concern for energetic residues. Also, no validated methods exist for this compound when dispersed in a soil matrix.

Table 2-8. Installations at which artillery ranges have been sampled for energetic residues.

| Installation | Year Sampled | Types of Areas Sampled | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Firing Points | Target areas | Areas with Partial Detonations | Firing Fan Areas[1] | Craters | Near-UXO items | Areas with Chunk Explosives |
| Fort Richardson, AK[2] | 1992 | x | x | | | | | |
| Fort Greely (Donnelly Training Area), AK[3] | 2000 | x | | | | | | |
| Fort Lewis, WA[4] | 2000 | x | x | | | x | | |
| Yakima Training Area, WA[4] | 2001 | x | x | | | x | x | |
| Camp Guernsey, WY[4] | 2001 | | x | x | | | | x |
| CFB Shilo, MB[5] | 2001 | | x | | x | | | |
| Fort Bliss, NM[6] | 2002 | x | x | x | x | | | x |
| Jefferson Proving Ground, IN | 2002 | | x | | x | | | |
| Schofield Barracks, HI[7] | 2002 | x | x | | x | | | |
| CFB Gagetown, NB[8,9] | 2002<br>2003 | | x | x | x | | | x |
| Fort Polk, LA[10] | 2003 | | x | x | x | | | x |
| Fort Hood, TX[11] | 2004 | | x | x | | | x | x |
| Fort Carson, CO[11] | 2004 | x | x | | | | | |
| 29 Palms, CA[11] | 2004 | | x | x | | | | x |
| Massachusetts Military Reservation, MA | 2004 | | x | | | | | |
| CFB Petawawa, ON | 2004 | x | | | | | | |

[1] Areas away from any known firing activity or detonations.
[2] Walsh et al. 1995.
[3] Walsh et al. 2001.
[4] Jenkins et al. 2001.
[5] Thiboutot et al. 2003.
[6] Pennington et al. 2003.
[7] Hewitt et al. 2004.
[8] Ampleman et al. 2003b.
[9] Thiboutot et al. 2004.
[10] Jenkins et al. 2004b.
[11] Hewitt et al. 2005.

The highest concentrations of 2,4DNT are for samples from Fort Lewis (Jenkins et al. 2001), but these were collected from an area just in front of 105-mm howitzers where 600 rounds had been fired in the preceding month, and the samples were collected from only the top 0.5 cm of soil. When the concentration of 2,4DNT in a sample was above 3 mg/kg, much lower concentrations of 2,6DNT were sometimes detected as well.

Table 2-9. Summary of sampling results for surface soils at artillery firing points.

| | | | Mean Surface Soil Concentration mg/kg | | |
|---|---|---|---|---|---|
| Installation | Weapon fired | Propellant type | 2,4DNT | 2,6DNT | NG |
| Fort Greely (Donnely Training Area), AK | 105-mm howitzer | single based | | | |
| FP BoWhale | | | 4.3 | NA | <0.01 |
| FP Big Lake | | | 9.1 | 0.35 | <0.01 |
| FP Mark | | | 1.1 | NA | NA |
| FP Sally | | | 0.66 | NA | NA |
| Yakima Training Center, WA | 120-mm tank gun | single, triple based | | | |
| MPRC: 10 m from fixed firing point | | | 24 | 0.40 | 4.6 |
| MPRC: 20 m from fixed firing point | | | 8.2 | 0.13 | 1.3 |
| MPRC: 30 m from fixed firing point | | | 2.2 | <0.01 | 0.64 |
| MPRC: 50 m from fixed firing point | | | 0.68 | <0.01 | 0.33 |
| MPRC: 75 m from fixed firing point | | | 0.19 | <0.01 | 0.50 |
| Yakima Training Center, WA | 155-mm howitzer | single, triple based | | | |
| 7 m from firing point | | | <0.03 | <0.02 | 26 |
| 12 m from firing point | | | <0.03 | <0.02 | 3.0 |
| 22 m from firing point | | | 3.2 | 0.05 | 6 |
| 32 m from firing point | | | 0.27 | <0.02 | 1.85 |
| Fort Bliss, NM (14 composite samples) | 155-mm howitzer | single, triple based | | | |
| Non detects: 12 samples | | | <0.002 | <0.001 | <0.001 |
| Maximum value found | | | 0.97 | <0.001 | <0.001 |
| Fort Lewis, WA (600 rounds fired)[1] | 105-mm howitzer | single based | | | |
| At muzzle of 105-mm howitzer | | | 63 | <0.01 | <0.01 |
| 5 m from muzzle | | | 84 | <0.01 | <0.01 |
| 10 m from muzzle | | | 57 | <0.01 | <0.01 |
| 15 m from muzzle | | | 15 | <0.01 | <0.01 |
| 20 m from muzzle | | | 4.0 | <0.01 | <0.01 |
| CFB Petawawa, Ontario | various mortars | single, double based | 0.91 | <0.01 | 3.58 |
| Schofield Barracks, HI | 105-mm and 155-mm | single, triple based | | | |
| Max in seven composite samples | | | 0.04 | <0.01 | 0.35 |
| Fort Richardson, AK | 105-mm howitzer | single based | | | |
| surface 0- to 3-cm depth | | | 9.6 | <0.01 | <0.01 |
| 3- to 6-cm depth[2] | | | 2.2 | <0.01 | <0.01 |
| 6- to 10-cm depth[2] | | | 0.063 | <0.01 | <0.01 |
| 10- to 20-cm depth[2] | | | 0.56 | <0.01 | <0.01 |
| Fort Carson, CO | mostly mortars | mostly double based | 0.11 | <0.01 | 12 |

[1] Surface samples collected from top 0.5 cm of surface soil.

[2] Soils collected at specified depths below surface.

2,6DNT is an impurity in military-grade 2,4DNT. Soil samples were collected primarily in surface soils, except at Fort Richardson, where soils were sampled as deep as 20 cm. In this case, the concentration of 2,4DNT declined from 9.6 mg/kg in the surface 0- to 3-cm sample to 0.56 mg/kg in the sample from 10 to 20 cm. To investigate the physical nature of these propellant residues, metal trays were placed in front of 105-mm howitzers during a firing event at Fort Richardson, AK. Microscopic analysis of the residues indicated that at least a portion of the residues was unburned or partially burned propellant fibers with fiber lengths ranging from 0.4 to 7.5 mm (Taylor 2004 and personal communication[1]). The unburned fibers contained much higher concentrations of 2,4DNT than did the partially burned ones.

At Yakima Training Center surface soil samples were collected at a multipurpose range complex in front of a fixed firing point for 120-mm tank firing (Pennington et al. 2002). Both 2,4DNT and NG were detected at 75 m, the farthest distance from the firing point sampled (Table 9). At Yakima an area was sampled where a 155-mm howitzer had recently been fired. In this case, the residue was largely NG although some 2,4DNT was also detected. The propellants used with 155-mm howitzers can be either single base for short range target practice or a combination of single base and triple base for longer range firing activities.

### Samples from areas at artillery ranges away from impact areas and firing points

At Camp Shelby, MS; Fort Bliss, NM; Fort Polk, LA; Fort Carson, CO; and Jefferson Proving Ground, IN, the U.S. AEC, and the U.S. Army CHPPM conducted Regional Range Studies to assess the overall environmental impacts of residues from firing activities on artillery ranges. The AEC/CHPPM group used a stratified random sampling strategy unbiased by any judgmental observations, and collected 5-point composite samples from 10-m × 10-m grids established at various points across these areas. Because target areas represent only a small fraction of the total area of artillery ranges and their sampling area selection was unbiased, most of the areas that they sampled were quite a distance from any recognizable activity. The ER-1155 team accompanied the AEC/CHPPM sampling teams at all of these sites with the exception of Camp Shelby, and random 30-increment samples were collected within some of the same

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[1] Personal communication, Susan Taylor, ERDC-CRREL. 2004.

10-m × 10-m grids that they sampled. Most of these samples, collected by both the AEC/CHPPM and CRREL protocols for these sampling locations, did not contain detectable energetic residues using either RP-HPLC or GC-ECD methods, indicating that most of the total area at these ranges is virtually uncontaminated (Table 2-10).

Table 2-10. Results for unbiased samples collected at artillery range areas that were within the firing fan but away from firing points and targets.

| Installation | Number of Samples Analyzed | Number of Samples With No Detectable Energetic Compounds | Maximum Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | RDX | TNT | HMX | 2,4DNT | NG | 4ADNT | 2ADNT |
| Camp Shelby, MS (AEC/CHPPM)[1] | 54 | 53 | <0.23 | <0.23 | 0.33 | <0.23 | <0.48 | <0.23 | <0.23 |
| Fort Bliss, NM (AEC/CHPPM)[2] | 161 | 151 | 8 | 0.20 | 2.7 | <0.001 | 0.35 | 0.27 | 0.19 |
| Fort Bliss, NM (ERDC)[3] | 23 | 14 | 0.009 | 0.049 | 0.066 | 0.011 | 0.97 | 0.011 | 0.012 |
| Jefferson Proving Ground, IN (AEC/CHPPM)[4] | 170 | 138/RDX<br>167/TNT<br>169/DNT | 0.098 | 0.06 | <0.05 | 0.58 | <0.05 | <0.05 | <0.02 |
| Jefferson Proving Ground, IN (ERDC) | 105 | 103/RDX<br>100/TNT | 0.036 | 0.232 | <0.05 | <0.001 | <0.05 | <0.001 | <0.001 |
| CFB Shilo, MN (DRDC/ERDC)[5] | 26 | 16 | 0.022 | 1.6 | <0.01 | 0.046 | 0.015 | <0.001 | <0.001 |
| CFB Gagetown, NB (DRDC/ERDC)[6] | 18 | 7 | <0.05 | 0.21 | <0.05 | 0.02 | 0.49 | <0.01 | <0.01 |
| Fort Greely (Donnelly Training Area), AK (ERDC) | | | | | | | | | |
| WA Range: 50-increment samples | 77 | 74 | 0.27 | <0.001 | 0.61 | 0.62 | <0.02 | <0.002 | <0.002 |
| WA Range: discrete samples[7] | 16 | 10 | 0.036 | 0.012 | 0.004 | 9.5 | <0.03 | 0.016 | 0.018 |
| Georgia Island Range: 50-increment samples[8] | 44 | 44 | <0.002 | <0.001 | <0.004 | <0.001 | <0.02 | <0.002 | <0.002 |
| West side of WA Range: 50-increment samples[8] | 24 | 24 | <0.002 | <0.001 | <0.004 | <0.001 | <0.02 | <0.002 | <0.002 |
| Total | 718 | 631 Maximum | 8 | 1.6 | 2.7 | 9.5 | 0.97 | 0.27 | 0.19 |

[1] CHPPM 2001.
[2] CHPPM 2004.
[3] Pennington et al. 2003.
[4] CHPPM 2003.
[5] Ampleman et al. 2003b.
[6] Thiboutot et al. 2003.
[7] Walsh et al. 2001
[8] Walsh et al. 2004.

At CFB Shilo, MB, and CFB Gagetown, NB, Thiboutot et al. (2003, 2004) collected sets of multi-increment samples at various distances between the firing points and targets. Here again, the concentrations of energetic compounds were generally near or below analytical detection limits

(Table 2-10), indicating that the largest portion of the range has very low concentrations of energetic residues. A set of 77 50-increment samples and a set of 16 discrete samples were also collected using a grid node sampling approach from the Washington Range at Fort Greely. This range is used to test artillery, mortar, TOW missiles, and a variety of other weapons under very low temperature conditions and has been used for many years. Of the 77 multi-increment samples, 74 had no detectable residues of energetic compounds, and the maximum concentrations for the other three samples were 0.61 mg/kg for HMX, 0.62 mg/kg for 2,4DNT, and 0.27 mg/kg for RDX. Of the 16 discrete samples, 10 had no detectable residues and the maximum concentrations for RDX, TNT, HMX, 2,4DNT, 2,6DNT, 4ADNT, and 2ADNT were 0.036, 0.012, 0.004, 9.5, < 0.03, 0.016, and 0.018 mg/kg, respectively (Walsh et al. 2001). Similar sets of 50-increment samples were collected on the west side of the Washington range and at the Georgia Island range using the grid-node approach. No energetic residues were detected in any of the 68 samples analyzed.

### Artillery range target areas

Because target areas receive the largest numbers of detonations per unit area, samples were systematically collected around targets at many of the artillery ranges visited. These targets are generally derelict trucks, tanks, and armored personnel carriers, and many have sustained enormous damage after years of target practice. Because of the danger of encountering buried UXOs and residue scattered over the surface by detonations, most of the soil samples from these areas were collected from surface soil.

Table 2-11 presents a series of results from the analysis of surface soils collected near targets at five artillery impact areas. At Camp Guernsey, WY, a series of duplicate 30-increment samples was collected at distances of 1, 5, 10, and 15 m from the perimeter of a truck target. HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB were detected in at least one of these samples, but (except for one HMX value at 0.14 mg/kg) concentrations were less than 0.05 mg/kg. At Fort Bliss, 30-increment samples were collected at distances of 2 and 5 m from the target perimeter.

Table 2-11. Analytical results for individual soil samples collected near artillery targets.

| Installation | Number of Increments Per Sample | Distance From Target m | Mean Concentration, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HMX | RDX | TNT | 4ADNT | 2ADNT | TNB |
| Camp Guernsey, WY[1] | 30 | 1 | 0.14 | <0.03 | <0.02 | <0.03 | <0.04 | <0.02 |
| | 30 | 5 | <0.03 | 0.003 | 0.003 | 0.02 | 0.01 | <0.003 |
| | 30 | 10 | <0.03 | <0.003 | 0.013 | 0.04 | 0.03 | <0.003 |
| | 30 | 15 | <0.03 | <0.003 | <0.001 | 0.01 | 0.007 | <0.003 |
| Fort Bliss, NM: (Target 1)[2] | 30 | 2 | 3.1 | 2.1 | 0.69 | 0.1 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 1) | 30 | 5 | 0.03 | 0.01 | 0.57 | 0.08 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 2) | 30 | 2 | <0.03 | <0.003 | <0.001 | <0.002 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 3) | 30 | 2 | <0.03 | <0.003 | <0.001 | 0.04 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 4) | 30 | 2 | 0.02 | 0.01 | 0.02 | 0.02 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 5) | 30 | 2 | 0.08 | 0.37 | <0.01 | 0.002 | <0.01 | <0.01 |
| Fort Bliss, NM: (Target 5) | 30 | 5 | 0.04 | 0.03 | <0.001 | <0.01 | <0.01 | <0.01 |
| Fort Hood, TX[3] | 10 | 0–2 | 0.010 | 0.016 | 0.006 | <0.01 | <0.01 | <0.01 |
| | 10 | 0–2 | <0.01 | 0.003 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10 | 0–2 | <0.01 | 0.013 | 0.008 | 0.004 | 0.007 | <0.01 |
| | 10 | 2–5 | <0.01 | 0.008 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10 | 2–5 | <0.01 | <0.01 | 0.021 | 0.004 | 0.004 | <0.01 |
| | 10 | 2–5 | <0.01 | 0.010 | 0.059 | 0.040 | 0.040 | <0.01 |
| | 10 | 2–5 | <0.01 | 0.007 | 0.007 | 0.004 | 0.007 | <0.01 |
| | 10 | 5–10 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10 | 5–10 | <0.01 | <0.01 | 0.013 | <0.01 | <0.01 | <0.01 |
| | 10 | 10–20 | 0.092 | 0.14 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10 | 10–20 | 0.011 | 0.037 | <0.01 | 0.009 | 0.009 | <0.01 |
| | 10 | 10–20 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10 | 10–20 | <0.01 | <0.01 | 0.005 | 0.007 | 0.007 | <0.01 |
| Fort Polk, LA[4] | 10 | 0–2 | 15 | 16 | 1.2 | 0.25 | 0.31 | <0.01 |
| | 10 | 0–2 | 1.40 | 1.20 | 0.14 | 0.17 | 0.21 | <0.01 |
| | 10 | 0–2 | 0.42 | 2.2 | 0.52 | 0.28 | 0.36 | <0.01 |
| | 10 | 2–5 | 0.36 | 0.50 | 19 | 0.91 | 1.20 | 0.082 |
| | 10 | 2–5 | 0.88 | 0.45 | 0.44 | 0.17 | 0.23 | <0.01 |
| | 10 | 2–5 | 0.24 | 0.72 | 0.076 | 0.074 | 0.096 | <0.01 |
| | 10 | 2–5 | 0.22 | 1.8 | 14 | 0.27 | 0.25 | <0.01 |
| | 10 | 2–5 | 0.12 | 0.42 | 0.23 | 0.18 | 0.27 | <0.01 |
| | 10 | 2–5 | 1.9 | 13 | 4.4 | 0.53 | 0.73 | <0.01 |
| | 10 | 2–5 | 0.23 | 1.2 | 2.2 | 0.61 | 0.88 | <0.01 |
| | 10 | 2–5 | 0.13 | 0.29 | 9.5 | 1.1 | 1.4 | <0.01 |
| | 10 | 2–5 | 0.064 | 0.11 | 0.78 | 0.30 | 0.40 | <0.01 |

| Installation | Number of Increments Per Sample | Distance From Target m | Mean Concentration, mg/kg | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HMX | RDX | TNT | 4ADNT | 2ADNT | TNB |
| Fort Greely, AK[5,6] | 7 | 5 | <0.01 | 0.002 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 5 | <0.01 | 0.004 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 10 | 0.11 | 0.002 | 0.002 | <0.001 | <0.001 | <0.001 |
| | 7 | 10 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 15 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 15 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 20 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 20 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 25 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 25 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 30 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 30 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 35 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 35 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 40 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 40 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 45 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 45 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 50 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 7 | 50 | <0.01 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |

[1] Pennington et al. 2002.
[2] Pennington et al. 2003.
[3] Hewitt et al. 2005.
[4] Jenkins et al. 2004b.
[5] Walsh et al. 2001.
[6] Wire-guided missile target.

Concentrations of HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB were always less than 1 mg/kg, except for one 2-m sample at Target Number 1 where HMX and RDX were 3.1 and 2.1 mg/kg, respectively. At Fort Hood, 10-increment samples were collected at distance intervals of 0–2 m, 2-5 m, 5–10 m, and 10–20 m. Concentrations for the same six analytes were always less than 0.14 mg/kg. Soil samples collected from 0–2 m and 2-5 m around a target area at Fort Polk had the highest concentrations of these target analytes, with maximum values for HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB of 15, 16, 19, 1.1, 1.4, and 0.082 mg/kg, respectively. At Fort Greely, AK, 20 seven-increment samples were collected at distances ranging from 5 to 50 m from a target used for testing TOW missiles. In only three of these samples were energetic compounds detected and the maximum concentration was 0.11 mg/kg for HMX.

Also collected was a set of six systematic 100-increment samples in a 100-m × 100-m area next to a target at Fort Hood, TX. This area had over 600 craters within the 10,000-$m^2$ area, 55 of which were considered to be recent (within the last several months). The mean and range (r) of values obtained for these six samples were RDX (mean = 1.2 mg/kg, r = 0.12 to 3.68 mg/kg), TNT (mean = 0.30 mg/kg, r = < 0.001 to 0.81 mg/kg), and HMX (mean = 0.21 mg/kg, r = 0.035 to 0.63 mg/kg). A set of 36 discrete samples was also collected within this area. RDX was detected in only seven of these samples, HMX was detected in eight, and TNT was not detected in any. However, the TNT transformation products (4ADNT and 2ADNT) were detected in two of these samples. It should be noted, though, that a small area that had visible chunks of Composition B was found within this 10,000-$m^2$ area, and this may account for the low levels of residues detected in the multi-increment samples, and the low frequency of detections in the set of discrete samples.

Overall, the concentrations of energetic compounds near artillery targets are low and there does not appear to be a defined concentration gradient. Surface soil samples from some targets can have concentrations in excess of one mg/kg, but the concentrations at most targets are less, sometimes below the detections limits of the analytical methods used. In many cases, SW846 Method 8095 (USEPA 1999) was used for samples from artillery range impact areas because the concentrations of energetic compounds were less than the detection limits of the RP-HPLC method, SW846 Method 8330 (USEPA 1994).

### Artillery ranges near low-order (partial) detonations

By far the highest concentrations of energetic residues that were encountered at artillery ranges were associated with rounds that had undergone a low-order detonation (Table 2–12). One example of these partial detonations is shown in Figure 2–8. In most cases, chunks of pure explosive were observed on the soil surface near these items and concentrations of energetic compounds in the surface soil (particles < 2 mm) were at the percent levels in a few cases (Table 2–12). The highest concentration that were encountered for a soil sample was from Fort Hood where the TNT concentration beneath a low-order 4.2-in. mortar was 143,000 mg/kg (14.3 percent). The areas influenced by these low-order detonations were explored in several cases. At Fort Polk, a set of 100 discrete samples was collected in a 10-m × 10-m area that was subdivided into 100 1-m × 1-m cells (Jenkins et al. 2004b). The visible mass of Composition B on the surface of each cell was collected and weighed separately from the soil samples. The RDX concentrations in these soil samples varied from 0.037 to 2,390 mg/kg (Figure 2–9) and the highest concentrations (i.e., those > 100 mg/kg) were

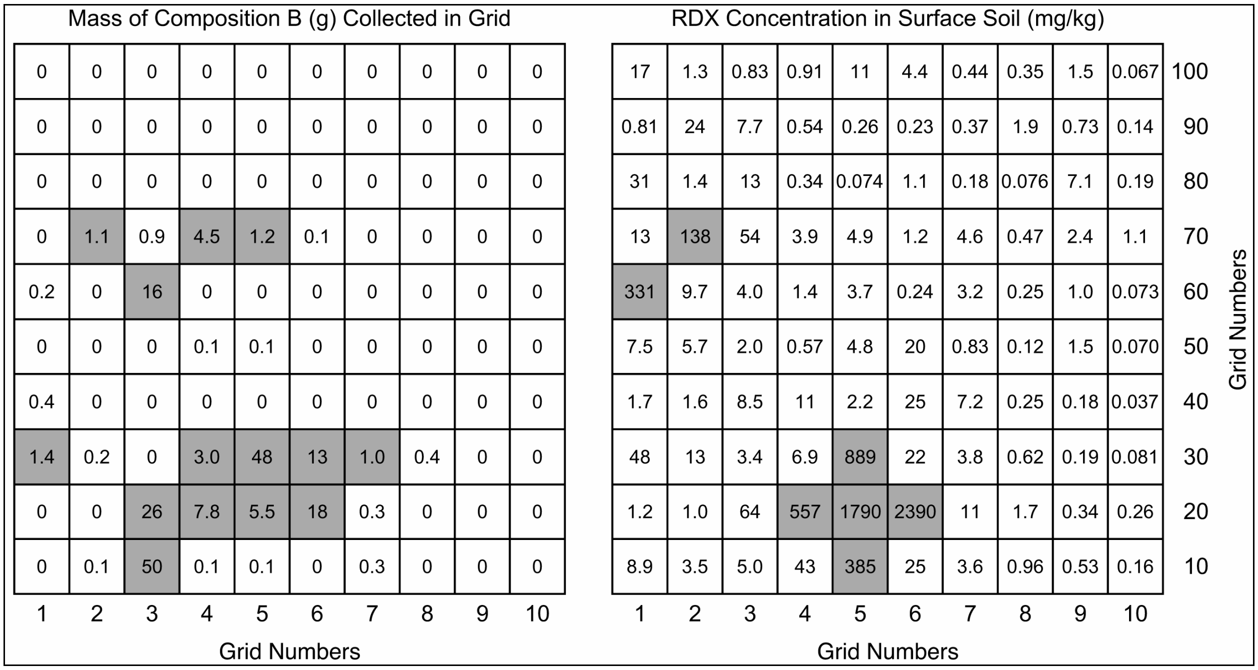
Table 2-12. Concentration of energetic compounds in surface soil samples near low-order detonations at artillery ranges.

| Installation | Description of Surface Soil Samples | Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | HMX | RDX | TNT | 4ADNT | 2ADNT | TNB | 2,4DNT |
| Fort Greely, AK[1] | Beneath a low-order 2.75-in. rocket warhead | 40 | 340 | 130 | 1 | 0.8 | 0.2 | 0.04 |
| Fort Lewis, WA[2] | Beneath a low-order 155-mm round | <10 | <10 | 15,100 | 110 | 102 | 15 | 40 |
| Camp Guernsey, WY[3] | Beneath a ruptured 500-lb bomb | <10 | <10 | 9,440 | <10 | <10 | 50 | <10 |
| Yakima Training Center, WA[3] | Near a low-order 155-mm round | 5.2 | 54 | <1 | <1 | <1 | <1 | <1 |
| Fort Bliss, NM[4] | Beneath a low-order 2.75-in. rocket warhead | 302 | 1,130 | 14 | 3.3 | 2.8 | <1 | <1 |
| Fort Bliss, NM[4] | Beneath a low-order 155-mm round | <10 | <10 | 2,520 | <10 | <10 | 148 | <10 |
| Fort Bliss, NM[4] | Beneath a 90-mm round | 149 | 678 | 1,110 | 12 | 18 | 9 | 1.3 |
| 29 Palms, CA[5] | Beneath a chunk of Composition B from low-order 155-mm | 94 | 825 | 537 | 0.05 | 0.11 | 4 | <0.1 |
| CFB Gagetown, NB[6] | Within a crater from a low-order 500-lb bomb | <10 | <10 | 42,200 | <10 | <10 | <10 | <10 |
| Fort Carson, CO[5] | Beneath a low-order 106-mm HEP round | 59 | <1 | 336 | <1 | <1 | <1 | <1 |
| Fort Carson, CO[5] | Beneath ruptured 8-in. round | 53 | 308 | 451 | 6 | 5 | 0.3 | 1 |
| Fort Hood, TX[5] | Beneath a low-order 4.2-in. mortar | 59 | 323 | 143,000 | <10 | 20 | 26 | 26 |

[1] Walsh et al. 2001.
[2] Jenkins et al. 2001.
[3] Pennington et al. 2002.
[4] Pennington et al. 2003.
[5] Hewitt et al. 2005.
[6] Thiboutot et al. 2003.

isolated in two small areas near where chunks of pure explosive were observed on the surface. About two-thirds of the total RDX present within this area was in the soil-sized fraction (< 2 mm) and only about one-third in the visible chunks found on the surface. Some of the locations of these low-order detonations were near targets, but many others were found in areas away from any recognizable targets. It is believed that these low-order detonations and UXO items that have been ruptured by subsequent detonations represent the main source of residues on artillery ranges.

Figure 2-8. Low-order 155-mm artillery round found at Fort Bliss.



Mass of Composition B (g) Collected in Grid

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 1.1 | 0.9 | 4.5 | 1.2 | 0.1 | 0 | 0 | 0 | 0 |
| 0.2 | 0 | 16 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.1 | 0.1 | 0 | 0 | 0 | 0 | 0 |
| 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1.4 | 0.2 | 0 | 3.0 | 48 | 13 | 1.0 | 0.4 | 0 | 0 |
| 0 | 0 | 26 | 7.8 | 5.5 | 18 | 0.3 | 0 | 0 | 0 |
| 0 | 0.1 | 50 | 0.1 | 0.1 | 0 | 0.3 | 0 | 0 | 0 |

Grid Numbers

RDX Concentration in Surface Soil (mg/kg)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Grid Numbers |
|---|---|---|---|---|---|---|---|---|---|---|
| 17 | 1.3 | 0.83 | 0.91 | 11 | 4.4 | 0.44 | 0.35 | 1.5 | 0.067 | 100 |
| 0.81 | 24 | 7.7 | 0.54 | 0.26 | 0.23 | 0.37 | 1.9 | 0.73 | 0.14 | 90 |
| 31 | 1.4 | 13 | 0.34 | 0.074 | 1.1 | 0.18 | 0.076 | 7.1 | 0.19 | 80 |
| 13 | 138 | 54 | 3.9 | 4.9 | 1.2 | 4.6 | 0.47 | 2.4 | 1.1 | 70 |
| 331 | 9.7 | 4.0 | 1.4 | 3.7 | 0.24 | 3.2 | 0.25 | 1.0 | 0.073 | 60 |
| 7.5 | 5.7 | 2.0 | 0.57 | 4.8 | 20 | 0.83 | 0.12 | 1.5 | 0.070 | 50 |
| 1.7 | 1.6 | 8.5 | 11 | 2.2 | 25 | 7.2 | 0.25 | 0.18 | 0.037 | 40 |
| 48 | 13 | 3.4 | 6.9 | 889 | 22 | 3.8 | 0.62 | 0.19 | 0.081 | 30 |
| 1.2 | 1.0 | 64 | 557 | 1790 | 2390 | 11 | 1.7 | 0.34 | 0.26 | 20 |
| 8.9 | 3.5 | 5.0 | 43 | 385 | 25 | 3.6 | 0.96 | 0.53 | 0.16 | 10 |

Grid Numbers

Figure 2-9. Mass of Composition B and soil RDX concentrations and their relative position in the 10-m × 10-m sampling grid near a low-order 81-mm mortar round at Fort Polk's artillery range impact area.

### Bombing ranges

Air Force ranges are very large, generally hundreds of square kilometers in size, but the areas currently used for training with HE-containing bombs are much smaller; generally only tens of hectares. Two live-fire bombing ranges were sampled: Cold Lake Air Weapons Range (CLAWR) in Alberta (Ampleman et al. 2003a, 2004) and Holloman Air Force Base (HAFB) in New Mexico (Jenkins et al. 2006). Also sampled were several other ranges where bombing with HE-containing bombs had been conducted (Donnelly Training Area, AK; Camp Guernsey, WY; Fort Polk, LA; CFB Gagetown, NB; 29 Palms, CA; and Fort Carson, CO). The Air Force regularly scheduled range maintenance activities where duds and chunks of HE (larger than golf-ball size) observed on the surface are gathered up and destroyed by detonating with C4, and craters are often filled in.

The HE present in U.S. and Canadian Air Force bombs is usually either tritonal (TNT, aluminum powder) or H-6 (TNT, RDX, aluminum powder). Some older bombs contained TNT. Although experiments documenting the residue deposited when a bomb detonates as designed have not been conducted, experimental results for large artillery rounds indicate that large mass HE detonations are very efficient, dispersing only microgram-to-milligram quantities of residue when they detonate high order (M. R. Walsh et al. 2005). As with other ordnance items, low-order detonations are the major source of residues from bombs.

Figure 2-10 shows a low-order bomb crater at CFB Gagetown where the TNT dissolving from chunks of tritonal in the bottom of the crater turned red as a result of photodegradation. Communication with range personnel at CLAWR indicates that low-order bomb detonations generally occur several times per year at their range. A low-order bomb can deposit kilogram quantities of residues as chunks and soil size particles. Low-order bombs were observed at Camp Guernsey (Figure 2-11) and at HAFB.

Because of the very large amount of explosive that remains after a low-order detonation, these occurrences are believed to produce the largest mass of residue at bombing ranges. Some of these low-order events probably occur during the bombing exercise, but the one observed at HAFB was apparently caused by a bomb detonation occurring in close proximity to a subsurface 2,000-lb dud (Figure 2-12). Bomb detonations

Figure 2-10. Reddish-colored crater formed from a low-order 500-lb bomb at CFB Gagetown.

Figure 2-11. Low-order bomb found on the impact range at Camp Guernsey, WY.

Figure 2-12. Soil sampling being conducted near a low-order 2,000-lb bomb at Holloman Air Force Base, NM.

produce many sharp metal fragments, as designed, and these high-velocity fragments can rupture UXOs present nearby. This phenomenon is believed to happen on a frequent basis on training ranges where intense live-fire training is conducted in areas where many UXOs have accumulated over the years. This activity has been simulated in a doctoral study (Lewis 2004) where munitions were easily broken by fragments from detonations of other rounds nearby, and the fate of explosive from broken shells was measured in soil columns (Pennington et al. 2004).

Results for soil samples collected at CLAWR, HAFB, near a low-order bomb at Camp Guernsey, at the bombing areas at Fort Polk, and near some low-order bomb craters at CFB Gagetown are presented in Table 2-13. The concentration of TNT in these samples from the single bombing target at CLAWR ranged from 3 to 408 mg/kg, with a mean value of 86 mg/kg for a 50-m-radius circle. The mean concentrations of RDX, HMX, 4ADNT, 2ADNT, 2,4DNT, and TNB in these samples were 0.27, 0.21, 0.71, 1.2, 0.20, and 0.13 mg/kg, respectively. Because the TNT concentrations were two orders of magnitude higher than RDX, and several small chunks of tritonal were present in the sampled area, it is believed

Table 2-13. Concentrations of energetic residues at live-fire bombing range impact areas.

| Installation | Distance from Target | Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | TNT | RDX | HMX | 4ADNT | 2ADNT | 2,4DNT | TNB |
| Cold Lake Air Weapons Range, AB[1] | 0–10 m (mean n = 2) | 32.2 | <0.01 | <0.01 | 1.14 | 1.78 | 0.17 | 0.08 |
| | 10–30 m (mean n = 8) | 83.3 | 0.56 | 0.14 | 0.91 | 1.39 | 0.20 | 0.06 |
| | 30–50 m (mean n = 16) | 94.1 | 0.1 | 0.23 | 0.62 | 1.04 | 0.1 | 0.17 |
| Cold Lake Air Weapons Range, AB[2] | 0–10 m (mean n = 2) | 41.1 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 10–30 m (mean n = 8) | 44.4 | 0.05 | <0.01 | 0.12 | 0.19 | <0.01 | <0.01 |
| | 30–50 m (mean n = 16) | 41.6 | 0.38 | 0.10 | <0.01 | <0.01 | <0.01 | <0.01 |
| Holloman AFB, NM[3] | Area sampled | | | | | | | |
| | within low-order bomb crater | 60.0 | <0.1 | <0.1 | 0.19 | 0.19 | 0.20 | 0.69 |
| | 100 m × 100 m[4] | 5.94 | 0.09 | 0.03 | 0.10 | 0.12 | 0.03 | 0.02 |
| | 100 m × 100 m[5] | 0.58 | 0.01 | <0.01 | 0.01 | 0.07 | <0.01 | 0.04 |
| | 10 m × 10 m[4] | 16.1 | <0.01 | <0.01 | 0.60 | 0.61 | 0.09 | 0.051 |
| | 10 m × 10 m[5] | 0.28 | <0.01 | <0.01 | 0.01 | 0.02 | <0.01 | <0.01 |
| Camp Guernsey, WY[6] | Low-order bomb | | | | | | | |
| | 3 m from bomb | 13.0 | 0.09 | 0.03 | 1.86 | 1.44 | 0.03 | 0.16 |
| | 5 m from bomb | 0.26 | <0.03 | <0.03 | 0.30 | 0.23 | <0.03 | <0.01 |
| | 10 m from bomb | 0.30 | <0.03 | <0.03 | 0.06 | 0.04 | <0.03 | <0.01 |
| Fort Polk, LA | Area near large bombing craters | | | | | | | |
| | inside/toe crater #1 | 0.01 | <0.01 | <0.01 | 0.02 | 0.02 | <0.01 | <0.01 |
| | rim crater #1 | <0.01 | <0.01 | <0.01 | 0.02 | 0.02 | <0.01 | <0.01 |
| | bottom crater #2 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | toe to rim crater #2 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | sides crater #2 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | sides crater #2 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| CFB Gagetown, NB | Low-order bomb crater | | | | | | | |
| | Crater #2 at 1 m | 276 | 0.08 | 0.25 | 2.8 | 4.5 | 0.57 | 0.59 |
| | crater #2 at 2 m | 334 | <0.01 | <0.10 | 1.2 | 1.8 | 0.20 | 0.45 |
| | Crater #3 at 1 m | 17.6 | <0.01 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| | Crater #3 at 2 m | 24.6 | <0.01 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| | Crater #4 at 1 m | 1860 | <0.01 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | Crater #4 at 2 m | 3720 | <0.01 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | Crater #4 at 5 m | 2540 | <0.01 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| Fort Carson, CO | 25-m × 25-m area with HE chunks | 15.3 | <0.01 | <0.01 | 1.8 | 1.7 | 0.04 | 0.14 |
| 29 Palms, CA | 100-m × 100-m area with H-6 chunks | 1.4 | 9.4 | 1.3 | <0.10 | <0.10 | <0.10 | <0.10 |

[1] Ampleman et al. 2003.

[2] Ampleman et al. 2004

[3] Jenkins et al. 2006.

[4] Area with chunks from 2,000-lb low order.

[5] Area away from 2,000-lb low order.

[6] Pennington et al. 2002

that these residues were from a tritonal-containing bomb. Because the soil around the target at CLAWR is tilled to reduce the chance of a wild fire, residue concentrations for different samples are less heterogeneous than those encountered at some other ranges.

Similarly, concentrations of TNT ranged from 0.58 to 5.94 mg/kg in two 100-m × 100-m grids at HAFB, one containing an area with a low-order 2000-lb bomb and one about 50 m from the bomb. Concentrations of RDX were less than 0.1 mg/kg in most samples from this range. The concentration of TNT within a crater containing a low-order bomb averaged 60 mg/kg, and the concentration within a 10-m × 10-m grid located just uphill from the crater averaged 16.1 mg/kg. Very different results were found for a 500-lb bomb crater sampled at Fort Polk. No energetic residues were detectable in soil samples from this crater, indicating that it was formed by a high-order detonation.

Explosives residues were detected in all of the samples collected near the target array located 2-km downstream from the Delta Creek Impact Area at Donnelly Training Area, AK (Walsh et al. 2004). In the composite samples, the following residues were determined: TNT (< 1-314,000 µg/kg); RDX (7–1,400 µg/kg); HMX (< 25–110 µg/kg); 2,4DNT (1–33 µg/kg), and NG (< 15–51 µg/kg). Only four of the samples had TNT above 1,000 µg/kg, and the median concentration was 80 µg/kg. The amino-DNT (ADNT) reduction products were detected in each sample as well, but concentrations were low (< 200 µg/kg). One of the discrete samples collected near a 500-lb bomb partial detonation had a TNT concentration of 17,300,000 µg/kg, a concentration far exceeding any other sample collected.

At Fort Carson, soil samples were collected in a 25-m × 25-m area where a large number of tritonal chunks were observed on the surface. These chunks were probably deposited from a low-order bomb. The mean TNT concentration within this area was 15.3 mg/kg; TNT transformation products TNB, 2ADNT, and 4ADNT were detectable at low concentrations as well. Chunks of explosive were not included in the soil samples. Here again, the concentration of RDX was less than 0.1 mg/kg.

The H-6 explosive from a low-order bomb was detected only at 29 Palms. In this area chunks of H-6 were observed and the mean concentrations of RDX, TNT, and HMX in a 100-m × 100-m area just downslope of where the largest mass of explosive was observed were 9.4, 1.4, and 1.3 mg/kg, respectively. RDX was detected on a bombing range only where H-6 bombs were detonated, or when BIP with C4 had occurred. TNT was the major energetic residue present at live-fire bombing ranges.

### Demolition ranges

Demolition ranges at active DoD training facilities are used by the military EOD technicians to destroy various munitions that are considered safe to move. Sometimes chunks of HE or unused propellants are also destroyed at these ranges, either by demolition or burning. Demolition ranges are generally only a few hectares in size and sparsely vegetated near demolition craters. Demolition craters are often used many times before being filled in. At active installations, a quantity of C4 explosive is usually placed on the item, and it is detonated using a blasting cap, eliminating any detonation hazards from these items. Results from studies reported by Pennington et al. (2004) indicate that substantial residues of energetic compounds can sometimes be deposited during demolition events, particularly if they result in a low-order detonation for the item being destroyed or if the C4 does not detonate completely.

At some Air Force demolition ranges, C4 explosive is used to blow a hole in practice bombs to ensure that they contain no HEs before these items can be removed from the range for recycling. Two areas were sampled where this practice was used, one at Eglin AFB, FL, and the other at HAFB, NM. Surface soil samples from both demolition ranges contain detectable concentrations of RDX and HMX (Table 2–14). At Eglin AFB, the mean concentrations for six discrete samples were 8.84 and 0.54 mg/kg for RDX and HMX, respectively. At HAFB, the mean concentrations of RDX and HMX for three 30-increment composite samples collected within a 25-m circle around the demolition crater were 11.4 and 1.84 mg/kg, respectively. Because the items being detonated do not contain any explosives or propellants, the residues deposited originate from the C4 demolition explosive. The C4 demolition explosive is unconfined, which may lead to lower destruction efficiencies than for detonation of confined charges. Unconfined charges lead to detonations of lower pressure and temperature, two parameters that influence strongly the efficiency of the transformation processes in the detonation fire ball.

Table 2-14. Concentrations of explosives residues in soils at ranges where C4 was used to demonstrate that practice bombs contain no high explosives prior to metals recycling.

| Installation | Date Sampled | Sample Number | Concentration, mg/kg | |
|---|---|---|---|---|
| | | | HMX | RDX |
| Eglin AFB | February 2003 | 1 | 0.18 | 1.81 |
| | | 2 | <0.01 | 0.48 |
| | | 3 | 0.52 | 1.60 |
| | | 4 | <0.01 | 0.58 |
| | | 5 | 0.61 | 13.9 |
| | | 6 | 1.94 | 34.6 |
| | | mean | 0.54 | 8.84 |
| Holloman AFB | May 2005 | 1 | 0.59 | 2.04 |
| | | 2 | 3.98 | 27.8 |
| | | 3 | 0.96 | 4.39 |
| | | mean | 1.84 | 11.4 |

Lower pressure and temperature cause incomplete oxidation processes and result in spreading of higher levels of unaltered energetic compounds in the environment.

Surface soil sampling was also conducted at a number of other demolition ranges at Fort Polk, LA; Schofield Barracks and Pohakuloa, HI; CFB Petawawa, ON; CLAWR, AB; and Camp Shelby, MS (Table 2–15). These ranges were used to destroy HE-containing munition items. With the exception of two samples from CLAWR, RDX and HMX were detected in all samples from these ranges, probably from the C4 demolition explosives. Concentrations of these two explosives varied significantly from < 0.03 at CLAWR to 60.2 mg/kg at Pohakuloa. At several ranges, pieces of C4 were observed on the surface. During a BIP test at Redstone Arsenal, small pieces of undetonated C4 were deposited over a small area when one of the two blasting caps failed and the secondary did not completely detonate the C4 block (Pennington et al. 2005). These events probably occur infrequently, but they are likely a source of the RDX residues in some cases.

TNT was also detected in some samples from these demolition ranges. Except for two high-concentration samples from Pohakuloa, however, the concentrations of TNT were less than 0.6 mg/kg. NG and 2,4DNT were detected in samples from several of these ranges. These compounds are

Table 2-15. Concentrations of explosives residues in surface soils at demolition ranges where C4 was used to detonate HE-containing munition items.

| Installation | Date | Type[1] | Concentration, mg/kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | HMX | RDX | TNT | 4ADNT | 2ADNT | 2,4DNT | NG | TNB |
| Cold Lake Air Weapons Range, AB | Aug. 2002 | MI-30 | <0.03 | <0.03 | 0.01 | <0.01 | <0.01 | <0.01 | 0.02 | <0.01 |
| | | MI-30 | <0.03 | <0.03 | 0.52 | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 |
| | | MI-30 | <0.03 | 0.82 | 0.07 | <0.01 | <0.01 | <0.01 | <0.02 | <0.01 |
| Schofield Barracks, HI | Nov. 2002 | MI-30 | 0.70 | 3.94 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | | MI-30 | 0.68 | 4.38 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Pohakuloa, HI | Nov. 2002 | MI-30 | 7.12 | 39.6 | 0.20 | 0.12 | 0.11 | <0.01 | <0.01 | 0.06 |
| | | MI-30 | 7.12 | 45.6 | 9.22 | 0.17 | 0.20 | <0.01 | 1.23 | 0.30 |
| | | MI-30 | 11.1 | 60.2 | 0.58 | 0.15 | 0.14 | 0.34 | 0.10 | 0.19 |
| | | MI-30 | 7.8 | 36.0 | 11.6 | 0.25 | 0.35 | 0.64 | 10.5 | 0.23 |
| Fort Polk, LA | June 2003 | MI-30 | 0.03 | 0.17 | 0.03 | 0.02 | <0.01 | 1.51 | 0.13 | <0.01 |
| | | MI-30 | 0.07 | 0.33 | 0.09 | 0.08 | 0.13 | 2.4 | <0.01 | <0.01 |
| CFB Petawawa, ON | Oct. 2004 | MI-50 | 1.06 | 30.5 | <0.01 | <0.01 | <0.01 | 12.0 | 1.15 | <0.01 |
| | | MI-50 | 0.08 | 0.72 | 0.05 | <0.01 | <0.01 | 2.05 | 0.44 | <0.01 |
| | | MI-50 | 0.55 | 2.45 | 0.05 | <0.01 | <0.01 | 1.00 | <0.01 | <0.01 |
| Camp Shelby, MS | April 2005 | MI-65 | 0.32 | 1.1 | <0.04 | <0.08 | <0.08 | <0.04 | <0.1 | <0.01 |
| | | MI-65 | 0.27 | 0.59 | <0.04 | <0.08 | <0.08 | <0.04 | 0.33 | <0.01 |
| | | MI-90 | 0.10 | 0.32 | <0.04 | <0.08 | <0.08 | 0.66 | <0.1 | <0.01 |

[1] MI: Multi-increment sample—number of increments.

generally components of propellant formulations where excess propellant is supposed to be destroyed by burning. Sometimes, however, these propellants are detonated instead, spreading propellant grains across the soil surface. It is not possible to determine whether the residues of NG and 2,4DNT found at these ranges were from burned propellant or propellant that was incorrectly detonated.

### Residue mobility

To investigate the mobility of energetic residues in the soil, soil samples were collected at depth below several low-order detonations at a variety of ranges (Table 2–16). The highest concentrations of TNT, RDX, or HMX were in the surface soil. Sometimes the highest concentrations for 4ADNT and 2ADNT were found in subsurface samples because these compounds are formed as dissolved TNT moves through the soil. In several of these data sets, HMX and RDX penetrated deeper into the soil profile than TNT.

Table 2-16. Concentrations with depth samples collected below low-order (partial) detonations or chunks of explosive at artillery ranges.

| Installation (location of samples) | Mean Concentration, mg/kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Depth cm | HMX | RDX | TNT | 4ADNT | 2ADNT | TNB | 2,4DNT |
| Fort Greely, AK (under 2.75-in. warhead) | surface | 40 | 340 | 130 | 1.0 | 0.84 | 0.17 | 0.036 |
| | 2–5 | 0.61 | 2.4 | 0.28 | 0.065 | 0.084 | <0.001 | <0.001 |
| | 5–7 | 0.06 | 0.38 | 0.013 | 0.015 | 0.024 | <0.001 | <0.001 |
| | 10 | 0.03 | 0.03 | <0.001 | 0.003 | 0.007 | <0.001 | <0.001 |
| Fort Bliss, TX (under chunk of TNT) | Surface | <1 | <1 | 2100 | <1 | <1 | 42 | <1 |
| | 1–2 | <1 | <1 | 194 | <1 | <1 | 21 | <1 |
| | 2–3 | <1 | <1 | 103 | <1 | <1 | 5.4 | <1 |
| Fort Bliss, TX (under 2.75-in. warhead) | Surface | 302 | 1,130 | 13.5 | 3.3 | 2.8 | 0.09 | <0.01 |
| | 3–4 | 17 | 111 | 1.5 | 1.2 | 1.9 | <0.01 | <0.01 |
| Fort Lewis, WA (under 155-mm round) | Surface | <0.01 | <0.01 | 15,100 | 110 | 102 | 15 | 40 |
| | 5 | <0.01 | <0.01 | 710 | 146 | 153 | <0.01 | 10 |
| | 10 | <0.01 | <0.01 | 46 | 20 | 30 | 0.14 | 20 |
| | 15 | <0.01 | <0.01 | 2.5 | 0.19 | 0.19 | 0.06 | 0.01 |
| Camp Guernsey, WY (under ruptured bomb) | Surface | <10 | <10 | 9,440 | <10 | <10 | <10 | <10 |
| | 1–3 | 4.2 | 0.6 | 240 | <10 | <10 | 3.2 | <1 |
| | 4–7 | 1.3 | <1 | 42 | 14.9 | 19 | 0.96 | 2.0 |
| Fort Hood, TX (under low-order 81-mm mortar) | Surface | 52 | 212 | 5.0 | 6.5 | 8 | <0.01 | 0.76 |
| | 1–3 | 6.3 | 26 | 0.48 | 2.2 | 3 | <0.01 | 0.23 |
| | 3–7.5 | 6.7 | 26 | 1.6 | 1.7 | 3.2 | <0.01 | 0.18 |
| | 7.5–10 | 4.2 | 13 | 0.30 | 1.1 | 2.0 | <0.01 | 0.14 |
| Fort Hood, TX (under chunk of Composition B) | Surface | 129 | 861 | 459 | 14 | 9.8 | <0.01 | <0.01 |
| | 1–4 | 31 | 173 | 31 | 8.7 | 5.1 | <0.01 | <0.01 |
| | 9–14 | 127 | 832 | 331 | 2.8 | 1.9 | <0.01 | <0.01 |
| | 16–20 | 12 | 56 | 9.5 | 2.2 | 1.4 | <0.01 | <0.01 |
| Fort Hood, TX (area with Composition B)[1] | Surface | 0.95 | 2.2 | 0.064 | 0.21 | 0.24 | <0.001 | <0.001 |
| | 2–6 | 0.40 | 3.7 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 6–9 | 0.12 | 0.33 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 9–12 | 0.13 | 0.25 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| | 12–16 | 0.10 | 0.22 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Fort Carson, CO (under 106-mm HEP round) | Surface | 59 | 336 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 3–4 | 19 | 97 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 4–5 | 8.9 | 49 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 5–6 | 1.3 | 5.8 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 6–7 | 1.1 | 4.6 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| | 7–8 | 1.4 | 6.0 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

[1] No chunks present at surface.

This is consistent with the lower soil/water partition coefficients for HMX and RDX relative to TNT (Pennington and Brannon 2002), and the susceptibility of TNT to attenuation reactions with soil components (Haderlein et al. 1996; Thorn et al. 2002). RDX and HMX have been found in groundwater below several training ranges (Jenkins et al. 2001; Clausen et al. 2004), but TNT has not.

At Fort Bliss (Pennington et al. 2003), a series of surface soil samples was taken downslope from low-order detonations of a 90-mm and a 155-mm round (Table 2–17). In both cases, some migration of energetic compounds was observed. Residues of HMX and RDX were considerably more mobile than TNT downslope of the 90-mm round. Residues of TNT were higher than RDX downslope of the 155-mm round because this round contained TNT.

### Detonation craters and UXO presence

A series of samples were taken at several installations to determine the residual concentrations of energetic compounds within impact craters and around their perimeter (Table 2–18). RDX, HMX, TNT, 2ADNT, and NG were detected in only 46, 6, 30, 48, and 6 of the 126 samples analyzed, respectively. Except for two samples, concentrations were always less than 1 mg/kg. Similarly, samples were collected next to intact UXO at Camp Guernsey (Table 2–18). Here again, residue concentrations were always below 1 mg/kg. When these UXOs at Camp Guernsey were detonated with C4 and soil samples collected in the area where the UXO had been prior to its destruction, much higher residue concentrations were found in two of the three cases (Table 18). Overall, areas near detonation craters and intact UXOs are not heavily contaminated with residues of energetic compounds, but the destruction of UXOs with C4 (BIP) can sometimes result in a substantial increase of energetic compound concentrations in the near vicinity where the detonations occur. The use of C4 for BIP detonations eliminates the safety issues associated with the presence of the UXO at training ranges; however, it can contribute to the environmental impact by distributing RDX in the environment.

Table 2-17. Concentration of energetic compounds for soil samples collected downslope of low-order (partial) detonations or chunks of explosive at Fort Bliss, TX.

| Installation (location of samples) | Downslope m | Mean Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | HMX | RDX | TNT | 4ADNT | 2ADNT | TNB | 2,4DNT |
| Fort Bliss, TX (low-order 155-mm with chunks of TNT)[1] | 0.2 | <0.03 | <0.03 | 6,270 | <0.03 | <0.04 | 98 | <0.003 |
| | 1 | <0.03 | <0.03 | 1.3 | 0.2 | 0.17 | <0.02 | <0.003 |
| | 2 | <0.03 | <0.03 | 38 | 0.8 | 0.07 | <0.02 | <0.003 |
| | 3 | <0.03 | 0.05 | 0.01 | <0.002 | <0.003 | <0.003 | <0.003 |
| | 4 | <0.03 | 0.10 | 0.03 | 0.003 | <0.003 | <0.003 | <0.003 |
| | 5 | <0.03 | 0.02 | 348 | 0.007 | 0.004 | <0.003 | <0.003 |
| | 12 | 0.04 | 0.03 | 0.04 | <0.002 | <0.003 | <0.003 | <0.003 |
| | 30 | <0.03 | <0.003 | <0.001 | <0.002 | <0.003 | <0.003 | <0.003 |
| Fort Bliss, TX (low-order 90-mm) | 0 | 149 | 678 | 1,100 | 12 | 18 | 9.0 | 1.3 |
| | 2 | 50 | 110 | 0.38 | 0.15 | 0.10 | 0.09 | 0.04 |
| | 3.7 | 41 | 39 | 0.21 | 0.12 | 0.06 | <0.001 | <0.001 |
| | 6 | 3.3 | 0.67 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |

[1] 155-mm round located in an arroyo.

Table 2-18. Summary of concentrations for energetic compounds (mg/kg) for crater samples and samples next to intact UXO items at artillery ranges in the United States and Canada.

| Installation | Year Sampled | Crater Samples Analyzed | Type of Craters | HMX | | RDX | | TNT | | 2ADNT | | NG | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Number <d[1] | Max Value | Number <d | Max Value | Number <d | Max Value | Number <d | Max Value | Number <d | Max Value |
| Fort Greely (Donnelly Training Area), AK | 2000 | 3 craters (13 samples) | BIP[2] mortar, TOW missile, SADARM | 13 | <0.026 | 5 | 0.016 | 6 | 0.008 | 12 | 0.003 | 12 | 0.37 |
| Fort Lewis, WA | 2000 | 12 craters (47 samples) | Live-fire, mortars, artillery | 47 | <0.026 | 30 | 0.093 | 28 | 1.75 | 16 | 0.031 | ND[2] | ND |
| Yakima Training Center, WA | 2001 | 5 craters (31 samples) | Live fire, artillery | 31 | <0.026 | 26 | 0.017 | 31 | <0.001 | 30 | 0.003 | 31 | <0.022 |
| CFB Gagetown, NB | 2002 | 8 craters (15 samples) | Artillery | 13 | 1.1 | 11 | 6.4 | 11 | 1.9 | 8 | 0.14 | 11 | 0.12 |
| Fort Polk, LA | 2003 | 5 craters (15 samples) | 105-mm, 155-mm, bombs | 14 | 0.060 | 4 | 0.061 | 12 | 0.27 | 11 | 0.46 | 13 | 0.005 |
| Schofield Barracks, HI | 2003 | 5 craters (8 samples) | | 8 | <0.026 | 4 | 0.015 | 8 | <0.001 | 1 | 0.013 | 8 | <0.022 |

| Installation | Year Sampled | Crater Samples Analyzed | Type of Craters | HMX |  | RDX |  | TNT |  | 2ADNT |  | NG |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Number <d[1] | Max Value | Number <d | Max Value | Number <d | Max Value | Number <d | Max Value | Number <d | Max Value |
| Camp Guernsey, WY | 2001 | 36 | three 155-mm rounds | 21 | 0.53 | 18 | 0.33 | 13 | 0.550 | 4 | 0.45 | 36 | <0.022 |
| Yakima Training Center, WA | 2001 | 10 | 105-mm, 155-mm, illumination | 9 | 0.026 | 7 | 0.72 | 10 | <0.001 | 8 | 0.049 | 10 | <0.022 |
| Camp Guernsey, WY | 2001 | 49 | three 155-mm rounds | 11 | 83 | 11 | 541 | 7 | 294 | 26 | 0.59 | 49 | <0.022 |

[1] Number of samples where concentrations were below analytical detection limits.

[2] BIP: Blow-in-place detonation crater.

## Summary and conclusions

The types of residues and their concentrations and distributions differ depending on the type of range and munition used. In general, the largest residue concentrations for all impact areas appear to be due to low-order detonations spreading particles and larger chunks of HE over the soil surface.

For hand grenade ranges, low-order detonations occur either when grenades are thrown during training or when duds are blown in place using C4 explosive. The C4 explosive used for detonating duds contains 91 percent military-grade RDX, of which about 10 percent is HMX. The major energetic residues on hand grenade ranges are RDX and TNT from Composition B, the explosive charge in M67 and C13 fragmentation grenades. For ranges where a recent partial detonation has occurred, concentrations are generally in the low mg/kg range and the distributions are more spatially homogeneous than at other types of impact ranges due to the thousands of individual detonations that continually redistribute the residue. Because grenade ranges are small in size, composite samples consisting of 30 increments have been found to be adequate for obtaining representative samples of surface soils.

At anti-tank rocket ranges, the major residue present in surface soils at the target area is HMX from the octol used as the HE in the warhead of 66-mm M72 LAW rockets. A concentration gradient is present in surface soils relative to the distance from targets. HMX concentrations in surface soils near targets are generally in the hundreds to low thousands of mg/kg, with TNT concentrations about one-hundredth that of HMX. The high levels of HMX in the soil at anti-tank rocket ranges can be attributed to the high dud and rupture rate of the M72 rockets. For sample collection, the impact area should be stratified into areas near targets, and areas in front of and in back of targets. Short-range spatial heterogeneity in residue concentrations at these sites is high, and in order to get representative samples, it is necessary to take multi-increment samples with a minimum of 30 increments.

At the firing points of anti-tank rocket ranges, NG is present from the double-based propellant used in the 66-mm M72 rockets. The major deposition of residue is behind the firing line due to the back blast from this weapon. Concentrations as high as the low percent level are sometimes found in soil up to 25 m behind the firing line. NG is also found between the firing line and the target, but the concentrations are generally several orders of magnitude lower than behind the firing line. Multi-increment samples have been found to provide adequate characterization for samples from impact areas and firing points at anti-tank rocket ranges.

Because the residues in these samples are largely present as particles of propellant, samples must be processed using larger sieves (10 mesh, 2 mm) than recommended in SW846 Methods 8330 and 8095 (USEPA 1994, 1999). It is also recommended that samples be thoroughly ground using a mechanical grinder prior to subsampling to preserve the representativeness of the portion of the sample to be used for extraction and analysis.

Most of the total artillery range acreage that is remote to firing points and targets is uncontaminated with residues of energetic compounds. At artillery and mortar firing points, the energetic residues are usually either 2,4DNT or NG, depending on the type of propellant used for the specific firing platform. Residues can be deposited at distances up to 100 m in front of the muzzle. For 105-mm howitzers, the major detectable residue is 2,4DNT, which can accumulate into the mg/kg range for fixed firing points. The residues from the single-based propellant used with this weapon are distributed primarily as burnt or unburnt propellant fibers. Residue deposition from 155-mm howitzers and mortars is primarily NG from double- or triple-based propellants. The NG does not seem to accumulate to concentrations as high as those for 2,4DNT from single-based propellants. Propellant residues are deposited at the soil surface and the highest concentrations remain at the surface unless the soil is disturbed. Both NG and 2,4DNT are deposited in an NC fiber matrix, thereby probably limiting their bioavailability and leachability.

Near targets at impact ranges, the majority of detonations of munitions are high-order detonations, and, as found by Hewitt et al. (2003), they appear to deposit very little residue. The major energetic residue deposition is due to low-order (partial) detonations that can deposit chunks of pure explosive. Residue concentrations of hundreds or thousands of mg/kg are often found in the surface soils next to these detonations. The major residues are TNT and RDX from military-grade TNT and Composition B, the major explosives used in mortar and artillery rounds. The distribution of residues in the area of the range where detonations occur is best described as randomly distributed point sources. Some of these point sources may be due to low-order detonations that are from BIP surface UXOs. At present, the detection of these point source areas has been visual, but research is underway to try to develop a near-real time detection capability. The collection of representative samples in areas subject to these partial detonations is a major challenge and approaches utilizing multi-increment sampling have not been adequate.

The major residue present at bombing ranges is generally TNT from the tritonal used as the HE in most bombs. Concentrations can be in the tens to hundreds of ppm in and near bomb craters where low-order detonations have occurred. RDX concentrations are generally low at these ranges unless a bomb containing H-6 explosive had undergone a low-order detonation.

RDX and HMX from C4 are generally the residues present at highest concentrations in demolition ranges where C4 explosive is used to blast small holes in practice bombs to ensure that they contain no HE prior to recycling activities. RDX is generally the residue present at the highest concentration at EOD demolition ranges due to use of C4 to destroy duds and other explosives-containing items. Concentrations can sometimes be in the low mg/kg in surface soils at these sites.

RDX and HMX appear to be the most mobile of the energetic compounds present at training ranges. This is true for both downward migration through the soil profile and also overland in runoff. This agrees with results reported for energetic compounds in groundwater (Clausen et al. 2004; Jenkins et al. 2001).

Results of these studies demonstrate that the potential for range contamination is specific to the type of range and the type of activity. Large areas of training ranges are uncontaminated, while residues in smaller areas, e.g., those around targets, firing points, and low-order detonations, are potentially significant. Range managers can, therefore, limit management practices for residue control to specific areas and specific types of firing activities.

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# 3 Transport Parameters for Firing Range Residues

## Introduction

Transport parameters quantitatively describe the potential movement of contaminants from the soil surface into the soil matrix and, subsequently, into surface or ground water. These parameters are required to adequately simulate transport by numerical modeling of vadose zone and groundwater systems. Transport parameters are also useful in environmental risk assessments to define the exposure potential for contaminant receptors.

During the execution of ER-1155 various transport parameters for munition constituents of interest were measured empirically in the laboratory. Parameters included the following: dissolution rate, solubility, adsorption kinetics, soil to water partition coefficients, and transformation rate coefficients. Photolysis studies of Composition B and its principal components were also conducted. The objective of this chapter is to summarize findings.

The *dissolution* of explosives from residues on the soil surface or from cracked or partially fragmented munitions is one of the main processes affecting the fate and transport of explosives on firing ranges. Concentration gradients observed in the soil profile are consistent with kinetic limitations on dissolution rates for TNT, RDX, and HMX (Jenkins et al. 1997). The data are limited, however. Thiboutot et al. (1998) have also shown that the rates of dissolution of TNT and HMX from the formulation (octol) differ substantially. Accurate dissolution kinetics for explosives and for explosives formulations are key to describing the fate and transport of explosives residues from firing ranges into groundwater and surface water. Therefore, a key objective of ER-1155 was to determine dissolution rates of the principal HEs and several of their solid formulations.

Once in solution, the main factor affecting fate and transport of explosives residues is advection; contributing factors are adsorption, transformation, and irreversible soil binding (Brannon and Myers 1997). The fate and transport process descriptors required for estimating the movement of explosives residues through soil and into groundwater are the partition coefficient and the transformation rate coefficient. The *partition coefficient* is a mathematical expression that describes the distribution of a chemical compound between soil and water at equilibrium, or at steady state. When transformation, degradation, and/or irreversible sorption are pronounced, equilibrium distribution is not attainable and no partition coefficient can be measured. Under these conditions, all processes that remove contaminant from solution are lumped together in a *transformation rate coefficient*. The transformation rate coefficient is a kinetic parameter that describes the removal of contaminant from solution when equilibrium is unattainable due to confounding processes. One example of this is the partitioning of TNT under certain conditions that promote reduction of nitro to amino groups with subsequent changes in partitioning and with chemical reactions between the reduction products and soil components. Transformation rate coefficients generally follow first-order kinetics (Brannon and Myers 1997).

This chapter summarizes process descriptors for the principal high explosives, explosive compositions, and selected propellants (Table 3–1). Both batch and column studies were conducted. A large-scale column study with mortars that had been cracked open by detonation of another mortar was heavily leveraged with funds provided by the Canadian DLE. Other column studies were heavily leveraged with funds from the U.S. Army Corps of Engineers Environmental Quality and Technology Program, Characterization/Assessment of Distributed Source Ordnance-Related Compounds on Ranges, “Transport of Explosives through the Vadose Zone.”

## Dissolution experiments

A series of dissolution experiments were conducted during ER-1155. In the first set, dissolution rates of TNT, RDX, and HMX were determined as a function of temperature, surface area, and energy input, i.e., stirring rate (Lynch et al. 2002a). Experiments were performed in stirred reactors by systematically changing one variable while holding the other two constant. Dissolution rate correlation equations were developed that incorporated the three variables both independently and collectively in one equation for each explosive. Rates for all three explosives increased as surface area, temperature, and mixing rate increased. TNT demonstrated the fastest dissolution rate followed by HMX and then RDX.

Table 3-1. Compounds of interest.

| Compound | CAS[1] Number | Abbreviation |
|---|---|---|
| High Explosives, Selected Transformation Products and Impurities | | |
| 2,4,6-Trinitrotoluene | 118-96-7 | TNT |
| 2-Amino-4,6-dinitrotoluene | 35572-78-2 | 2ADNT |
| 4-Amino-2,6-dinitrotoluene | 19406-51-0 | 4ADNT |
| 2,4-Diamino-6-nitrotoluene | 6629-29-4 | 2,4DANT |
| 2,6-Diamino-4-nitrotoluene | 59229-75-3 | 2,6DANT |
| 1,3,5-Trinitrotoluene[2] | 99-35-4 | 1,3,5TNB |
| 1,3-Dinitrobenenze[2] | 99-65-0 | 1,3DNB |
| Nitrobenzene[2] | 98-95-3 | NB |
| 3,5-Dinitroanaline[2] | 618-87-1 | 3,5DNA |
| Hexahydro-1,3,5-trinitro-1,3,5-triazine | 121-82-4 | RDX |
| Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine | NA[4] | MNX |
| Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine | NA | DNX |
| Hexahydro-1,3,5-trinitroso-1,3,5-triazine | 13980-04-6 | TNX |
| Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine | 2691-41-0 | HMX |
| Octahydro-1,3,5-trinitro-7-nitroso-1,3,5,7-tetrazocine | 5755-28-2 | MN-HMX |
| 2,4-Dinitrotoluene[2] | 121-14-2 | 2,4DNT |
| 2,6-Dinitrotoluene[2] | 606-20-2 | 2,6DNT |
| N-Methyl-N,2,4,6-tetranitroaniline, or tetryl[2] | 479-45-8 | NA |
| 2,4,6-Trinitrophenol, or picric acid[2] | 88-89-1 | PA |
| Pentaerythritol tetranitrate[2] | 78-11-5 | PETN |
| Propellants and Propellant-Related Compounds | | |
| Nitrocellulose | | NC |
| 1,2,3-Propanetriol trinitrate, or nitroglycerin[2] | 55-63-0 | NG |
| Nitroguanidine[3] | 556-88-7 | NQ |
| Diphenylamine[3] | 122-39-4 | DPA |
| N-Nitrosodiphenylamine[3] | 86-30-6 | NNDPA |
| N,N'-Diethyl-N,N'-diphenylurea, or Ethyl Centralite[3] | 85-98-3 | ECL |
| Ammonium perchlorate[3] | 7790-98-9 | |
| Solid Formulations of High Explosives | | |
| C4 (91% RDX, 5.3% plasticizer, 2.1% binder, 1.6% petroleum oil) | NA | C4 |
| Composition B (59.5% RDX, 39.5% TNT, 1% wax) | NA | Comp B |
| Octol (70% HMX, 30% TNT) | NA | NA |
| LX-14 (95.5% HMX, 4.5% polyurethane (Estane)) | NA | NA |

[1] Chemical Abstracts Service.

[2] Explosive-related compounds for which process descriptors were limited or lacking at the beginning of ER-1155 (Pennington et al. 2001).

[3] Propellants added to the process descriptor database later in ER-1155.

[4] Not applicable.

The rate approximately doubled with every 10 °C increase in temperature. The authors suggest that the Levins and Glastonbury (1972) correlation is a viable method for estimating dissolution rates when diffusivities are known and particles of explosive compounds are of uniform diameter. Using this equation for 25 °C yielded the following best-fit diffusivities: $6.71 \times 10^{-6}$ $cm^2s^{-1}$ for TNT, $2.2 \times 10^{-6}$ $cm^2s^{-1}$ for RDX, and $1.5 \times 10^{-4}$ $cm^2s^{-1}$ for HMX. The relationships developed in this study serve as an initial approximation of expected dissolution rates under field conditions.

In the second set of experiments, effects of pH and temperature on aqueous solubilities and dissolution rates of TNT, RDX, and HMX were determined (Lynch et al. 2001). Results indicated that neither solubilities nor dissolution rates were significantly affected by pH over the range of the study (pH of 4.2 to 6.2), but were significantly affected by temperature over the range of 3.1 to 33.3 °C. TNT was the most soluble and had the highest dissolution rate; RDX had the second highest solubility, but the slowest dissolution rate. Correlation equations were proposed to estimate the aqueous solubilities and dissolution rates of these high explosives as a function of temperature.

In a third set of experiments, solubilities and dissolution rates were determined for poured molds of TNT and of the explosive formulations octol, Composition B, and LX-14 and for mixtures of the crystalline forms of the three explosive compounds (TNT, RDX, and HMX) that variously make up the formulations (Lynch et al. 2002b). Experiments were performed over a temperature range of 10 to 30 °C and at a constant stirring rate of 2.5 revolutions per second. Average dissolution rates and solubilities are given in Table 3–2. Dissolution rates of the explosive compounds in the various mixtures of crystalline forms were comparable to the rates determined independently. However, dissolution rates for the explosives from the molded formulations were generally lower than those determined independently (Table 3–3). None of the combinations studied, either in the formulations or as a mixture, resulted in significant changes in explosive compound solubility compared with those of the independent determinations.

Solubility of the solid propellant compounds, diphenylamine, N-nitrosodiphenylamine and ethyl centralite, were determined in stirred reactors at 10, 24, and 30 °C (Brannon et al. 2004; Table 3–4). Solubilities increased with temperature. Values were generally somewhat lower than

Table 3-2. Dissolution rates (± standard deviation of three replicates) at 20 °C, mg $s^{-1}$ $cm^{-2}$, and solubility (± standard deviations of three replicates) at 26.3 ± 0.2 °C, mg $L^{-1}$

| Explosive | Dissolution rate | Solubility |
|---|---|---|
| TNT | 23.3 E-5 (4.7 E-5) | 127.3 (1.1) |
| RDX | 5.37 E-5 (0.21 E-5) | 52.6 (0.74) |
| HMX | 15.3 E-5 (2.3 E-5) | 4.52 (0.06) |

Table 3-3. Dissolution rate, r (E-5 mg $s^{-1}$ $cm^{-2}$), of TNT, RDX and HMX from molded discs of three explosive formulations and TNT. Stirring rate was 2.5 revolutions per second (Lynch et al. 2002b).

| 10 °C | | | 20 °C | | | 30 °C | | |
|---|---|---|---|---|---|---|---|---|
| TNT | RDX | HMX | TNT | RDX | HMX | TNT | RDX | HMX |
| *TNT mold* | | | | | | | | |
| 7.4 | NA[1] | 0.092 | 19 | NA | 0.47 | 36 | NA | 0.24 |
| 7.6 | NA | 0.093 | 21 | NA | 0.52 | 43 | NA | 0.35 |
| 8.5 | NA | 0.071 | 23 | NA | 0.50 | 43 | NA | 0.19 |
| *LX-14 mold* | | | | | | | | |
| NA | NA | 0.48 | NA | NA | 0.91 | NA | NA | 2.8 |
| NA | NA | 0.46 | NA | NA | 0.94 | NA | NA | 2.8 |
| NA | NA | 0.41 | NA | NA | 0.93 | NA | NA | 2.7 |
| *Octol mold* | | | | | | | | |
| 6.4 | NA | 0.22 | 16 | NA | 0.48 | 30 | NA | 0.81 |
| 7.2 | NA | 0.22 | 16 | NA | 0.48 | 34 | NA | 1.0 |
| 7.4 | NA | 0.24 | 15 | NA | 0.48 | 34 | NA | 1.1 |
| *Composition B mold* | | | | | | | | |
| 5.1 | 1.1 | 0.19 | 9.9 | 2.1 | 0.37 | 18 | 2.8 | 0.40 |
| 5.3 | 1.3 | 0.21 | 13 | 2.6 | 0.48 | 20 | 4.3 | 0.75 |
| 4.9 | 1.3 | 0.20 | 12 | 2.7 | 0.49 | 23 | 4.6 | 0.82 |

[1] This formulation/mold did not contain the compound in this column.

Table 3-4. Mean (standard error) solubility values for propellant constituents, mg $L^{-1}$.

| Temperature, °C | Diphenylamine | N-nitrosodiphenylamine | Ethyl Centralite |
|---|---|---|---|
| 30 | 53.7 (0.71) | 8.4 (1.9) | 35.2 (1.4) |
| 24 | 39.9 (0.99) | 12.3 (0.61) | 23.0 (1.6) |
| 10 | 27.0 (3.4) | 9.1 (0.19) | 17.5 (2.7) |

those reported at similar temperatures in other literature (e.g., Verschueren 1983; Yalkowsky and He 2002; and Fedoroff et al. 1983).

Accurate modeling of explosive compound dissolution in the field environment depends on mathematically replicating natural processes (Lynch et al. 2003). In order to make predictions of the persistence of TNT and HMX in solid form, both as individual explosive compounds and components of octol, Lynch et al. (2003) used three exploratory modeling approaches. The study identified the range in predicted solid persistence and flux loading from the solid into solution. Results indicated that contaminant fate and transport at sites contaminated with multiple explosive compounds from more than one type of explosive formulation will be challenging to simulate with a model. Each specific explosive formulation is expected to dissolve differently depending on composition and manufacturing process (Lynch et al. 2003).

## Transport parameters

### Background and methods

The *partition coefficient* and the *transformation rate coefficient* are two important fate and transport process descriptors required for estimating the movement of explosives residue through soil and into groundwater. The partition coefficient is a mathematical expression describing the distribution of the compound between soil and water phases at steady state. When the relationship is linear, the equation typically takes the form

$$q = K_d C \tag{1}$$

where $q$ is the solid phase (soil) concentration (mg $kg^{-1}$), $K_d$ is the partition coefficient (L $kg^{-1}$), and $C$ is the solution phase concentration (mg $L^{-1}$) at steady state. The transformation rate coefficient is a kinetic parameter describing the removal of the compound from the solution phase when equilibrium is unattainable due to confounding processes, such as transformation, degradation, or irreversible sorption. Processes that remove compounds from the solution phase can be expressed by pseudo first order kinetics of the form

$$dc/dt = -kc \tag{2}$$

where $c$ is the concentration of the reacting chemical, $k$ is the pseudo first order reaction constant, and $t$ is time. Pseudo first order kinetics reduces to

$$\ln(c_o/c) = kt \tag{3}$$

where $c_o$ is the concentration of the reacting compound at time $0$. Once a value of $k$ is obtained, the half-life of the reacting compound, $t_{1/2}$, can be calculated using the equation

$$k = 0.693/t_{1/2} \tag{4}$$

These parameters are useful in transport models to estimate persistence of explosives, explosives-related compounds, and propellants. They are also useful in estimating the exposure component of environmental risk assessments and have been incorporated into the U.S. Army Groundwater Modeling System (GMS) and into the Adaptive Risk Assessment Modeling System (ARAMS, http://el.erdc.usace.army.mil/arams/).

Partition coefficients and transformation rate coefficients were determined for three groups of compounds. These included high explosives and related compounds, propellants and propellant-related compounds, and solid formulations of HEs (Table 3–1). These compounds were selected on the basis of a literature review conducted early in the project (Pennington et al. 2001). Partition coefficients were determined in shake tests at a 1:4 ratio of soil to water. Typically, only the solution phase was analyzed. Transformation rate coefficients were determined in shake tests similar to those for determination of partition coefficients, but were sampled over time. Details of methods for specific data may be found in the references given in Table 3–5 for each compound.

In addition to these shake tests, a set of experiments were performed to determine the effects of Eh and pH on partitioning of perchlorate in a high clay soil (Brannon et al. 2004). The stirred reactors were amended with organic matter (OM) (0.5 percent w/w) from a natural source. Tests were conducted in triplicate at two Eh levels (+500 and -150 mV) and three pH values (5.5, 7.0, and 10.0). The solution phase was assayed (EPA SW-846 Method 9058, USEPA 1996) eight times over 336 hr. A second soil, freshly acquired to ensure an active biomass, was tested at pH 7 and two Eh levels (+500 and -150 mV).

Table 3-5. Partition coefficients, $K_d$, and pseudo first-order transformation rate coefficients, $k$, for explosives, explosives-related compounds, and propellants determined during ER-1155. Selected soil properties are included.

| Compound$^1$ | Soil Origin | Soil Properties | | | $K_d$ (R$^2$) L kg$^{-1}$ | $k$ (R$^2$), h$^{-1}$ | References |
|---|---|---|---|---|---|---|---|
| | | CEC meq 100 g$^{-1}$ | TOC % | Clay % | | | |
| Explosives and Explosives-Related Compounds | | | | | | | |
| TNT | Sharkey Clay2 | 38.9 | 0.2 | 48.7 | 10 | 0.0163 (0.94) | *Kd*, Pennington and Patrick 1990;<br>*k*, Brannon and Myers 1997 |
| | LAAP-SM3 | 5.5 | 0.02 | 7.5 | 0.17 | 0.0007 (0.78) | *Kd*, *k*, Pennington et al. 1999 |
| | WES-silt | 12.4 | 0.57 | 7.5 | 4.5 | 0.144 (NA$^8$) | $K_d$, $k$, Myers et al. 1998 |
| RDX | Sharkey Clay$^2$ | 38.9 | 0.2 | 48.7 | 2.73 (NA) | 0 | $K_d$, $k$, Price et al. 1998 |
| | LAAP-SM$^3$ | 5.5 | 0.02 | 7.5 | 0.33 (0.95) | 0.00009 (0.27) | $K_d$, $k$, Pennington et al. 1999 |
| | WES-silt | 12.4 | 0.57 | 7.5 | 0.77 (NA) | 0.144 (NA) | $K_d$, $k$, Myers et al. 1998 |
| HMX | Sharkey Clay$^2$ | 38.9 | 0.2 | 48.7 | 19.8 (NA) | 0 (0.55) | $K_d$, $k$, Price et al. 1998 |
| | LAAP-SM$^3$ | 5.5 | 0.02 | 7.5 | 0.20 (0.77) | 0 (0.02) | $K_d$, $k$, Pennington et al. 1999 |
| | WES-silt | 12.4 | 0.57 | 7.5 | 1.17 (NA) | 0.004 (NA) | $K_d$, $k$, Myers et al. 1998 |
| PETN | Sharkey Clay | 38.9 | 0.2 | 48.7 | NSS$^4$ | 0.05 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | LAAP-D$^3$ | 5.5 | 0.2 | 7.5 | 1.32 (0.89) | 0.0017 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | Picatinny | 9.8 | 0.634 | 5 | NSS | 0.011 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | Grange Hall | 16.7 | 0.3 | 10 | 15.6 (0.86) | 0.034 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| Tetryl | Sharkey Clay | 38.9 | 0.2 | 48.7 | NSS | 0.852 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 1.1 (0.74) | 0.0062 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | Picatinny | 9.8 | 0.634 | 5 | NSS | 0.031(NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| | Grange Hall | 16.7 | 0.3 | 10 | 0.77 (0.70) | 0.0017 (NA) | $K_d$, $k$, Brannon and Hayes 2003 |
| 2,4DNT | Sharkey Clay | 38.9 | 2.4 | 48.7 | 12.5 (0.95) | TRR$^5$ | $K_d$, $k$, Pennington et al. 2001 |
| | LAAP-C$^3$ | 6.6 | 0.08 | 12 | 0.67 (0.85) | 0.0021 (0.75) | $K_d$, $k$, Pennington et al. 1999 |
| | LAAP-D$^3$ | 5.5 | 0.2 | 7.5 | 1.67 (0.75) | 0.0005 (0.23) | $K_d$, Pennington et al. 2001<br>$k$, Pennington et al. 1999 |

| Compound[1] | Soil Origin | Soil Properties | | | $K_d$ ($R^2$) L $kg^{-1}$ | $k$ ($R^2$), $h^{-1}$ | References |
|---|---|---|---|---|---|---|---|
| | | CEC meq 100 $g^{-1}$ | TOC % | Clay % | | | |
| 2,6DNT | Sharkey Clay | 38.9 | 2.4 | 48.7 | 5.96 (0.99) | 0.0235 (0.85) | $K_d$ $k$, Pennington et al. 2001 |
| | LAAP-C | 6.6 | 0.08 | 12 | 0.96 (0.96) | 0.0023 (0.80) | $K_d$, $k$, Pennington et al. 2001 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 1.83 (0.88) | 0.0035 (0.99) | $K_d$, $k$, Pennington et al. 2001 |
| 1,3,5TNB | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 0.1800 (0.995) | $K_d$, $k$, Pennington et al. 2001 |
| | LAAP-C | 6.6 | 0.08 | 12 | 0.49 (0.99) | 0.0027 (0.74) | $K_d$, $k$, Pennington et al. 1999 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.27 (0.88) | 0.0005 (0.38) | $K_d$, $k$, Pennington et al. 1999 |
| 1,3DNB | Sharkey Clay | 38.9 | 2.4 | 48.7 | 17.7 (0.95) | 0.0476 (0.97) | $K_d$, $k$, Pennington et al. 2001 |
| | LAAP-C | 6.6 | 0.08 | 12 | 0.32 (0.59) | 0.0013 (0.53) | $K_d$, $k$, Pennington et al. 1999 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | NSA[6] | 0.0019 (0.61) | $K_d$, $k$, Pennington et al. 1999 |
| NB | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 0.0498 (0.88) | $K_d$, $k$, Brannon et al. 2004 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.50 (0.97) | Stable[7] | $K_d$, $k$, Brannon et al. 2004 |
| | Grange Hall | 16.7 | 0.3 | 10 | NSS | 0.00804 (0.91) | $K_d$, $k$, Brannon et al. 2004 |
| MNX | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 0.225 (0.754) | $K_d$, $k$, Brannon et al. 2002 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.85 (0.96) | Stable | $K_d$, $k$, Brannon et al. 2002 |
| | Picatinny | 9.8 | 0.634 | 5 | NSA | Stable | $K_d$, $k$, Brannon et al. 2002 |
| DNX | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 0.333 (0.76) | $K_d$, $k$, Brannon et al. 2002 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.43 (0.94) | Stable | $K_d$, $k$, Brannon et al. 2002 |
| | Picatinny | 9.8 | 0.634 | 5 | NSA | Stable | $K_d$, $k$, Brannon et al. 2002 |
| TNX | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | Stable | $K_d$, $k$, Brannon et al. 2002 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.29 (0.50) | Stable | $K_d$, $k$, Brannon et al. 2002 |
| | Picatinny | 9.8 | 0.634 | 5 | NSA | Stable | $K_d$, $k$, Brannon et al. 2002 |

| Compound[1] | Soil Origin | Soil Properties | | | $K_d$ ($R^2$) L $kg^{-1}$ | $k$ ($R^2$), $h^{-1}$ | References |
|---|---|---|---|---|---|---|---|
| | | CEC meq 100 $g^{-1}$ | TOC % | Clay % | | | |
| Propellants and Propellant-Related Compounds | | | | | | | |
| NG | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 7.3 (NA) | $K_d$, $k$, Brannon et al. 2002 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 4 (NA) | 335 (NA) | $K_d$, $k$, Brannon et al. 2002 |
| | Picatinny | 9.8 | 0.634 | 5 | 3.8 (NA) | 84 (NA) | $K_d$, $k$, Brannon et al. 2002 |
| NQ | Sharkey Clay | 38.9 | 2.4 | 48.7 | 0.43 (0.89) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 0.26 (0.73) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | Grange Hall | 16.7 | 0.3 | 10 | 0.15 (0.69) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| DPA | Sharkey Clay | 38.9 | 2.4 | 48.7 | NSS | 1.098 (0.999) | $K_d$, $k$, Brannon et al. 2004 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 3.8 (0.99) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | Grange Hall | 16.7 | 0.3 | 10 | 1.66 (0.88) | 0.00271 (0.90) | $K_d$, $k$, Brannon et al. 2004 |
| NNDPA | Sharkey Clay | 38.9 | 2.4 | 48.7 | 11.4 (0.99) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 1.4 (0.98) | 0.0036 (0.41) | $K_d$, $k$, Brannon et al. 2004 |
| | Grange Hall | 16.7 | 0.3 | 10 | 0.25 (0.62) | 0.00186 (0.74) | $K_d$, $k$, Brannon et al. 2004 |
| ECL | Sharkey Clay | 38.9 | 2.4 | 48.7 | 14.4 (NA) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | LAAP-D | 5.5 | 0.2 | 7.5 | 9.15 (NA) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | Grange Hall | 16.7 | 0.3 | 10 | 3.09 (NA) | Stable | $K_d$, $k$, Brannon et al. 2004 |
| Perchlorate | Sharkey Clay | 38.9 | 2.4 | 48.7 | NA | Stable | $K_d$, $k$, Brannon et al. 2004 |
| | Lake Park | 22.3 | 1.4 | 17.5 | NA | Stable | $K_d$, $k$, Brannon et al. 2004 |

Note: CEC = cation exchange capacity; TOC = total organic carbon.

[1] Data for TNT, RDX, and HMX were not acquired during ER-1155.

[2] In some references, this soil is called "Yokena Clay."

[3] Data were acquired under anaerobic conditions using an aquifer soil.

[4] Steady-state concentrations were not attained.

[5] Transformation rate was too rapid to measure.

[6] No significant adsorption occurred.

[7] Stable; no significant change in solution phase concentration over time. Rate constant is not statistically ($p<0.05$) different from zero.

[8] Not available.

### TNT-related compounds

Both partition and transformation rate coefficients for the TNT-related compounds were higher in a high clay surface soil than in a low clay aquifer soil (Table 3–5) (Pennington et al. 2001). One compound, 1,3,5TNB, failed to reach steady-state concentrations in the clay. Another compound, 1,3DNB, exhibited no significant adsorption in one of the aquifer soils.

One of the dinitrotoluenes, 2,4DNT, transformed so rapidly in the high clay soil that the transformation kinetic coefficient could not be determined. Results suggest that these compounds will be readily degraded and/or strongly adsorbed in surface soils, but relatively mobile once in aquifer soils.

### RDX transformation products

The transformation products of RDX (MNX, DNX, and TNX) were generally stable in all three soils (one aquifer and two surface soils), except for MNX and DNX in one of the surface soils. This soil was high in cation exchange capacity (38.9 milliequivalent (meq) $100g^{-1}$), total organic carbon (TOC) (2.4 percent), and clay content (49 percent). The first-order transformation coefficients were 0.225 $h^{-1}$ ($r^2 = 0.75$) and 0.333 $h^{-1}$ ($r^2 = 0.76$) for MNX and DNX, respectively (Brannon et al. 2002). $K_d$ values for all three compounds (0.29 to 0.85 L $Kg^{-1}$) were similar to values determined earlier for RDX (0.33 L $Kg^{-1}$; Pennington et al. 1999). Transformation rate coefficients were first-order with very short half-lives, 0.225 $h^{-1}$ ($r^2 = 0.75$) for MNX and 0.33 $h^{-1}$ ($r^2 = 0.75$) for DNX in the high clay soil. Hexahydro-1.3.5-trinitroso-1,3,5-triazine (TNX) was stable in all three tested soils.

### Tetryl

Solution phase concentrations of tetryl in a high clay soil (Sharkey clay), declined to zero within the first 15 minutes of contact (Brannon and Hayes 2003). Half-life values (hr) were 0.81, 23, 111, and 415 for tetryl in Sharkey clay, Picatinny, LAAP D, and Grange Hall soils, respectively. Partition coefficients were not determined with Sharkey clay nor Picatinny soil because of the continuing decline in solution phase concentration, an indication of decay or continuing adsorption of tetryl to the soils (Table 3–5). Partition coefficients for the other two soils were 1.1 ($r^2 = 0.74$) and 0.77 ($r^2 = 0.70$) for an aquifer and a surface soil, respectively. Results suggest that transformation/decay may be significant fate processes for tetryl. When these mechanisms are not active, as in certain soils, transport will occur easily.

### Propellants and propellant-related compounds

*NG*

The behavior of NG was similar to that of tetryl; solution phase concentrations in Sharkey clay declined to zero within the first hour of contact (Brannon et al. 2002). Therefore, no partition coefficient could be determined in this soil. Partition coefficients for the aquifer (LAAP D) and the other surface soil (Picatinny) were 3.8 and 4.0 L $kg^{-1}$, respectively. Values for k are presented in Table 3–5. Half-life values were 7.3, 84, and 335 hr for Sharkey clay, Picatinny, and LAAP D soils, respectively. NG will likely be degraded and/or adsorbed in surface soils and aquifer soils.

*PETN*

PETN was rapidly degraded in surface soils and degraded at a slightly slower rate in aquifer soils (Brannon and Hayes 2003). Half-life values ranged from 13.8 to 398 hr with the greatest persistence in an aquifer soil. $K_d$ values were determined for one aquifer and one surface soil and were 1.32 ($r^2 = 0.89$) and 15.6 ($r^2 = 0.86$) L $kg^{-1}$, respectively.

*NQ*

That concentrations of NQ in solution phase did not change over time (Brannon et al. 2004) reflects the previously reported lack of susceptibility of NQ to aerobic biodegradation in activated sludge (Kaplan et al. 1982). Partition coefficients were, in like manner, very low, ranging from 0.15 to 0.43 L $Kg^{-1}$. These values are consistent with a value reported by Haag et al. (1990) of < 0.1 L $Kg^{-1}$. This propellant will not be attenuated in soils by sorption or degradation.

*DPA*

Diphenylamine (DPA) rapidly disappeared from the solution phase in the high clay soil, and more slowly from another surface soil (Brannon et al. 2004). Concentrations were relatively stable in the aquifer soil. Partition coefficients for DPA were 3.8 ($r^2= 3.28$) and 1.66 ($r^2 = 0.88$) L $Kg^{-1}$ in an aquifer and a surface soil, respectively. Results suggest that DPA will not persist once in solution in certain soils, but may be stable in others.

### *NNDPA*

The N-nitrosodiphenylamine (NNDPA) propellant was very stable in solution phase after an initial very rapid drop in solution phase concentration in the high clay soil (Brannon et al. 2004). Partition coefficients ranged from 0.25 to 11.4 L $Kg^{-1}$ with the highest values attained in the high clay, high organic carbon (OC) soil. Therefore, persistence of this propellant will depend upon properties of the soil in which it occurs.

### *ECL*

Solution phase concentrations of ethyl centralite (ECL) rapidly reached steady state in all three soils (Brannon et al. 2004). After the initial adsorption, no discernable processes removed ECL from solution. $K_d$ values tended to be relatively higher than for other propellants, ranging from 3.09 to 14.4 L $Kg^{-1}$ (Table 3–5).

### *Perchlorate*

A slight decrease in solution phase concentration was observed with -150 mV and pH 7.0 in the Sharkey clay, but no other changes in solution concentrations of perchlorate were evident in any of these experiments (Brannon et al. 2004). Perchlorate has been reported to degrade under reducing conditions with sufficient carbon source (Tipton et al. 2003); however, degradation also requires an active perchlorate-degrading microbial population, which may have been absent from the tested soils. Although perchlorate-degrading microbial populations are reported to be nearly ubiquitous (Coates et al. 1999), enrichment may be necessary to achieve degradation. Results indicate that factors affecting perchlorate degradation in soils may be more complex than just having highly reducing anaerobic conditions, an adequate carbon source, and freshly collected soils with an active microbial population.

## Summary

Partition coefficients for all of the explosives, explosives-related compounds, and propellants were rarely greater than 10 and generally less than 1 L $Kg^{-1}$. However, values are increased by properties of the soil such as high OC and clay content. Partitioning of these compounds to soils is limited compared to partitioning of organic contaminants such as polychlorinated byphenols (PCBs) and polycyclic gromatic hydrocarbons (PAHs) for which partition coefficients often exceed $10^5$ L $Kg^{-1}$. For some compounds, transformation is an important process (e.g., 2,4DNT and NG), while other compounds were very stable in the soils (e.g., TNX, NQ, ECL and perchlorate). Some were stable in all soils except for the high clay, high OC soil (e.g., MNX and DNX).

## Site-specific parameters

TNT was readily transformed to mono amino dinitrotoluenes in the high cation exchange capacity (CEC)/TOC soils (Yakima and Guernsey) and in the high clay soils (Fort Bliss and Jefferson Proving Ground) (Table 3–6). (Jefferson Proving Ground soil was also high in TOC.) In these soils, no steady state distribution between solution and soil was reached because the solution phase concentration continued to decrease throughout the test. RDX failed to reach steady state in Guernsey and Jefferson Proving Ground soils; HMX failed to reach steady state in Guernsey soil.

Table 3-6. Partition coefficients, $K_d$, of TNT, RDX, and HMX and properties of soils from selected training ranges.

| Site | Soil Properties | TOC % | Clay % | Explosive | $K_d$ L kg$^{-1}$ | References |
|---|---|---|---|---|---|---|
| | CEC, meq 100 g$^{-1}$ | | | | | |
| Fort Lewis, WA | 6.8 | 0.26 | 9.9 | TNT | 1.6 ± 0.8 | Brannon et al. 2002 |
| | | | | RDX | 0.6 ± 0.2 | |
| | | | | HMX | 3.5 ± 0.6 | |
| Yakima Training Center, WA | 23.6 | 1.06 | 15 | TNT | NSS[1] | Brannon and Hayes 2003 |
| | | | | RDX | 1.5 ± 0.064 | |
| | | | | HMX | 2.5 ± 0.04 | |
| Camp Guernsey, WY | 30.3 | 1.6 | 25 | TNT | NSS[1] | Brannon and Hayes 2003 |
| | | | | RDX | NSS[1] | |
| | | | | HMX | NSS[1] | |
| Fort Bliss, TX | 9.6 | 0.4 | 41 | TNT | NSS[1] | Brannon et al. 2004 |
| | | | | RDX | 1.72[2] | |
| | | | | HMX | 3.92[2] | |
| Jefferson Proving Ground, IN | 20.0 | 3.3 | 29 | TNT | NSS[1] | Brannon et al. 2004 |
| | | | | RDX | NSS[1] | |
| | | | | HMX | 2.7[3]<br>2.4[2] | |

[1] Steady-state concentrations were not attained.

[2] $K_d$ determined from measured solution concentration and calculated soil concentration (by difference at the first desorption step in the kinetics test producing a derived single-point $K_d$).

[3] $K_d$ determined by measuring both solution and soil concentrations. $R^2$ value for this slope-determined $K_d$ was 0.75.

When steady state was achieved, the $K_d$ values were generally low, ranging from 0.2 to 3.5 L $Kg^{-1}$. These results indicate that the fate of these three compounds is strongly affected by soil properties, especially CEC, TOC, and clay content.

## Column leaching studies

### DRDC study

The objectives of these column studies were to determine long-term (up to 12 months) leaching rates of Composition B from cracked mortars on the soil surface. The following two methods were used to generate broken mortars: C4-containing shaped charges or C4 in ball, block, or hemispherical shapes, and secondary detonations whereby one mortar was initiated and fragments from it struck another mortar, breaking its casing (Lewis et al. 2005). Cracked mortars containing Composition B were used in two columns, crushed Composition B from the detonations was used in two columns, and crushed Composition B that was not from detonations (clean) was used in two columns. A column with potassium bromide (KBr) and no Composition B was also included. Columns for this study were large, 60 cm in diameter and 75 cm deep. Test parameters reflected local soil (a silty sand) and climatic conditions. The columns were run under unsaturated conditions. To expedite infiltration cycles, the annual periods of no infiltration (December through March while the ground is frozen, and June through September while in the summer dry season) were compressed so that 2 years of activity were simulated in 1 year. This compression was accomplished by doubling the rate of infiltration and halving the dry periods between infiltration events.

High concentrations of energetic materials were found in the effluent of the soil columns during the initial groundwater recharge event that simulated the springtime snowmelt. The retardation factor was 1.56, and the $K_d$ was 0.27 L $kg^{-1}$ for all energetic compounds together. No significant difference was observed between the three energetic materials in terms of the volume of infiltration prior to breakthrough. Concentrations of TNT transformation products were 2 to 3 orders of magnitude lower than the concentration of TNT.

Effluent concentrations of columns containing cracked mortars did not differ from concentrations of columns containing crushed Composition B. Therefore, the small amounts of soot and metal fragments occurring with the cracked mortars did not impact mass transport. While cracked shells represent a potential source of energetic materials, the relatively small exposed surface area and the protection afforded by the metal casing prevent the energetic material from contributing substantially to the initial slug of dissolved explosives. Therefore, the energetic material inside the shell may be a long-term source of explosives, but does not contribute substantially to the first infiltration event. The extremely fine detonation particles were dissolving preferentially and entered into solution quite quickly. Once they were gone, the concentration in the effluent dropped off. The masses of energetic materials lost during the springtime infiltration event were up to 1,000 mg of RDX, 2,200 mg TNT, and 48 mg HMX. The total mass of energetic materials lost from crushed Composition B (> 0.75-mm diameter) was approximately 3.2 g of an initial mass of 45 g, or 7.1 percent. If this rate of mass transport were sustainable, the whole mass would be depleted in about 15 years. If the fine fraction is dissolving preferentially, however, then the high initial rate of mass transport will be followed by a significant slow down when the fine fraction is exhausted. This finding would suggest that substantial amounts of the coarser fractions of detonation residue would still be found in surface soils, which is consistent with observations on the ranges.

### ERDC study

Leaching properties of residues from low-order detonations of Composition B-filled artillery shells (see Chapter 5) were compared with leaching properties of dissolved RDX, TNT, and Composition B in saturated columns. Column results were also compared with partition coefficients determined in batch shake tests. Two soils were used; a silt loam (Camp Edwards, MA) and a loamy sand (Vicksburg, MS). Columns were 10.16-cm internal diameter by 17.00-cm height stainless steel cylinders, fitted with porous stainless steel plates and caps on the top and the bottom. Radiolabeled $^{14}$C-RDX and $^{14}$C-TNT were added to dissolved RDX and TNT test solutions. To determine the longitudinal dispersivity ($\lambda$) for each soil and monitor for signs of preferential flow, all solutions were prepared with a tritiated tracer ($^3H_2O$). Experiments were analyzed using the HYDRUS-1D code for simulating the one-dimensional movement of water, heat and multiple solutes in variably saturated porous media (Šimunek et al. 2005).

### *Conservative tracer*

Longitudinal dispersivity and physical nonequilibrium were assessed by HYDRUS-1D analysis of the conservative tracer concentrations. Coefficients of determination for most breakthrough curves were high ($R^2 > 0.99$). Dispersivity was generally small as expected for short repacked columns. Breakthrough of the conservative tracer occurred at 1 pore volume, indicating the absence of preferential pathways for flow. Breakthrough curves were plotted on a time basis in order to accurately present interrupted flow experiments. $^3H_2O$ outflow concentrations resumed at similar values after the flow interruption, indicating that no or only limited physical nonequilibrium occurred in the soil column. Mass balance calculations indicated recovery of all of the tritiated water (100 ± 5 percent).

### *RDX*

Breakthrough for $^{14}$C-RDX was later than for the conservative tracer indicating adsorption to the soil. Average $K_d$ values determined from the breakthrough curves were small (approximately 0.19 ± 0.024 L $Kg^{-1}$). $^{14}$C-RDX exhibited little retardation, as is generally reported in the literature (Brannon and Pennington 2002; Selim et al. 1995; Tucker et al. 2002). High mobility of $^{14}$C-RDX was also supported by the mass balance. For the silt loam, sorption was reversible; recovery of $^{14}$C-RDX varied between 98 and 105 percent. Furthermore, irreversible attenuation was not statistically significant when modeled by HYDRUS-1D. For the loamy sand, however, some irreversible attenuation was observed, as indicated by lower $^{14}$C-RDX recovery in outflow (81–91 percent) and significant values for the irreversible attenuation rate coefficient (0.012 ± 0.002 $h^{-1}$). Incomplete recovery of $^{14}$C-RDX in the loamy sand is consistent with the 8 percent unextractable $^{14}$C-RDX after 168 days observed by Singh et al. (1998) and some irreversible attenuation of RDX in this same soil (7.4 percent) reported by Speitel et al. (2002). The asymmetric shape of the breakthrough curves, particularly for the loamy sand, and results of HYDRUS-1D simulations support rate-controlled adsorption and desorption. An estimated 30 percent of adsorption sites in loamy sand and 33 percent in the silt loam exhibited kinetic adsorption, with the rate of exchange in the 0.12 to 0.16 $h^{-1}$ range. The decrease in concentration following flow interruption also indicated chemical nonequilibrium.

### *TNT*

$^{14}$C-TNT exhibited greater attenuation than $^{14}$C-RDX as indicated by a delay in the breakthrough curve and smaller outflow concentrations. Part of the attenuation was attributed to reversible adsorption, and part to irreversible attenuation. Average $K_d$s were 3.2 times greater for $^{14}$C-TNT than for $^{14}$C-RDX in both soils suggesting a greater affinity of TNT for adsorption sites. This difference was close to the 2.4-fold difference in log $K_{ow}$ of the compounds (2.06 and 0.87 for TNT and RDX, respectively) suggesting that partitioning of TNT to the organic matter may be a significant mechanism for reversible adsorption. The 4.4-fold difference in irreversible attenuation rate between soils was consistent with difference in OC content (0.2 and 0.78 percent for the silt loam and the loamy sand, respectively), which is a matrix for irreversible attenuation by reduced TNT amines (Thorn et al. 2002). An asymmetric breakthrough curve, as well as a decrease in concentration when flow was interrupted, indicated rate-controlled sorption of $^{14}$C-TNT. In the mass balance, 73 to 75 percent of $^{14}$C-TNT was recovered in silt loam and 41 to 42 percent in the loamy sand. Unrecovered $^{14}$C-TNT is assumed to be in the form of amines covalently bound to the soil OM by reactions reported by Thorn et al. (2002). Formation of coplanar complexes of TNT with K-exchanged phyllosilicate clays in soils is also possible (Weissmahr et al. 1999); however, in the studied soils only 0.5–1.2 percent of exchange sites were occupied by $K$.

### *Solution phase Composition B*

TNT and RDX from dissolved Composition B behaved like pure TNT and RDX with respect to the following parameters: $K_d$s, irreversible attenuation rates, degradation rates, and fraction of sites with instantaneous adsorption. The rates of exchange for kinetic sites for $^{14}$C-RDX radiotracer, and for RDX and TNT in Composition B did not significantly differ from the ones obtained for pure explosives. The only difference was in the rate of irreversible attenuation and mass balance of $^{14}$C-RDX radiotracer in loamy sand soil. Unlike pure $^{14}$C-RDX in the loamy sand that exhibited a statistically significant rate of irreversible attenuation ($0.012 \pm 0.002$ h$^{-1}$), $^{14}$C-RDX in Composition B had no significant irreversible attenuation (irreversible attenuation rate, $\mu_w$, was not significantly different from zero). In addition, all of $^{14}$C-RDX was recovered in Composition B (105 ± 0 percent), while in pure $^{14}$C-RDX some was retained (8–18 percent). Some competition for irreversible attenuation sites between TNT and RDX is possible, since products of TNT transformation actively react with OM.

While irreversible attenuation of RDX was reported before, little is known about the mechanism.

HMX, which was not studied separately, was stable with no significant degradation or irreversible attenuation and 100 percent recovery (96 to 103 percent). HMX $K_d$s (0.43 to 0.48 $cm^3$ $g^{-1}$) were in general agreement with batch values summarized by Brannon and Pennington (2002).

Degradation products of TNT accounted for 65 percent of outflow constituent mass in silt loam and 25 percent in the loamy sand. They included ADNTs, which predominated (with more 4ADNT than 2ADNT and earlier breakthrough by 4ADNT), and azoxy compounds. RDX degradation products were only a small part of the outflow constituent mass: 0.4 to 4 percent of RDX input; 0.4 to 5 percent of the RDX outflow.

#### *Solid phase Composition B*

Breakthrough curves from solid Composition B indicated that despite the small range of Composition B particle sizes, variability in dissolution rate of Composition B among the experiments was significant. A sharp initial peak in concentration for an interrupted flow experiment in the silt loam can be explained by the presence of microscopic Composition B particles that dissolved in an initial flush. (This was also observed in the DRDC column studies described previously under “DRDC study.”) Adsorption coefficients for HMX, RDX, and TNT determined from solid Composition B were generally smaller than in dissolved Composition B. Two processes can explain this difference, saturation of sorption sites at high concentrations (inflow in dissolved Composition B was below 10 mg $L^{-1}$, while in solid Composition B, outflow was as high as 40 mg $L^{-1}$), and competition between RDX and TNT at high concentrations for nonspecific sorption sites. The dissolution rates of TNT, RDX, and HMX were correlated (i.e., tended to vary with each other).

While physical nonequilibrium was negligible, chemical nonequilibrium (kinetic sorption) contributed to transport and distribution of both RDX and TNT. The contribution of chemical nonequilibrium was confirmed by interrupted flow experiments. The behavior of dissolved Composition B was similar to that of pure RDX and TNT. Great variability in outflow concentrations in experiments with solid phase Composition B indicated that dissolution controlled transport.

## Conclusions

Although the fate and transport properties of compounds encountered on firing ranges tend to be compound-specific and influenced by soil characteristics, several important generalizations can be offered. Partition coefficients are in general relatively small, typically less than 20 L $Kg^{-1}$, and many less than one L $Kg^{-1}$, an indication that partitioning to soils will not appreciably attenuate most of these residues. For many of the compounds, partitioning between soil and solution phases failed to reach a steady state. In these cases, adsorption was confounded by other processes (e.g., transformation or degradation), which continued to remove compounds from the solution phase. In these cases, any adsorption occurring is overwhelmed by degradation or other attenuation mechanisms (e.g., covalent bonding of TNT transformation products to soil OC). These processes tend to be compound specific and related to relatively high soil OC and clay content. Transformation products of RDX and many of the propellants and propellant-related compounds were completely stable in the soil water system. Once dissolved, these compounds will be readily transformed with no, or only limited, potential for degradation.

Results of dissolution experiments provide relationships that may be used in approximating dissolution rates on the ranges. Dissolution rates were independent of pH within the range of typical range soils (4.2–6.2), but increased significantly with temperature. Predictive models were explored, but the various compositions and physical configurations of formulations complicate predictions of their dissolution rates in the field.

Results of column studies confirm the importance of dissolution rate on transport of high explosives from solid forms. An initial peak in effluent concentration as smaller particles are dissolved by the first rainfall event is likely to be followed by a smaller and slower release in subsequent events. RDX exhibited only limited retardation in the column studies. TNT, however, exhibited marked attenuation, probably due to covalent bonding of transformation products with OC and coplanar complexing with clays. These results explain the occurrence of RDX to the exclusion of TNT in groundwater on ranges where Composition B predominates. The behavior of TNT and RDX in Composition B differed little from their behavior independently, except that limited competition between the two for adsorption and irreversible attenuation sites was observed in one soil. Transformation products of TNT were observed in both sets of column experiments and may, therefore, be expected in soils when TNT is present.

Results of these studies have contributed empirical process descriptors for transport of explosives in soils of training ranges. These parameters have been integrated into environmental risk assessment models to define the exposure potential for contaminant receptors. Results have also contributed to understanding of the relative importance of transport processes and dissolution to the environmental fate of explosives and explosives-related compounds and propellants.

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# 4 Residues in Groundwater, Surface Waters and Sediments

## Introduction

Twenty-seven military firing ranges in the United States and Canada were investigated during the SERDP Project ER-1155 "Distribution and Fate of Energetics on DoD Testing and Training Ranges." The main goals of these range studies were to determine where residues are deposited during military training and testing activities and to develop a scientifically sound approach for establishing their concentrations in the most heavily impacted areas (Jenkins et al. 2001, 2005; Walsh et al. 2004, 2005; Hewitt et al. 2005). Overall, the SERDP project established that the largest sources of energetic residues on impact ranges are ruptured (low-ordered or breached) warheads of mortars, artillery rounds, bombs, and shoulder-fired rockets (Jenkins et al. 2001; Thiboutot et al. 2003a, 2004; Pennington et al. 2001-2006). Since artillery and mortar rounds and bombs often contain military-grade TNT, tritonal (80 percent TNT and 20 percent aluminum) or Composition B (60 percent RDX and 39 percent TNT) as secondary explosives, TNT and RDX are often the major residues deposited in the impact area of artillery and bombing ranges (Pennington et al. 2001-2006; Clausen et al. 2004). At anti-tank impact ranges, the major energetic constituents distributed into the environment include HMX and TNT from the octol (70 percent HMX: 30 percent TNT) in the warhead of the M72 66-mm LAW rockets, and NG from the double-based rocket propellant (Thiboutot et al. 2003a, 2004; Jenkins et al. 2004). At demolition ranges, RDX, TNT, NG, and 2,4DNT are prevalent because C4 (91 percent RDX) is frequently used for the sympathetic detonation of obsolete munitions, inert or dud rounds, and excess propellants (Clausen et al. 2004; Pennington et al. 2004; Jenkins et al. 2005).

At firing points, impact areas, and demolition ranges, energetic residues are initially deposited on the surface as particles of unconsumed HEs and propellant formulations (Taylor et al. 2004; Walsh et al. 2005). Therefore, most of the samples collected in the SERDP program were from the top 2 to 5 cm of the surface. However, occasionally it was possible to collect samples of surface water, groundwater, and sediments from artillery, anti-tank, and demolition ranges. This collection allowed assessment of the potential for energetic residue transport away from the deposition location. This report summarizes the results for surface water, groundwater, and sediments on these three types of military training ranges.

## Methods

### Water and sediment sample collection

Water samples were collected in 0.5- or 1-L small-neck amber glass bottles with Teflon-lined caps. Sediment samples were collected in 120 mL or larger wide-mouthed amber glass jars with Teflon-lined caps. Surface water samples were collected by holding the mouth of the bottle at the water surface (air-water) interface, with a glove-covered hand or by attaching to a metal pole for extended reach. Sediment samples from dry stream channels were collected with a stainless steel scoop. Sediment samples from wet stream channels and bodies of water were collected by attaching the scoop to a metal pole. Typically, several subsamples were collected at the same general location ($<1\ \mathrm{m}^2$).

Groundwater samples were collected from monitoring wells following development and purging. Sampling methodologies included the high-flow method, using a Waterra inertial pump, or the low-flow method, using a peristaltic suction pump. Hollow-stem augers, direct-push methods, and air-rotary drills have all been used when deemed appropriate for local geology. Well screens were typically located at the top of the aquifer, except in locations designated for deep wells. Well construction followed industry standards, with 100 percent silica filter packs surrounding the well screen and extending 1 m above the top of the screen. Bentonite grout or hydrated chips were used as a hydraulic plug to within 0.6 m of the surface. A concrete well head with a steel casing was installed at the surface to protect wells from damage. Ground and surface waters and sediments were chilled in coolers and shipped by overnight courier to a laboratory for chemical analysis.

### Extraction and analysis

Sediment samples were air dried at room temperature on aluminum foil or pans and passed through a #10 mesh (2-mm) sieve. The sieved fraction of the smaller sediment samples (i.e., < 200 g) were placed in the appropriately sized glass containers with Teflon-lined lids, weighed, and a volume (mL) of acetonitrile, approximately double the mass (g) of the sample, was added. The < 2-mm fraction of the larger samples (> 200 g) were ground in a puck mill for 90 sec, after which the entire sample was mixed and spread out on a fresh sheet of aluminum foil (Walsh et al. 2002). Subsamples of 10.0 g were obtained by combining 20 or more increments in a 60-mL bottle. Acetonitrile (20 mL) was added to each of the 10.0-g subsamples. Sediment samples were extracted over an 18-hr period while being agitated on a tabletop shaker set at 150 revolutions/min (RPMs). Following the extraction step, the samples were allowed to settle. An aliquot of the sample was removed and filtered through a 0.45 µm Millex FH filter.

When energetic residues were observed on the soil near or within surface bodies of water, samples were filtered through a 0.45-µm Millex HV membrane before analysis. Most of the water samples, including all of the groundwater samples, were pre-concentrated by solid phase extraction ([SPE] Jenkins et al. 1995) on a Porapak RDX cartridge (Sep-Pak, 6-cm$^3$, 500 mg, Water Corporation). Typically, a 500-mL volume of water was passed through the cartridge. Analytes of concern were recovered from the cartridge with 5 mL of acetonitrile, for a 100-fold preconcentration.

Sample extracts were analyzed by reverse-phase high performance liquid chromatography (RP-HPLC), Method 8330 (USEPA 1994) and or by gas chromatography with an electron capture detector (GC-ECD), Method 8095 (USEPA 2000). Additional information addressing instrument configuration and operational parameters have been reported elsewhere (Jenkins et al. 2004; Walsh et al. 2005). Estimated water and sediment (soil) reporting limits for the analytes covered in this report by these two methods are listed in Table 4–1.

Table 4-1. Estimated reporting limits for soil and water.

| Analyte | Soil, µg/Kg | | Water, µg/L[1] | |
|---|---|---|---|---|
| | RP-HPLC[2] | GC-ECD | RP-HPLC | GC-ECD |
| HMX | 40 | 10 | 0.2 | 0.05 |
| RDX | 40 | 6 | 0.2 | 0.04 |
| TNT | 40 | 10 | 0.2 | 0.02 |
| 2,4DNT | 40 | 2 | 0.2 | 0.01 |
| 2ADNT | 80 | 2 | 0.4 | 0.03 |
| 4ADNT | 80 | 2 | 0.4 | 0.02 |
| NG | 100 | 10 | 0.5 | 0.2 |

[1] SPE; 500-mL sample to 5-mL extract.

[2] Estimated direct analysis of water samples (µg/L) by RP-HPLC is 0.5x soil (µg/Kg) values.

## Site descriptions and results

### Artillery/bombing impact ranges

*Monitoring wells*

Along the borders of the central artillery impact range at Fort Lewis, WA, water samples were collected from springs emerging along slopes and cliffs below the range and from groundwater monitoring wells (Jenkins et al. 2001; Pennington et al. 2001). Surface soils collected in the impact area within about 1 km of the wells contained RDX up to 0.09 mg/kg and TNT up to 15,000 mg/kg. (Hydrologic connections between the range and these wells were not investigated.) RDX was the only energetic compound found in groundwater or spring water (Table 4–2).

Two reports describe ground and surface water conditions at CFB Gagetown following sampling conducted in August 2001 and October 2002 (Thiboutot et al. 2003b; Lewis et al. 2005). In total, 53 monitoring wells have been installed at this facility, and 129 groundwater and 30 surface water samples have been collected and analyzed. To date, energetic contamination of groundwater has not been observed. However, several potential sources of explosives residues in surface soils have been identified (Thiboutot et al. 2003a; Pennington et al. 2004). Therefore, these wells will continue to be monitored.

Table 4-2. RDX concentration (µg/L) in groundwater and spring water along the boundary of an artillery impact range[1].

| Monitoring Wells | Springs |
|---|---|
| 0.28 | 0.31 |
| 0.19 | 0.15 |
| 0.18 | 0.26 |
| 0.51 | 0.73 |
| <0.04 | <0.04 |

[1] Analytes for which values were below detection limits for the GC/ECD method conducted by CRREL (reported above) included the following: HMX, TNT, NG, 2,4DNT, 2,6DNT, 2ADNT, and 4ADNT. All samples were split and also analyzed at EL by HPLC for the following additional undetected analytes: TNB, DNB, tetryl, NB, 2NT, 3NT, 4NT, DNA, 2,4DANT, 2,6DANT, 4,4′-AZOXY, MNX, DNX, and TNX. A contract laboratory also reported less than detection limits for all of these analytes by HPLC and concentrations of RDX comparable to CRREL and EL results.

In March 2004, groundwater from 14 monitoring wells at the Jimmy Lake/Shaver River range complex and the Alpha/Bravo range complex of CLAWR was sampled. RDX was detected in one of the 14 groundwater samples (Table 4–3). In the August 2004 round of sampling, 19 monitoring wells were sampled, including the 14 sampled in March. Only RDX was detected, and it was for a sample collected from the same monitoring well that previously showed the presence of this energetic residue. This well is about 200 m downgradient from the primary target position on Shaver River Range where most of the live munitions are dropped.

Table 4-3. Summary of results for CLAWR groundwater (GW).

| Date of Campaign | No. of GW Samples Collected | No. of GW with ER[1] | Energetic Residues | Concentrations (µg/L) |
|---|---|---|---|---|
| March 2004 | 14 | 1 | RDX | 3.2 |
| August 2004 | 19 | 1 | RDX | 7.0 |
| August 2003 | 6 | 1 | 1,3DNB | 0.60 |
| | | | 2,6DNT | 0.38 |
| | | | 2,4DNT | 6.5 |
| | | | TNT | 13.1 |
| | | | RDX | 2.0 |
| March 2004 | 5 | 1 | NG | 0.5 |
| August 2004 | 7 | 0 | 0 | <d |

[1] Dissolved energetic residue.

Thirty monitoring wells were installed in October 2003 at the Western Area Training Center (WATC) Wainwright, in Alberta, Canada (Martel et al. 2004b); 28 wells were sampled at that time. No energetic residues were detected.

In October 2000, 42 monitoring wells were installed at CFB Shilo, a large army maneuver area and artillery training base in Canada (Thiboutot et al. 2001); 38 were sampled at that time. No energetic residues were detected in any of these samples. In 2001, 36 additional monitoring wells were installed for a total of 78 (Ampleman et al. 2003). In September 2001, 89 groundwater samples were collected. These samples were taken from 70 of the 78 newly installed wells, 14 previously existing wells, 2 drinking water supply wells, 2 wells in neighboring Spruce Woods Provincial Park, and 1 private well. No energetic residues were detected. In September 2002, 67 groundwater samples were collected. These samples included 52 of the 78 monitoring wells, 6 previously existing wells, 3 drinking water supply wells, 1 well in Spruce Woods Provincial Park, and 5 private wells. Again, no energetic residues were detected.

### *Lakes, ponds, rivers, and streams*

In October 2000, nine surface water samples were collected from CFB Shilo (Thiboutot et al. 2001). In 2001, 17 surface water samples, and, in 2002, 20 surface water samples were collected, 17 of which were previously sampled in 2000 and/or 2001. No energetic residues were detected in any of these samples.

Of the five surface water samples taken in March 2004 from ice covered lakes and rivers at the impact area of CLAWR, one sample showed evidence of NG (Table 4–3). No energetic residues were detected in the seven August 2004 surface water samples from this site, which included the same sites tested in March.

Twenty surface water samples were taken in October 2003 from lakes, streams, and ponds across the Western Area Training Center (WATC) Wainwright in Alberta, Canada (Martel et al. 2004b). One sample from Battle River, the major river running along the western border of the training area, had TNT at a concentration of 0.2 µg/L. Three samples taken from the same river at other locations showed no energetic residues.

Water samples were collected from a stream downgradient of an impact range where 105-mm howitzers were fired (air-to-surface) from C-130 gunships. Samples were collected on three occasions over a 2-year period. All six samples exhibited explosives detections of < 1 µg/L (Table 4–4). Two seeps between the stream and target also contained explosive residues (Table 4–4).

Water samples were collected in a stream immediately below a heavily cratered area (more than 600 craters around a target) of a central artillery impact range. One sample was collected from the headwaters of the stream near the area, and one from at least 1 km downstream. This stream was joined by several tributaries that drained other target areas of the range. Except for detection of 2.9 µg/L RDX, detections were less than 1 µg/L (Table 4–4).

Table 4-4. Concentrations of energetic residues in a steam downgradient from an air-to-surface range.

| Location | Concentration, µg/L | | | | |
|---|---|---|---|---|---|
| | HMX | RDX | TNT | 2ADNT | 4ADNT |
| Air-to-surface stream | 0.061 | 0.691 | <0.021 | 0.181 | 0.921 |
| | 0.051 | 0.601 | 0.041 | 0.221 | 0.221 |
| | 0.051 | 0.571 | 0.081 | 0.211 | 0.201 |
| | <0.2 | 3.0 | <0.2 | <0.4 | <0.4 |
| | <0.2 | 0.6 | <0.2 | <0.4 | <0.4 |
| | 0.3 | 1.0 | <0.2 | <0.4 | <0.4 |
| Air-to-surface seeps | <0.2 | 0.9 | <0.2 | <0.4 | <0.4 |
| | 0.6 | 2.4 | <0.2 | 0.5 | <0.4 |
| Heavily-cratered artillery (near) | 0.11 | 0.88 | <0.02 | 0.05 | 0.03 |
| Heavily-cratered artillery (far) | 0.46 | 2.9 | <0.02 | 0.07 | 0.12 |

[1] GC-ECD analysis; all others, RP-HPLC analysis.

### *Dry stream beds and drainage channels*

Sediment samples were collected in two locations on the Dona Ana Range at Fort Bliss, TX, in dry channel beds downgradient of ruptured artillery shells surrounded by chunks of energetic residues (Pennington et al. 2003). One round was a 155-mm howitzer shell partially filled with TNT located on the side of a ravine; the other was a 90-mm recoilless rifle shell partially filled with Composition B and located on the side of a small hill. TNT concentrations decreased by more than five orders of magnitude within 4-m downgradient from the 155-mm howitzer shell (Table 4–5). Over 6 m from the 90-mm recoilless rifle shell, the HMX and RDX concentrations in the surface sediments dropped by about three orders of magnitude; TNT decreased by more than four orders of magnitude (Table 4–6). Based on the sediment sample results, particulate residues are unlikely to have been transported a substantial distance from these sources.

At an air-to-surface firing range where 105-mm howitzers were fired from C-130 gun-ships, a drainage channel extended about 78 m downslope near the targets. The channel varied in width from 1 to 10 m. Soil in the channel was wet from recent rainfall. Ten 20-increment samples were collected in this channel. Results indicate low mg/kg concentrations of several explosives, explosive transformation products, and propellants (Table 4–7).

Table 4-5. Energetic residue concentrations in a dry channel downslope of a ruptured 155-mm TNT-filled artillery round.

| Distance from Round (m) | Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| 0.2[1] | <0.04 | <0.04 | 6,200 | <0.1 | <0.04 | <0.08 | <0.08 |
| 1[1] | <0.04 | <0.04 | 1.3 | <0.1 | <0.04 | 0.17 | 0.20 |
| 2[1] | <0.04 | <0.04 | 38 | <0.1 | <0.04 | 0.07 | 0.08 |
| 3 | <0.01 | 0.046 | 0.02 | <0.01 | 0.006 | <0.002 | <0.002 |
| 4 | <0.01 | 0.10 | 0.03 | <0.01 | 0.004 | <0.002 | <0.002 |
| 5 | <0.01 | 0.022 | 0.35 | <0.01 | <0.002 | 0.004[1] | 0.007[1] |
| 12 | 0.04 | 0.027 | 0.04 | <0.01 | <0.002 | <0.002 | <0.002 |
| 30 | <0.04 | <0.006 | <0.04 | <0.01 | <0.002 | <0.002 | <0.002 |
| 50 | <0.01 | <0.006 | 0.01 | <0.01 | 0.008 | <0.002 | <0.002 |
| 100 | <0.01 | <0.006 | 0.10 | <0.01 | 0.008 | 0.004 | 0.005 |

[1] RP-HPLC analysis; all others, GC-ECD analysis.

Table 4-6. Energetic residue concentrations in a dry channel downslope of a ruptured 90-mm Composition-B-filled recoilless rifle shell.

| Distance from Round (m) | RP-HPLC Sediment Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| 0* | 150 | 680 | 1,100 | <0.1 | 1.3 | 18 | 12 |
| 2 | 50 | 110 | 0.38 | <0.1 | 0.04 | 0.10 | 0.15 |
| 3.7 | 41 | 39 | 0.21 | <0.1 | <d | 0.05 | 0.12 |
| 6 | 3.3 | 0.67 | <0.04 | <0.1 | <0.04 | <0.08 | <0.08 |

* Sample collected beneath ruptured round.

Fourteen multi-increment sediment samples were collected in an arroyo located downslope from the most heavily impacted area on a U.S. Air Force bombing range (Jenkins et al. 2006). Sampling began beyond the north edge of the heavily cratered area and continued south for about 340 m. In addition, depth profile samples were collected from the lowest lying location within the arroyo.

Table 4-7. Energetic residue concentrations in a drainage channel downslope of targets for C-130 air-to-surface firing of 105-mm howitzers.

| Distance from Target (m) | Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| 0 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | 0.004 | 0.004 |
| 12 | 0.05 | <0.006 | 1.6 | <0.01 | 0.002 | 0.018 | 0.018 |
| 20 | 0.18 | 1.5 | 0.05 | <0.01 | <0.002 | 0.010 | 0.008 |
| 28 | 0.04 | <0.006 | 0.25 | 0.060 | 0.006 | 0.012 | 0.010 |
| 37 | 0.03 | 0.006 | <0.01 | <0.01 | 0.004 | 0.024 | 0.016 |
| 48 | 0.01 | <0.006 | <0.01 | <0.01 | <0.002 | 0.008 | 0.006 |
| 51 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | 0.004 | 0.004 |
| 57 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | 0.010 | 0.006 |
| 64 | <0.01 | <0.006 | 0.02 | 0.34 | 0.008 | 0.016 | 0.008 |
| 76 | <0.01 | <0.006 | <0.01 | <0.01 | 0.008 | 0.016 | 0.008 |

[1] Analyses were by GC-ECD.

Within the heavily impacted area immediately up-gradient from the arroyo, two ruptured bombs were found – one 2,000 lb and the other 250 lb. Near these bombs and in several other locations, more than 200 individual and clusters of energetic residue pieces were present. The energetic residues were Tritonal (Jenkins et al. 2006). Two separate 100-m × 100-m areas located within the heavily impacted area were sampled. Mean TNT concentrations were 5.9 and 0.28 mg/kg for the grids with and without the low-ordered 2,000-lb bomb, respectively.

In the arroyo, the concentration of energetic compounds was less than 0.2 mg/kg except for one sample collected 210 m north of the access road where the TNT concentration was 2.3 mg/kg (Table 4–8). This higher concentration area appears to be isolated from the up- or down-stream sediment samples and may be due to a small piece of Tritonal from a low-order detonation. Energetic compounds in the arroyo profile samples were generally below detection. Overall, there is no evidence that particles of TNT or any other energetic compounds are being transported off the range through the arroyo.

Table 4-8. Energetic residue concentrations (mg/kg) in sediment samples from arroyo next to bombing range impact area.

| Distance from Target (m) | Concentration, mg/kg | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| 340 | <0.01 | <0.006 | <0.01 | 0.02 | <0.002 | 0.18 | 0.92 |
| 290 | <0.01 | <0.006 | <0.01 | 0.10 | <0.002 | 0.22 | 0.22 |
| 240 | <0.01 | <0.006 | 0.01 | <0.01 | <0.002 | 0.21 | 0.20 |
| 210 | <0.01 | <0.006 | 2.3 | 0.09 | <0.002 | 0.02 | 0.03 |
| 170 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | <0.002 | <0.002 |
| 120 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | <0.002 | <0.002 |
| 70 | <0.01 | <0.006 | <0.01 | <0.01 | <0.002 | <0.002 | <0.002 |
| 15 | <0.01 | <0.006 | 0.02 | 0.01 | <0.002 | <0.002 | <0.002 |

[1] GC-ECD analysis.

### *Craters*

In 2002 samples were collected in the Argus Impact Area at CFB Gagetown several weeks after the live-fire Staunch Gladiator exercise (Thiboutot et al. 2003a; Pennington et al. 2004). This live-fire exercise involved both surface- and air-launched munitions. Among the locations sampled was a fresh crater containing pinkish-colored water. Partly submerged in the crater pool was a ruptured 250-lb air-to-surface bomb partially filled with TNT. Multi-increment soil samples collected 0–2 m from the crater rim contained TNT concentrations up to 4,200 mg/kg. The TNT concentration in the crater pool was 20 mg/L, which is about one-fifth the solubility of this compound.

During an investigation of a central impact range used for training with mortars, howitzers, and air-to-surface bombing, two craters with pooled water were sampled. One crater was approximately 1.5 m deep and 3 m in diameter; the other was approximately 2 m deep and 6 m in diameter. In addition, soil samples were collected inside and around the rim of both craters. In the soil within the smaller crater, HMX, RDX, TNT, and it breakdown products, 2ADNT and 4ADNT, were detected. Within the larger crater pool (water) much lower concentrations of TNT and break down products were detected (Table 4–9).

Table 4-9. Energetic residue concentrations (µg/L) in water sample from two craters within a central impact range.

| | RP-HPLC Water Concentration, µg/L | | | | | | |
|---|---|---|---|---|---|---|---|
| Location | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| Crater - Small | 1.3 | 3.1 | 1.3 | <0.2 | <0.2 | <0.4 | <0.4 |
| Crater - Large | 0.7 | 0.4 | 0.7 | <0.2 | <0.2 | 0.5 | 0.6 |

At another central artillery impact area of an artillery range, a target surrounded by > 600 craters was intensively studied. The target was positioned on a gentle slope near the bottom of a hill. The first day of sampling occurred soon after a rainstorm. Several craters were filled with water and surface runoff. Water cascaded from one crater to the next. Three surface water samples were collected within the sampling area around the target. One was a composite water sample comprised of approximately 40-mL aliquots from 12 different crater pools (Table 4–10). The other two samples were from a crater pool (Crater A), which was next to a breached 2.75-in. rocket (Composition B) that was missing the nose (fuze), exposing the main charge. These two samples were collected from Crater A on two consecutive days. The mean soil concentrations for HMX, RDX, and TNT in the area surrounding the sampled crater pools were 0.20, 1.2, and 0.30 mg/kg, respectively. All of the water samples contained HMX and RDX. Crater A had much reduced concentrations on the second day when the pool contained a smaller volume of water and surface runoff had stopped. During the investigation of this central impact range, more than a dozen ruptured rounds were observed.

Table 4-10. Energetic residue concentrations in water samples from a stream and crater pools within a central impact range.

| | GC-ECD Water Concentration, µg/L[1] | | | |
|---|---|---|---|---|
| Sample Type | HMX | RDX | 2ADNT | 4ADNT |
| 12 Craters (composite) | 0.72 | 1.7 | <0.03 | <0.02 |
| Crater A (1st day) | 0.69 | 3.9 | <0.03 | <0.02 |
| Crater A (2nd day) | 0.25 | 0.66 | <0.03 | <0.02 |
| Stream (near) | 0.11 | 0.88 | 0.05 | 0.03 |
| Stream (far) | 0.46 | 2.9 | 0.07 | 0.12 |

[1] The following analytes were not detected: TNT, NG, 2,4DNT.

Craters sampled on an air-to-surface range where 105-mm howitzers were fired from C-130 gunships. Some craters were not fresh and were filled with aquatic vegetation. Of the seven samples collected in craters, only two exhibited detectable residue. These two samples contained 0.41 and 0.40 µg/L RDX only.

## Anti-tank ranges

### *Monitoring wells*

Groundwater data were acquired by DRDC for the Arnhem anti-tank range, CFB Valcartier. These were the only groundwater data from an anti-tank range that were available to the study group. This range is a training facility for 66-mm M72 LAW rockets containing octol. In June 1998, 25 monitoring wells were installed on or downgradient from the range. Beginning in July 1998, 13 sets of groundwater samples were collected from these wells at 2-wk intervals (Table 4–11). No surface water samples were taken during this study. Of all studies published to date, the results from the 1998-1999 Arnhem study show the most conclusive evidence of the presence of HMX, TNT, and RDX in the groundwater on a Canadian Forces base (Martel et al. 1999; Mailloux et al. 2002). Concentrations of HMX were in the high µg/L range, while TNT concentrations were relatively lower. These levels are consistent with observations of the ratio of HMX to TNT observed in surface soils associated with LAW rockets (Jenkins et al. 2003).

Table 4-11. CFB Valcartier groundwater (GW) sampling summary.

| Sampling Campaign | No. of GW Samples | No. of GW with ER* | No. Energetic Residues | Concentrations (µg/L) |
|---|---|---|---|---|
| 1998-1999 | 325 | 55 | HMX (55 hits) | 2.4-230 |
| | | | TNT (7 hits) | 0.25-6.35 |
| | | | RDX (8 hits) | 1-5.8 |

* Dissolved energetic residue.

### *Lakes, ponds, rivers, and streams*

At the Arnhem anti-tank (LAW rocket) range, a water sample was collected from a small intermittent stream (Jenkins et al. 2004). The stream flowed about 50 m, starting on the slope behind the target closest to the firing point, and disappeared into gravel at the base of the hill.

Surface soil samples were collected within this impact range using several different sampling designs. In the soil samples, HMX was present in the greatest amounts, ranging from 10 to 1,200 mg/kg. TNT and NG ranged from < d to 10 mg/kg, and RDX ranged from < d to 5 mg/kg (Jenkins et al. 2004). HMX, TNT and RDX were detected in the water samples (130, 1.6, and 2.4 µg/L, respectively), but no NG was detected. All three explosives were detected in groundwater at this site (see sections "monitoring wells" above).

Three surface water samples were collected at the anti-tank and machine gun range at CFB Petawawa. Two samples were from a small stream on the side of the range used for LAW rocket training. The other was from a small pond on the side of the range designated for machine gun training. The headwaters for the stream appeared to be several seeps near the anti-tank training target closest to the firing point. A multi-increment soil sample collected in front of the anti-tank training target closest to the firing point contained 2,500 mg/kg HMX and 27 mg/kg NG (Pennington et al. 2006). The two stream samples were collected about 100 and 500 m away from this target. Both of these stream samples had detectable levels of HMX (1.9 and 0.5 mg/L, respectively); the pond on the other side of the range did not.

#### *Craters*

Surface water and sediment samples were collected at an anti-tank range at CFB Gagetown in front of the four targets closest to the firing point (Thiboutot et al. 2004; Pennington et al. 2005). Two of the frequently used weapons at this range are LAW rockets and 84-mm armor piercing rounds. Six surface water samples were collected at this anti-tank range from three stagnant shallow pools. Two of the pools were ditches created by strafing adjacent to two separate targets; the third was a crater that may have been the result of a BIP operation and was about 20 m from the nearest target.

The ground surface near the pools by the targets was heavily littered with shell casings and pieces of rocket propellant. Soil samples collected near these two pools had the following energetic residue concentrations (mg/kg): HMX, 50 to 1,000; NG, 2 to 80; and both TNT and RDX, < 1 (Thiboutot et al. 2004). All water and subsurface sediment samples had detectable levels of HMX and NG, consistent with the two constituents present at the highest concentration in the adjacent surface soils (Tables 4–12 and 4–13).

Table 4-12. Energetic residue concentrations in water from craters at CFB Gagetown anti-tank impact range.

| Sample Type/Location | Concentration[1], µg/L | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| Pool 1 / 4m N[2] | 16 | <0.2 | <0.2 | 2.1 | <0.2 | <0.4 | <0.4 |
| Pool 1 / 10m N | 19 | <0.2 | <0.2 | 33 | <0.2 | <0.4 | <0.4 |
| Pool 1 / 3m S[2] | 570 | 2.7 | 1.0 | 1800 | <0.2 | 1.4 | 5.6 |
| Pool 2 / 12m N | 59 | <0.2 | <0.2 | 42 | <0.2 | <0.4 | <0.4 |
| Pool 2 / 2m S | 73 | <0.2 | <0.2 | 65 | <0.2 | <0.4 | <0.4 |
| Crater pool | 410 | 3.9 | <0.2 | 98 | <0.2 | <0.4 | <0.4 |

[1] Analyses by RP-HPLC.

[2] N/S – North or South side of pool.

Table 4-13. Energetic residue concentrations in sediment from craters CFB Gagetown anti-tank impact range.

| Sample Type/Location | Concentration[1], µg/L | | | | | | |
|---|---|---|---|---|---|---|---|
| | HMX | RDX | TNT | NG | 2,4DNT | 2ADNT | 4ADNT |
| Pool #1/2m N[2] | 34 | <0.04 | 1.2 | 67 | <0.04 | <0.08 | <0.08 |
| Pool #1/2m S[2] | 9.0 | <0.04 | 0.75 | 33 | <0.04 | <0.08 | <0.08 |
| Pool #1/3m S | 64 | <0.04 | 0.16 | 18 | <0.04 | 0.08 | 0.096 |
| Pool #1/3m N | 28 | <0.04 | 0.33 | 67 | <0.04 | <0.08 | <0.08 |
| Pool #2/2m N | 640 | <0.04 | 2.8 | 110 | <0.04 | <0.08 | <0.08 |
| Pool #2/2m S | 230 | 0.08 | 1.4 | 48 | <0.04 | 0.11 | 0.13 |
| Pool #2/10m N | 21 | <0.04 | 0.10 | 8.0 | <0.04 | <0.08 | <0.08 |
| Pool #2/10m S | 78 | <0.04 | 0.51 | 19 | <0.04 | 0.10 | 0.12 |

[1] Analyses by RP-HPLC.

[2] N/S – North or South side of pool.

TNT was present in all of the sediment samples, although at much lower concentrations than HMX and NG. In pools created by strafing, concentrations of energetic residues present in both the water and sediment matrices were variable, most likely because of localized chunks of residue and poor circulation of the water.

## Demolition and open burning/open detonation facilities

### *Monitoring wells*

Sixteen monitoring wells were installed at the Canadian Forces Ammunitions Depot (CFAD) Dundurn open burning/open detonation (OB/OD) facility in November 1995. Fourteen more were installed in December 1996 (Ampleman et al. 1998; Martel et al. 1998). Four rounds of sampling have been performed since 1995. Results of the last two sampling rounds are considered to be more representative of the groundwater condition than results of the first two (Table 4–14). Groundwater contamination by RDX is believed to be limited to shallow depths (the top 1.5 m of the aquifer) and downgradient of the OB/OD site.

Table 4-14. CFAD Dundurn groundwater (GW) sampling summary.

| Sampling Campaign | No. of GW Samples | No. of GW with ER* | Energetic Residues | Concentrations (µg/L) |
|---|---|---|---|---|
| September 1996 | 16 | 2 | RDX | 6.6, 79 |
| December 1996 | 35 | 3 | RDX | 40, 160, 3.4 |

* Dissolved energetic residue.

## Summary

Energetic residues can be transported away from locations where they are initially deposited on artillery and bombing impact, anti-tank, and demolition ranges. Dissolved energetic residues were present in seeps and, in some cases, in monitoring wells located downgradient from artillery and bombing impact, anti-tank, and demolition ranges. The concentration of dissolved energetic residues in surface and groundwaters were often associated with residues in the surrounding surface soil. The energetic residues were specific to the type of range. RDX was present most frequently in surface water, groundwater, and sediment on impact and demolition ranges; HMX was present most frequently on anti-tank ranges. TNT was typically detected at lower concentrations than RDX. TNT is much more subject to soil attenuation processes than RDX or HMX (Pennington et al. 1995; Major 1999; Thorn et al. 2002). In general, these findings are consistent with those reported for groundwater sampling program at the MMR where RDX and HMX were detected more frequently than TNT (Clausen et al. 2004).

Groundwater data were limited to a few sites, most in Canada, and may not be representative of all ranges across the United States and Canada. A more systematic and comprehensive sampling program for ground and surface waters would support greater confidence in data interpretation. For those sites sampled in this study, however, far more monitoring wells exhibited no detections than detections. RDX was the most frequently detected explosive. Detections were generally in the low ppb levels except for the data on the OB/OD range where concentrations were in higher ppb levels. In surface water bodies (including lakes, ponds, rivers, and streams), either on or near training ranges, very few detections of explosives were observed. Detections were typically in the low ppb levels. Nevertheless, detections suggest transport of energetic residues via surface runoff or groundwater transport. Standing water in craters frequently contained dissolved energetic compounds at low concentrations and may, therefore, be point sources for transport.

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# 5 Residues Resulting from Blow-in-Place of Specific Munitions

## Introduction

Observations and data from field characterization studies on various training ranges suggest that incomplete detonations of rounds are significant contributors to residues of energetic materials. Therefore, special efforts were made during ER-1155 to understand the mass and distribution of energetic materials resulting from incomplete detonations. When a weapon is fired and the ammunition performs as intended (i.e., a high-order detonation is achieved), only very small amounts of residual energetic material are expected. Most of the energetic material is consumed by the detonation or in the fireball (or after-burn). When the ammunition fails to perform perfectly and detonation is incomplete, the resulting residual can range from fragmented shells still containing some of the energetic material (low-order detonations) to intact shells still containing all of the original energetic material. The latter are considered UXOs. Fragmented shells, or remnants of low-order detonations, are typically left lying on the range since they pose little detonation hazard. However, UXOs are usually rendered safe by EOD personnel who typically detonate the round with a donor charge where it lies (BIP). If this BIP detonation is imperfect, the procedure may leave undesirable energetic residues behind. Such residues, together with residues from low-order detonations and detonations caused by shrapnel from local high-order detonations, are a potentially significant source of energetic materials on live-fire ranges. Depending on the hydrogeology and climate for a given range, these residues may be available for transport to groundwater and for exposure to environmental receptors.

During the execution of ER-1155, studies were conducted to determine the mass and distribution of energetic materials resulting from fired artillery rounds and from BIP detonations, both low-order and high-order. The studies included primarily mortar rounds (60- and 81-mm) and larger artillery projectiles (105- and 155-mm), but also included rifle grenades, hand grenades, landmines (anti-personnel and anti-tank), and detonations of unconfined charges. The objective of this chapter is to integrate and summarize the data acquired during these studies.

## Fired munitions

Residues resulting from live-firing of munitions were collected on snow after detonations (Jenkins et al. 2002b). Munitions studied were 60-mm mortar rounds at Fort Drum, NY; 60-mm mortar rounds, 120-mm mortar rounds, and 40-mm rifle grenades at Camp Ethan Allen, VT; 60-mm mortar rounds, 81-mm mortar rounds, 120-mm mortar rounds, and 105-mm artillery rounds at Fort Richardson, AK; 155-mm howitzer rounds fired at the former Fort Greely, AK; and hand grenades at Fort Drum, NY (Hewitt et al. 2003, 2004; Walsh et al. 2005a, 2005b). All of these tests were conducted on a snow-covered surface to facilitate recovery of residual explosives. For smaller items, a large percentage of the soot-covered snow was sampled; for larger items, a smaller percentage was collected. Average total mass of RDX and TNT for each type of round ranged from µg to mg quantities (Table 5–1). These data demonstrate that the HEs in the main charge of howitzer rounds, mortar rounds, and hand grenades are efficiently consumed (on average 99.997 percent or more) during live-fire operations that result in high-order detonations. The HEs that are not consumed during these detonations are spread over an area that would, on average, contribute 10 µg/kg/detonation or less to the ground surface. This amount of explosives residue is consistent with the very low concentrations of energetic residues that have been detected on most of the active impact ranges, with the exception of soil samples collected near munitions that have been blown in place or have partially detonated (i.e., low-order,

Table 5-1. Estimated RDX and TNT mass (± standard deviation) from live-fire detonations of various munitions.

| Item | n | Average RDX/round µg | Average TNT/round µg |
|---|---|---|---|
| 60-mm mortar rounds | 14 | 93 | 5.0[1] |
| 81-mm mortar rounds | 14 | 8,500 | 1,100 |
| 120-mm mortar rounds | 17 | 12,000 | 1,700 |
| 105-mm howitzers rounds | 13 | 95 | 170 |
| 155-mm howitzers (TNT) rounds | 7 | 0.0 | 0.0 |
| 155-mm howitzers (Comp-B) rounds | 7 | 300 | 9.0 |
| 40-mm rifle grenades | 3 | 1,610 (1,700) | 5.2 (3.6) |
| M67 hand grenades | 7 | 25 (16) | ND[2] |
| Claymore mines | 8 | 16,000 (1,600) | NA[3] |

[1] One replicate was not analyzed for TNT; therefore, n for TNT was 13.

[2] None detected.

[3] Not applicable.

breached casing, and presence of unconsumed main charge). Therefore, high-order detonations from live-fire training do not distribute large amounts of explosives residues to Army training ranges on a per round basis.

## Unconfined charges

Unconfined donor charges were investigated at various times during the execution of ER-1155 (Brochu et al. 2004; Hewitt et al. 2003; Walsh et al. 2005b). Detonation is a complex phenomenon that is likely to be affected by the size and shape of the main explosive charge, the position and orientation of the detonator, the characteristics and quantity of the donor charge, and even the weather conditions at the time of detonation. To better understand the influence of such parameters on BIP detonations, controlled experiments were conducted with unconfined charges in various configurations. Testing with unconfined charges was elected to avoid the complexities and hazards of working with real munitions. Detonation of unconfined charges represents a "worst case" scenario for residue generation because, without a casing, pressure cannot build up and high temperature is not achieved. The objectives of these studies were to estimate the quantities of residues resulting from the detonations, to define the relationship between the size of a charge and the residue generated upon detonation, and to determine whether the shape of a charge affects the quantity and distribution of residues.

A general description of the tests conducted by DRDC-Val is given in Table 5–2; details of explosives compositions, formulations, and detonation procedures are presented in Brochu et al. (2004). Data were acquired with high-speed video (Kodak CR2000 and Sony Betacam), two pressure gauges (PCB 113B51, PCB Piezotronics, Inc., Depew, NY), and a meteorological station (Weather Monitor II, Davis Instruments, Corp., Hayward, CA). Detonations were executed on a heavy steel plate (1.34 × 1.77 × 0.1 m) positioned in the center of four polyethylene tarps to isolate tests from potentially contaminated underlying soil. Residue was collected on aluminum witness plates (1 m × 1 m × 3 mm) positioned around the detonation center. Residues were recovered from the witness plate surface with acetone-soaked swabs (10.2 cm square). Residues from all witness plates from a single detonation were combined, extracted, and analyzed by HPLC (Method 8330, USEPA 1994). Explosives included C4, TNT, Composition B, octol, PBX, and XRT.

Table 5-2. General description of tests for unconfined charges.1

| Explosive | Number of Tests | Quantity of Explosive, g | Shape | Diameter, cm | Length, cm |
|---|---|---|---|---|---|
| C4 | 22 | 20, 30, 40, 50, 75, 100 | Spheres<br>Cylinders<br>Blocks | 2.5-9.0 | 1.9-12.5 |
| TNT | 7 | 20, 30, 40, 50, 75, 100 | Cylinders | 2.5, 5.6 | 2.6-13.1 |
| Comp B | 8 | 20, 30, 40, 50, 75, 100 | Cylinders | 2.5, 5.6 | 1.8-12.4 |
| Octol | 7 | 20, 30, 40, 50, 75, 82, 100 | Cylinders | 2.5, 5.6 | 1.7-11.3 |
| PBX | 7 | 20, 30, 40, 50, 75, 100 | Cylinders | 2.5, 5.6 | 1.8-12.4 |
| XRT | 14 | 20, 30, 40, 50, 75, 100 | Cylinders | 2.5, 5.6 | 1.8-12.4 |

[1] Primers were used with some but not all detonations. Detonators were oriented vertically for some tests and horizontally for others. The number of witness plates used with each test varied from 8 to 12 according to the size of the charge. Three of the 55 tests were duplicated.

Total residue recovered was generally small. For example, RDX values for all tests ranged from nondetect to 350 mg, but the median value was only 5 mg. Based on the total amount of each compound initially present, the maximum residues were 3.4 percent TNT (TNT cylinders), 19 percent RDX (XRT cylinders), and 2.8 percent HMX (XRT cylinders). Median values were much lower, 0.006 percent TNT, 0.02 percent RDX, and negligible HMX. Larger charges often yielded smaller amounts of residue; however, trends were inconsistent. Based on median total mass (mg), PBX and Composition B generated the greatest mass, 26 and 13 mg RDX, respectively. All other charges exhibited medians less than 10 mg. Based on residues of RDX recovered from C4 detonations, spheres generated the smallest residues (mean 1.8 mg, median 1.2 mg), cylinders next (mean 5.0 mg, median 1.8 mg), and blocks the greatest (mean 140 mg, median 9.5 mg).

Several tests were conducted by CRREL with C4 alone in conjunction with other BIP studies at Camp Ethan Allen, VT, and Fort Richardson, AK. Details are presented in Hewitt et al. (2003) and Walsh et al. (2005b). Detonation efficiencies were generally greater than 99.9 percent. Results are included in Appendix A.

## BIP of 60-mm mortar rounds

Three sets of experiments have been performed during ER-1155 to evaluate the quantity and distribution of explosive residues resulting from BIP of 60-mm mortar rounds. Two of the studies, one on snow and one on witness plates, were conducted at CFB Valcartier, Quebec (Lewis et al. 2003; Dubé et al. 2004); the third was conducted at Redstone Arsenal, AL (Pennington et al. 2006a).

### Valcartier tests on snow

Detonations of the 60-mm TNT-containing mortar rounds were initiated in the following two ways: (1) by packing a relatively small amount (50 g) of C4 into the fuze well, and (2) by placing a block of C4 (150 g) on the round (Lewis et al. 2003). The first approach was intended to simulate fired munitions; the second represented typical BIP detonations. Surface snow samples (approximately 2 cm deep) were taken in three or four 1- or 2-$m^2$ areas within the soot "footprint" of residue. This resulted in a sampled area of 3 to 6 $m^2$. Selected areas were biased to greater soot density to improve likelihood of detections. For analyses, the snow samples were allowed to melt, soot was filtered out, and a well-mixed subsample of the filtrate was recovered using a Sep-Pak cartridge to absorb the explosive analytes. Analytes were eluted with acetonitrile and analyzed by EPA Method 8330 (USEPA 1994).

No difference was observed between mass ($mg/m^2$) of residues obtained by the two approaches. Recoveries of RDX, TNT (including transformation products), and HMX were less than 0.2 percent of the original content of the mortar rounds. HMX was rarely detected. It is concluded that the configuration intended to simulate fired munitions was actually closer to typical BIP. The mortar rounds contained TNT only, but RDX was detected in residues. Therefore, C4 contributed RDX to the detonation residues.

### Valcartier tests with witness plates

The 60-mm mortar rounds contained 351 g of TNT. Detonations were achieved with C4, shaped charges, and a binary explosive. The C4 (50, 100, or 150 g) was placed laterally along the body of the mortar round, except for one test with C4 placed in the nose of the mortar round. The binary explosive was FIXOR, comprised of two components that become explosive once mixed. The two components are a flammable liquid and an inert powder. The three sizes (6.5, 16.5, and 36 g) of commercial shaped charges and the standard military C4, linear M7 shaped charges contained RDX. Mortar rounds were both fuzed and unfuzed. Residues from detonations were captured on 1 × 1 m witness plates surrounding the steel detonation plate (1.34 × 1.77 × 0.1 m). Plates were sampled and analyses conducted in a manner similar to that described in "Residues from unconfined charges" above, except that a compositing scheme was implemented to achieve resolution of residue with distance from the detonation center. Details of tests, site configurations, and analytical methods are given by Dubé et al. (2004).

Six of the 14 detonations were judged low-order based on pressure readings. At least 150 g of C4 in contact with the casing or a 16.5-g shaped charge were needed for the efficient destruction of the 60-mm mortar rounds. Residues for high-order detonations with 150 g C4 were $\leq$ 0.2 g TNT recovered collectively from all witness plates. Residues for low-order detonations with 75 or 100 g of C4 or with the 50 g of C4 placed into the nose ranged from 0.6 to 9.5 g of TNT. High-order detonations with the 16.5- and 36-g shaped charges deposited about 0.5 g TNT, while the low-order detonation with the 6.5-g shaped charge generated 4.7 g of TNT. FIXOR generated between 0.25 and 1.25 g of TNT. RDX concentrations were generally very low (µg to low mg quantities) and HMX was only rarely detected and then at low levels. Distribution with distance was heterogeneous and inconsistent.

### Redstone Arsenal tests

The objective of this study was to optimize BIP by determining which of four donors produced the greatest consumption of explosives constituents. Residues resulting from detonation of fuzed Composition B-filled 60-mm mortar rounds with the following donor charges were compared: shaped charges (30 g RDX, Halliburton Energy Services, Houston, TX); C4 (91 percent RDX, 5.3 percent plasticizer, 2.1 percent binder, and 1.6 percent petroleum oil) in 1.25-lb (0.567-Kg) blocks; block TNT (1 lb, or 0.454 Kg); and a binary explosive (Kinepak, Slurry Explosive Corp., Oklahoma City, OK) consisting of a solid base (K-1-S, 99–100 percent ammonium nitrate, Chemical Abstracts Service (CAS) No. 6484-52-2) and a liquid activator (K-1-L, minimum of 95–100 percent nitromethane, CAS No. 75-52-5). Detonations were executed on the surface of clean sand contained in a large steel bucket. The bucket was placed on a tarp to facilitate recovery of residues. The residue mass was collected with distance from the detonation center by sweeping sand from the tarp in concentric circles (3, 6, 9, 12, and 15 m radii) around the detonation center. Sand from each ring was thoroughly mixed in a cement mixer and subsampled for HPLC or GC/MS analysis (USEPA 1994; USEPA 2000, respectively). Each round was tested with each donor charge in seven replicates. Details can be found in Pennington et al. (2006a).

The most successful donor charge for the 60-mm mortar rounds was the binary. No constituent residue was detected in any replicates of the mortar round with this donor. All other donors left milligram (mg) quantities of RDX and microgram (µg) to mg quantities of TNT. Without considering the binary charge, the C4 donor produced the smallest quantity of residue and the TNT donor produced the greatest. The TNT donor also generated significant TNT residues. When residue mass was analyzed by analyte (RDX, HMX, and TNT) and donor (TNT, shaped charge; C4 > binary charge), differences between donors were significant for RDX (TNT, shaped charge; C4 > binary charge) and TNT (TNT > shaped charge; C4 > binary charge). No consistent trend in the distribution of mass with distance was observed with the 60-mm mortar rounds.

## BIP of 81-mm mortar rounds

Six sets of experiments were performed during ER-1155 to evaluate the quantity and distribution of explosive residues resulting from BIP of 81-mm mortar rounds. Two studies were conducted at Camp Ethan Allen, VT (Jenkins et al. 2000; Hewitt et al. 2003). Another was conducted at Fort Richardson, AK (Walsh et al. 2005a). Two other studies, one on snow and one on witness plates, were conducted at CFB Valcartier, Quebec (Lewis et al. 2003; Dubé et al. 2004). The last study was conducted with sand at Redstone Arsenal, AL (Pennington et al. 2006a).

### Camp Ethan Allen tests on snow

The following two tests were conducted:  one with three M374 fuzed cartridge and one with a single M374 fuzed charge (Hewitt et al. 2003). Both tests were conducted over snow with a single block of C4 (M112) on the side of the projectile body as the donor charge. In the first test, between 4.6- and 24.4-m$^2$ (6.2 to 15 percent) of the visible plume was sampled. In the second test, 7 m$^2$ (2.3 percent) of the plume was sampled. In the first test, 42 mg of RDX residue was observed; in the second test, 14 mg (see

Table B1, Appendix B). HMX was 6.8 and 3.4 mg, respectively. Only 0.3 and 0.081 mg of TNT, respectively, were observed in the two sets of tests.

### Fort Richardson

Seven fuzed M374 mortar cartridges were detonated on snow-covered ice (Walsh et al. 2005a). Multiple sampling methods were used in each plume including three methods of replicate multi-increment sampling and discrete samples of 1-$m^2$ areas. Quality control tests included multi-increment sampling outside the visible plume, testing for biasing based on proximity to the detonation point and density of the soot, and sampling beneath previously sampled areas. All areas were sampled prior to tests to ensure no contamination from previous activities. From 2 to 4 percent of the visible plume was sampled. Residue estimates were 130 mg RDX, 23 mg HMX, and no TNT (see Table B1, Appendix B).

### Valcartier tests on snow

Tests were conducted in a manner similar to that described in “Residues from 60-mm mortar rounds” above (Lewis et al. 2003). The 81-mm mortar rounds contained 857 g Composition B (416 g RDX, 57 g HMX, and 343 g TNT). The mortar rounds were tested with the propellant and fuze removed. The donor charges were 60 or 150 g of C4 positioned on the casing or 40 g placed in the nose of the mortar round. No relationship was observed between the amount of C4 and the amount of residue. The median amount of RDX recovered relative to the amount initially in the mortar round for all six detonations was 0.0022 percent (11 mg); the amount of TNT recovered was 0.026 percent (88 mg).

### Valcartier tests with witness plates

The same kind of 81-mm mortar rounds used in snow tests were used for the witness plate tests (Dubé et al. 2004). Detonations were achieved with C4, shaped charges, and a binary explosive. The C4 (100 or 150 g) was placed laterally along the body of the mortar round, except for four tests with 75 g C4 placed in the nose. The binary explosive, FIXOR, was used in two detonations. The C4 linear M7 shaped charge was used once, and the 6.5, 16.5, and 36 g shaped charges were each used once. Tests were both fuzed and unfuzed. Residues from detonations were captured on witness plates and analyzed as described previously.

In general the residue generated by C4 (an average of approximately 900 mg RDX and 1,200 mg TNT, which included two possible low-order detonations) was unrelated to the mass of C4 used. Residues generated by FIXOR were comparable to those generated by C4. The linear shaped charge produced the greatest amounts of residues: 18.13 g RDX, 12.159 g TNT, and 1.105 g HMX. Although data are limited, a trend of decreasing residue mass with increasing shaped charge size was evident.

### Redstone Arsenal tests

Detonations of the unfuzed, but capped, Composition B-filled 81-mm mortar rounds used two M81 igniters, two M14 blasting caps, and a 16-in. 80-grain detonation cord (Pennington et al. 2006a). Other test conditions were as described for 60-mm mortar rounds in “Redstone Arsenal tests” above, except that a 36-g shaped charge was used rather than the 30-g used on the 60-mm mortar rounds.

The 81-mm mortar round generated more residue than any other round (60-mm mortar rounds, 105-mm and 155-mm artillery projectiles) in this set of tests. The shaped charge was the most effective donor. Only µg to low mg quantities of RDX were deposited after detonations with the shaped charge. Differences between donors were significant for HMX (C4 binary > TNT, shaped charge), RDX (C4 > TNT, > shaped charge; binary > shaped charge) and TNT (TNT, C4 binary > shaped charge). The binary charge, so successful with the 60-mm mortar rounds, produced significant (mg) quantities of RDX. C4 produced mg quantities of both RDX and TNT. As observed with the 60-mm mortar rounds, the TNT donor left mg quantities of TNT. Results with C4 were 46.8 ± 45.9 and 15.1 ± 21.0 mg for RDX and TNT, respectively.

## BIP of 105-mm projectiles

Tests with 105-mm artillery projectiles were conducted at three sites: Valcartier, Quebec (Lewis et al. 2003); Fort Richardson, AK (Walsh et al. 2005b); and Redstone Arsenal, AL (Pennington et al. 2006a). The test at Valcartier consisted of a single detonation of a Composition B-filled projectile with C4 in the fuze well. Results showed 24 mg RDX and 2,500 mg TNT (Lewis et al. 2003). The TNT mass is relatively high, but with a single test, variability was uncontrolled.

Tests at Fort Richardson were conducted on snow-covered ice on the Eagle River Flats impact area (Walsh et al. 2005b). Seven fuzed M1 105-mm Composition B-filled projectiles with 136-g TNT supplemental charges were detonated over 2 days. All plumes were sampled using at least four different incremental sampling protocols with replication of some of the protocols. Quality control methods were randomly applied to the tests and included sampling outside the demarcated plume and sampling below previously sampled points. Estimated residues were 41 mg RDX, 8.8 mg HMX, and no TNT (see Table B1, Appendix B).

Tests at Redstone Arsenal were conducted as described for 60-mm mortar rounds except that the 36-g shaped charge, and two rather than one block of C4 and TNT were used (Pennington et al. 2006a). The rounds were unfuzed, but capped. The smallest amount of residue from 105-mm projectiles was produced by the shaped charge; however, except for the binary charge, which generated significantly greater residue than other donors, differences among donor charges were not significant. Unlike with the mortar rounds, the TNT donor generated almost no TNT residue, but mg quantities of RDX. The shaped charge produced 725 µg TNT, but 17 mg of RDX. C4 generated both RDX and TNT, 28 and 11 mg, respectively. The binary charge was too small for the 105-mm projectiles, often resulting in low-order detonations. Detonations with the binary charge were considered high-order by EOD personnel, but residues of RDX, TNT, and HMX were in the g levels.

## BIP of 155-mm projectiles

Studies of the BIP of 155-mm artillery projectiles were conducted at Camp Ethan Allen, VT, Fort Richardson, AK, and Redstone Arsenal, AL. Tests at the first two sites were conducted on snow, while tests at the last site were conducted on a tarp.

### Camp Ethan Allen

Eight unfuzed 155-mm rounds containing TNT were suspended 1.3 m above the snow by a chain attached to a wooden frame (Hewitt et al. 2004). The rounds were blown in place with a 0.57-kg block of C4. Aluminum trays were positioned at the four compass points about 15 m from the suspended round. Surface snow samples, typically 15, were collected after 7 of the detonations. The surface area sampled was approximately 1 to 2 percent of the post-detonation visible soot plume. The mass of TNT averaged 20 ± 38 g. The median mass was 200 mg, which represents 0.003 percent of the mass originally present in the round. The distribution of mass values was strikingly high, ranging over five orders of magnitude. Surface soil composite samples analyzed later in the year after the snow had melted showed elevated TNT concentrations where deposition on snow had been high.

### Fort Richardson

Three sets of tests were conducted on snow-covered ice at the Eagle River Flats impact area at Fort Richardson. In the first set, seven Composition B-filled 155-mm fuzed projectiles (M107 with M739 fuze) were detonated on ice blocks (1 m × 0.6 m × 0.6 m) using a 570-g block of C4 placed near the nose of each round (Walsh et al. 2005a). Snow was sampled according to two multi-increment sampling protocols: a large-increment (about 100 increments) and a multi-increment (about 40 increments). Quality control procedures used during sampling included replicate sampling, sampling outside the visible plume, sampling below previously sampled points, and sampling based on soot density within the plume. The second set of tests was conducted using seven TNT-filled fuzed projectiles. The protocols followed for these tests were the same as with the Composition B tests above. The final set of tests examined residues from Composition B-filled rounds blown in different configurations. Three fuzed rounds were detonated vertically (nose up) using one block of C4 in a test similar to that conducted at Camp Ethan Allen. Three more fuzed rounds were detonated horizontally with two blocks of C4. The last round was detonated with a single block of C4 and no fuze. Replicate multi-increment sampling was used for all tests. Quality control measures included sampling outside the demarcated plume and soot-density gradient sampling within the plume. For the first set of tests, residues averaged 14 mg RDX with a median value of 10 mg and less than 1 mg HMX in the detonation plumes where detected. No TNT was detected. For the TNT tests, detonation plume residues averaged less than 6.5 mg RDX with a median value of 5.9 mg where detected and 6.7 mg TNT with a median of 5.9 mg. The source of RDX in these tests is the fuze (21 g RDX), the C4, or both. Evidence of TNT particles were detected in subsurface samples and samples taken outside the plume, similar to findings from Camp Ethan Allen. The alternative BIP tests agreed well with the first set of tests, with only the one unfuzed detonation having residue levels elevated above the residues from the other configurations. The alternative BIP tests indicate that tests done over the course of this project using different detonation configurations using blocks of C4 should give similar results (see Table B1, Appendix B).

### Redstone Arsenal

Tests were conducted as described for 60-mm mortar rounds except that only two donors were tested: two blocks of C4 and the 36-g shaped charge (Pennington et al. 2006a). The rounds were unfuzed, but capped. The sampling protocol described for 105-mm projectiles was used with the 155-mm projectiles. The C4 generated less residue than the shaped charge; however, differences between the two donors were not significant. Both the shaped charge and the C4 were more effective with this large round than with the previous smaller ones (60- and 81-mm mortar rounds, 105-mm projectile). The significantly greater mass of the 155-mm projectile promotes the consumption of explosives in the detonation and in the afterburn. Nearly all observed residue was generated by only two of the five replicate detonations. All residue was RDX and TNT; no HMX was detected. The C4 generated an average of 2.1 ± 1.9 mg of RDX and 0.045 ± 0.028 mg of TNT, while the shaped charge generated an average of 9.8 ± 7.9 mg of RDX and 11 ± 9.3 mg of TNT.

## BIP of mines

Several types of mines were investigated as opportunities permitted during the execution of ER-1155. On separate occasions at Camp Ethan Allen, the following mines were detonated: two unfuzed anti-tank mines and a Claymore mine, seven Claymore mines, and eight anti-personnel mines consisting of two each of four different types (Hewitt et al. 2004; Jenkins et al. 2002a). Furthermore, on separate occasions a set of seven mimics of PMA-1A (Dubé et al. 2004) and eight PMA-2 anti-personnel mines (Lewis et al. 2003) were detonated at CFB Valcartier.

### Anti-tank mines

The two anti-tank mines were an M19, which contained 0.53 kg Composition B, and an M15, which contained 10.3 kg of Composition B. The mines, positioned upside down on snow-covered ground, were blown in place with 0.28 kg (half a block) of C4. Ten snow samples were collected after denotation of the M19 mine and nine after detonation of the M15 mine. The estimated mass of the residue from the M19 was 2.7 mg RDX and no TNT. For the M15 the estimated mass was 40 mg RDX and 0.076 mg TNT.

### Anti-personnel mines

At Camp Ethan Allen, two each of the following anti-personnel mines were detonated unfuzed: PMA-1A (200 g TNT), PPM-2 (130 g TNT), PMA-2 (100 g TNT and 13 g RDX), and VS-50 (43 g RDX). Mines were detonated over a steel plate buried under 20 to 30 cm of snow. The PMA-1A and PMA-2 were detonated with blasting caps in the fuze well; the PPM-2 and VS-50 were detonated with half a block of C4. The surface snow samples taken after each detonation represented about 5 percent of the visible plume. The greatest amount of TNT residue was generated from the PMA-1A and PPM-2 mines (Table 5–3). The VS-50 generated the greatest amount of RDX (Hewitt et al. 2004). At Valcartier in 2003 seven PMA-2 mines (100 g TNT only) were detonated in various configurations with C4 (Lewis et al. 2003); in 2004 eight PMA-1A mines were detonated with C4 (Dubé et al. 2004). Both sets of Valcartier data show primarily g quantities of TNT residues across the various test configurations.

### Claymore mines

Four composite surface soil samples were collected at Yakima Training Center, WA, from an area where a single Claymore mine (0.68 Kg Composition B) had been detonated with an electrically initiated fuze the previous week (Jenkins et al. 2002a). No residue from the mine was detected. At Camp Ethan Allen, seven mines were detonated with a 5-min time fuze (Hewitt et al. 2004). About 10 snow samples were collected after each detonation. Deposition of RDX averaged 15.9 + 16.0 mg. This mass was estimated to represent 0.002 percent of the original contents of the mine and a soil concentration of 10 µg/kg RDX.

## BIP of Bangalore torpedoes

Two Bangalore torpedoes containing 4.86 kg Composition B were detonated with a timed fuze, one at Fort Drum, NY, and one at Fort Richardson, AK (Hewitt et al. 2004). At Fort Drum, ten snow samples were collected within the soot plume and three from the walls of the crater. At Fort Richardson, eight snow samples (about 1percent of the plume) were collected. Recoveries of RDX were 110 and 90 mg, respectively. TNT (0.15 mg) was recovered from the first torpedo only.

Table 5-3. Mass (g) of residue generated by BIP of unfuzed anti-personnel mines.

| Location | Mine | Detonation Description | Mass (mg) | | |
|---|---|---|---|---|---|
| | | | RDX | TNT | HMX |
| Camp Ethan Allen, VT | PMA-1A | blasting cap in fuze well | - | 280 | - |
| | PMA-1A | | - | 1,100 | - |
| | PMA-2 | | 0.77 | 2.3 | - |
| | PMA-2 | | 1.60 | 550 | - |
| | PPM-2 | 280 g C4 | 49 | 1,100 | - |
| | PPM-2 | | 44 | 7,900 | - |
| | VS-50 | | 170 | - | - |
| | VS-50 | | 100 | - | - |
| | Claymore | 5-min time fuze | 15.9 | - | - |
| CFB Valcartier 2003 | PMA-2 | 20 g C4 | 990 | 40,000[1] | <dl |
| | PMA-2 | 5 g C4 | 120 | 1,700[1] | <dl |
| | PMA-2 | 20 g C4 | 33 | 3,700[1] | <dl |
| | PMA-2 | 20 g C4 | ND[2] | ND | ND |
| | PMA-2 | 20 g C4 | 19 | 3,700[1] | <dl |
| | PMA-2 | 20 g C4 | 15 | 32[1] | <dl |
| | PMA-2 | 20 g C4 | ND | ND | ND |
| CFB Valcartier 2004 | PMA-1A | 25 g C4 lying on mine | 1.2 | 281.4 | <dl |
| | PMA-1A | 30 g C4, 5 g in lateral hole | ND | 16.8 | <dl |
| | PMA-1A | 4 g C4 in lateral hole | ND | 235.8 | ND |
| | PMA-1A | 20 g C4 on top center hole | 7.2 | 3,117.6 | <dl |
| | PMA-1A | 20 g C4 on top center hole | 0.0 | 1,946.4 | <dl |
| | PMA-1A | C4 linear shaped charge | 0.0 | 9,964.8 | <dl |
| | PMA-1A | 4 g C4 in lateral hole | 84.8 | 6,900.8 | 0.8 |
| | PMA-1A | FIXOR lying on mine | 14.43[3] | 1,404.0 | 0.1[3] |
| Yakima Training Center, WA | Claymore | Electric fuze | <dl[4] | <dl | <dl |

[1] Includes mass of TNT transformation products.

[2] ND = no data, sample lost.

[3] Possible sample contamination.

[4] Less than detection limit.

## BIP of hand grenades

Hand grenades (M67) containing 185 g of Composition B were blown in place in two sets of experiments at CFB Valcartier. In spring 2001, five grenades were detonated in various configurations (Table 5–4). In autumn 2002, eight additional grenades were detonated. Residues were collected on witness plates (see Dubé et al. 2004 for details). If the values with

Table 5-4. Hand grenades blown-in-place with various configurations of donor charges.

| Experimental Set | Donor | Configuration | Mass of Residue (mg) | | |
|---|---|---|---|---|---|
| | | | RDX | TNT | HMX |
| Spring 2001 | none | Detonator inside grenade | ND[1] | 35 | ND |
| | 145-g C4 | Lateral | 7 | 25 | 2 |
| | 2 bottles FIXOR | 1 bottle each side | 565[2] | 211[2] | 58[2] |
| | none | Detonator inside grenade | 4 | 3 | 1 |
| | 100-g C4 | Lateral | 1 | 2 | 0 |
| Autumn 2002 | 100-g C4 | Lateral[3] | 0[4] | 267[4] | ND |
| | none | Detonator inside grenade | 34 | 17 | 2 |
| | none | Detonator inside grenade | 17 | 11 | 1 |
| | 20-g C4 | Lateral | 15[4] | 8[4] | 1[4] |
| | 2 bottles FIXOR | 1 bottle each side[3] | 23 | 10 | 2 |
| | 36-g RDX shaped charge | Lateral | 12 | 306 | ND |
| | 6.5-g RDX shaped charge | Lateral | 11[4] | 485[4] | ND |
| | 16.5-g RDX shaped charge | Lateral | 17 | 12 | 1 |

[1] Not detected.

[2] Sample possibly contaminated.

[3] Fuzed grenade tested.

[4] Residue may be due to a previous low-order detonation.

potential for sample contamination are ignored, only one detonation exhibited a relatively high TNT residue (306 mg). Others were less than 40 mg TNT and also less than 40 mg RDX. Consistently less than 0.01 percent of the original mass of RDX remained in the residue.

## Controlled low-order detonations

A series of controlled low-order detonation tests were conducted under ER-1155 (Pennington et al. 2005; Pennington et al. 2006b). Detonations were conducted on a raised table in the center of a tarp. Residue was recovered by sweeping the tarp. The final round of testing included detonation of four 60-mm, three 81-mm and four 120-mm mortar rounds, five 105-mm and seven 155-mm projectiles (Pennington et al. 2006b). All detonations had a target energy yield of 75 percent except for the 105-mm projectiles for which the target was 50 percent. Achieving a specific energy yield was challenging, especially for the smaller rounds. Although a general trend of increasing mass with decreasing energy was evident, the relationship was significant for the 155-mm rounds only. Mass distribution within 3 m of the table was typically small. Distribution with distance for the smaller rounds was relatively uniform, while the larger rounds tended to reach a maximum at 6–9 m. In planning remediation strategies, a 15-m radius around low-order detonation debris seems a reasonable starting area. Since most of the residue was of large diameter, remediation and modeling should focus on particles, or chunks, ranging from 12.5 mm up to the diameter of the round (i.e., 60, 81, 105, 120, and 155 mm).

The ratio of TNT to RDX in the original Composition B was conserved in the residue. However, the ratio in the < 0.25-mm size fraction exhibited significantly less TNT than is typical of Composition B. This reduction in TNT may be related to the much lower melting point of TNT (80 °C) relative to RDX (205 °C). Finer particles not only melt more readily than larger particles, but melted TNT is also more sensitive to detonation forces than solid TNT (Urbanski 1964).

Analytes other than TNT and RDX detected in residues included HMX, an impurity in Composition B, which was detected in every detonation. Other detections were in mg quantities only and included transformation products of TNT (2-amino-4,6-dinitrotoluene) and RDX (MNX), 2,4DNT, and two photodegradation products of TNT (1,3,5-trinitrobenzene and 1,3-dinitrobenzene) that probably formed during sample recovery. The source of the 2,4DNT may be boosters or supplemental charges in certain rounds, or 2,4DNT present as an impurity in military grade TNT.

## Conclusions

Results of these studies establish the importance of achieving high-order detonations when disposing of UXOs on live-fire training ranges. Fired munitions that perform as designed (high-order detonations) leave only µg quantities of HE residues and are, therefore, a minor source of range contamination on a per-round basis. Low-order detonations leave significant quantities of explosive residues. Therefore, BIP must be performed using sufficient donor to achieve high-order detonations. RDX predominates in Composition B residues resulting from BIP demolition. Unfortunately, RDX is highly mobile in the environment, posing a threat to groundwater and other receptors. The C4 tends to leave mg quantities of RDX after BIP detonations, even when high-order detonations are achieved. This may be due to the lack of confinement of the C4 or to the booster in the fuze. Depending on initial content, mines, torpedoes, and hand grenades blown in place leave both TNT and RDX in mg to g quantities. Under most circumstances, the original ratio of RDX to TNT in Composition B munitions is reflected in the post-blast residue.

To ensure environmental protection from residues of explosives on live-fire ranges, every effort should be made to minimize low-order detonations. When executing BIP procedures, the donor should be sufficient to produce maximum consumption of the UXO. Munition-specific BIP protocols should be developed to reliably achieve high-order detonations that consume both the donor and the UXO explosive. Furthermore, whenever possible, range debris should be removed if it contains residual explosives. Chunks of undetonated explosive should be collected and destroyed without using unconfined detonations.

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# 6 Conclusions

## Background

Suspension of training at MMR in 1997 due to detection of explosives residues in groundwater alerted the DoD to the potential for undesirable residuals at live-fire training ranges (USEPA 1997). The partnerships forged among the various stakeholders over the subsequent years have resulted in a gradually developing but definite awareness of the issues and implications of explosives residues on training ranges for the military, regulatory agencies, and public interest groups. In 1999 when SERDP announced a Statement of Need in this area of research, the need was great for data to characterize and define the extent of HE residues resulting from live-fire training.

Previous studies demonstrated the presence of RDX, HMX, TNT, and 2,4DNT on training ranges. Low concentrations of RDX, HMX, and TNT were detected in surface soils, and groundwater at MMR (CHPPM 1994). 2,4DNT and several other munitions-related compounds were found near weapons firing positions at Fort Richardson, AK and at Aberdeen Proving Ground, MD (Racine et al. 1992; Phillips and Bouwkamp 1994). HMX and TNT were detected at three anti-tank firing ranges in Canada and at Fort Ord, CA. (Jenkins et al. 1997, 1998; Thiboutot et al. 1998). Several challenges to effective characterization of explosives residues in soils of firing ranges were immediately apparent from these data. Achieving representative data with the extreme spatial heterogeneity in explosives distribution and concentrations on the ranges is a significant challenge. Therefore, development of special sampling protocols specific to the distribution of residues associated with various aspects of training became a specific objective of this study. Another challenge, adequate subsampling before analysis of soils in the laboratory, was occasioned by solid particles of explosives in the samples. Environmental contaminants of concern have typically resulted from liquid spills, which result in a relatively homogeneous distribution of the contaminant in the soil matrix. Explosive fill is typically solid; therefore, scattered particles of various sizes must be characterized. The inability to represent the distribution of sizes within each soil sample leads to complications and loss of representativeness when subsampling in the laboratory (Jenkins et al. 2005a). Therefore, development of special sample processing methods was essential to achieving reproducible range characterization data.

Another observation of earlier studies was a dramatic difference between the relative amounts of HMX and TNT in the original octol explosive composition and in the soil. For example, the ratio of HMX to TNT changed from 70:30 percent in the original octol explosive to 100:1 in the soil. The difference was postulated to arise from differences in the behavior of the two compounds in the environment, specifically differences in dissolution and degradation rates. Consequently, the importance of understanding the environmental fate processes was recognized and included in the SERDP proposal.

## Summary of principal results

### Characterization of energetic residues on live-fire ranges

Much of the total acreage at artillery ranges is remote to firing points and targets and is, therefore, uncontaminated by residues of energetic compounds. Explosive and energetic residues tend to be heaviest in the vicinity of targets and at firing points. Most detonations during live-fire testing and training are high-order (i.e., the round performs as intended). It has been demonstrated that, when high-order detonations are achieved, most of the explosive is consumed and very little residue remains. Experiments conducted as part of this project indicated that only a relatively small percentage ($10^{-3}$ to $10^{-6}$ percent) of the initial explosive mass is deposited on the range after high-order detonations of artillery rounds, mortars, and hand grenades (Hewitt et al. 2005; Walsh et al. 2005). Therefore, high-order detonations contribute insignificantly to total range residues.

The explosive compounds present in residues are characteristic of the type of training conducted, specifically, the type of weapon systems used. The most important factor controlling residues is the incidence of low-order or incomplete detonations, which varies among weapon systems. Low-order detonations from fired rounds, from incomplete detonations during BIP of UXO, and as a result of UXO detonation from metal fragments of incoming rounds are the greatest sources of residues on the ranges. As a consequence of incomplete detonations, the residues tend to consist of large chunks and smaller particles of the original formulations present in the rounds that have been scattered over the soil surface (Taylor et al. 2006; Pennington et al. 2005). The introduction of solid chunk material into the environment exerts a dramatic influence on the approaches necessary to collect representative samples, maintain representativeness during laboratory analyses, and evaluate fate and transport processes. Low-order detonations deposit large amounts of very fine explosive solid residue around the cracked shells. Because the deposition occurs as particles are being dispersed over the range surface, it is the surface soil that contains the major source of energetic residues. An exception is demolition ranges where residues may occur at the surface and at depth because the soils are reworked to fill demolition craters. Demolition range surface sampling alone is therefore inadequate for estimating residue mass.

### *Sampling*

For grenade ranges, which are small in size and relatively well-mixed from intensive grenade detonations, multi-increment sampling consisting of 30 increments generated representative samples of surface soil. At anti-tank rocket ranges, where HMX from LAW rockets is the principal residue, short-scale spatial heterogeneity is high. Therefore, multi-increment sampling with a minimum of 30 increments was necessary to assure representativeness. Multi-increment sampling was also adequate for firing points at anti-tank rocket ranges. The number of increments and mass of soil needed per composite sample depended on residue deposition and the size of the area investigated. Generally, 30 to 50 increments were adequate for 10-m × 10-m (100-$m^2$) areas, and 50 to 100 increments were often adequate for larger areas, e.g., 100 m × 100 m (10,000 $m^2$). Collection of representative samples in areas subject to partial detonations was a major challenge due to the presence of large numbers of particles of explosive. Multi-increment sampling greatly improved representativeness over discrete sampling and reduced uncertainty tremendously. However, the remaining uncertainty was still not as low as needed to make decisions on the proper course of action. Discrete samples were used for depth profiling near these high-concentration sources.

### *Sample processing*

Sample processing and subsampling have also evolved to address heterogeneity, size distribution, and the composition of explosives and propellant particles (Walsh et al. 2002). Currently, air-dried soils are sieved (#10, < 2 mm) to remove oversized particles, then the < 2-mm fraction is mechanically ground on a ring mill. Soils from impact ranges are ground for 90 sec. Soils from firing points, where residues may include fibrous propellant, are ground for five 60-sec intervals with a short cooling period between. Ground samples are mixed thoroughly, spread to form a 1-cm layer, and 10-g subsamples are formed by combining ≥ 30 random increments. Analyses were conducted by EPA Method 8330 (HPLC; USEPA 1994) or Method 8095 (GC-ECD; USEPA 2000). For greater detail on site characterization, see Chapter 2 in this report or Jenkins et al. (2005b and 2006).

*Soil concentrations*

Concentrations of explosives residues in surface soils were highly dependent on the weapon system. On artillery ranges, RDX, TNT, and HMX concentrations near the targets generally ranged from nondetections to less than 1 mg $kg^{-1}$, exclusive of low-order detonations; at firing points, concentrations of 2,4DNT and NG ranged from nondetections to 10 mg $kg^{-1}$. Where low-order detonations were observed, concentrations were three or four orders of magnitude greater than near targets. For anti-tank rocket range target areas, HMX concentrations were typically in the hundreds of mg $kg^{-1}$, while RDX and TNT were usually detected at low mg $kg^{-1}$. At firing points of anti-tank rocket ranges, NG was the primary residue, producing surface soil concentrations from 0 to 25 m behind the firing line as high as the hundreds or thousands of mg $kg^{-1}$. On hand grenade ranges, RDX concentrations ranged from < 1 mg $kg^{-1}$ to about 50 mg $kg^{-1}$. The principal source of explosive residues (RDX, TNT, HMX) was low-order detonations or duds that were blown in place by EOD personnel.

Heavy metals were often present with explosives in firing range soils. The metals present and their concentrations were highly dependent on the weapon system used in each specific range. Metals should be taken into account when developing remediation approaches or when evaluating the environmental toxicity of munitions residues.

*Groundwater, surface water, and sediments*

Dissolved energetic residues were present in seeps and, in some cases, in monitoring wells located downgradient from artillery and bombing impact, anti-tank, and demolition ranges. The concentration of energetic residues in surface and groundwaters were specific to the type of range. RDX was present most frequently in surface water, groundwater, and sediment on impact and demolition ranges; HMX was present most frequently on anti-tank ranges. TNT was typically detected at lower concentrations than RDX. Groundwater data were limited to a few sites, most in Canada; however, far more monitoring wells for those sites exhibited no detections than detections (Ampleman et al. 2003; Thiboutot et al. 2004). RDX was the most frequently detected. Detections were generally in the low ppb levels except for the data on the OB/OD range where concentrations were in higher ppb levels. In surface water bodies (i.e., lakes, ponds, rivers, and streams), either on or near training ranges, very few detections of explosives were observed. Detections were typically in the low ppb levels. Nevertheless, detections suggest transport of energetic residues via groundwater transport and, to a lesser degree, surface runoff. Standing water in craters frequently contained dissolved energetic compounds at low concentrations and may, therefore, be point sources for transport (Ampleman et al. 2004).

### *Blow-in-Place*

To ensure environmental protection from residues of explosives on live-fire ranges, every effort should be made to minimize low-order detonations. When executing BIP procedures, the donor should be sufficient to produce maximum UXO consumption. Munition-specific BIP protocols should be developed to reliably achieve high-order detonations that consume both the donor and the UXO explosive. Furthermore, whenever safe to do so, range debris should be removed if it contains residual explosives. Chunks of undetonated explosive should be collected and destroyed. Since surface UXOs have proven to be a potential source of explosives through cracking of their shells, regular range clearance with appropriate BIP procedure is critical to prevent high UXO density in impact areas.

### *Summary*

Careful consideration must be given to both sample collection and analysis when characterizing soils for explosives residues. Concentrations in surface soils are generally associated with targets and firing points rather than with the range at large. Detections are specific to weapon systems. Concentrations in ground and surface water are typically below detection or, when observed, were in the low ppb levels. BIP is a potentially significant source of residues. Therefore, high-order detonations should be achieved. Observable residues of energetic materials and UXOs should be actively removed from the range on a regular basis.

### Transport parameters

Just as residues are specific to the type of weapon systems fired, fate and transport properties of explosives tend to be compound-specific and influenced by soil characteristics (organic carbon, clay content, cation exchange capacity) and local hydrogeology (rainfall, temperature). Adsorption coefficients of the HEs are relatively small in typical range soils, an indication that partitioning to soils will not appreciably attenuate most of these compounds. Determining adsorption coefficients was sometimes confounded by other fate processes such as transformation and degradation.

#### *Dissolution*

Since the explosives residues occur as solid chunks on the soil surface, dissolution is a critical step in mobilization of the explosive compounds. Dissolution rates for the principal HEs (TNT, RDX, and HMX), were relatively rapid in laboratory experiments (Lever et al. 2005; Lynch et al. 2001, 2002a, 2002b, 2003). Rates for all three explosives increased as surface area, temperature, and mixing rate increased. TNT demonstrated the fastest dissolution rate followed by HMX and then RDX. The rate approximately doubled with every 10 $^{o}$C increase in temperature. Rates were independent of pH. The authors suggest that the Levins and Glastonbury (1972) correlation is a viable method for estimating dissolution rates when diffusivities are known and particles of explosive compounds are of uniform diameter. However, predicting dissolution rates on the range is complicated by the compositional and physical complexities of the various explosive formulations and the heterogeneity in particle-size distribution.

#### *Column studies*

Results of column studies confirm the importance of dissolution rate on transport of the HEs from solid formulations. An initial peak in effluent concentration as smaller particles are dissolved by the first rainfall event is likely to be followed by a smaller and slower release in subsequent events. RDX exhibited only limited retardation in the column studies. TNT, however, exhibited marked retardation, probably due to covalent bonding with OC and coplanar complexing with clays. These results explain the occurrence of RDX to the exclusion of TNT in groundwater on ranges where Composition B predominates. The behavior of TNT and RDX in Composition B differed little from their behavior independently, except that limited competition between the two for irreversible attenuation sites was observed in one soil. Transformation products of TNT were observed in both sets of column experiments and may, therefore, be expected in soils when TNT is present.

### *Photolysis*

Crusts of pink to red photolysis products on particles of TNT and in pools of pink to red TNT photoproducts in standing water have often been observed on ranges. Results of photolysis studies illustrate that products of TNT photolysis are numerous and complex. The rate of photolysis is relatively rapid and may be enhanced by the presence of the soil. The most prominent compounds observed in this study include previously identified photoproducts as well as newly characterized photoproducts.

### *Summary*

Results of fate and transport studies have contributed empirical process descriptors for transport of explosives and explosives-related compounds in soils of training ranges. These parameters have been integrated into environmental risk assessment models to define the exposure potential for contaminant receptors. Results have also contributed to the understanding of the relative importance of transport processes, dissolution, and photolysis to the environmental fate of explosives, explosive-related compounds, and propellants.

## Implications

This project has produced data from the ranges for a realistic evaluation of explosives residues as environmental contaminants. Sources of variability and bias inherent in range data acquisition have been described. Protocols for characterizing environmental contamination from liquid-source releases were inappropriate for characterizing concentrations and distributions of the solid explosives on live-fire ranges. Therefore, new protocols for characterizing soils containing the highly distributed solid formulations found on the ranges were developed and are currently being promulgated. Descriptions of residues associated with several specific types of firing activities are now available. Differences in residue generated by successful and failed performance of various types of artillery projectiles have been quantified. Results of studies of BIP and sympathetic detonations provide guidance for minimizing residue releases. Environmental fate and transport process descriptors place energetic contaminants in perspective among other environmental contaminants and support site-specific groundwater transport and risk assessment models. Results of this project provide the Army with concepts and approaches on which to base reasonable control measures for explosives residues on ranges. Results of the numerous studies conducted in the field and in the laboratory during the life of this project have contributed to the development of a realistic concept of the characteristics and distribution of explosives residues on test and training ranges.

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# Appendix B: CRREL Munitions Detonation Residues Summary

Table B-1. CRREL munitions detonation residues summary. All rounds were Composition B-filled except as noted.

| Location/year | Number of Detonations | Explosives Load, g[1] | Mean Plume Area, $m^2$ | Average Estimated Residue, mg | | | Detonation Efficiency, % | Residue Remaining, % |
|---|---|---|---|---|---|---|---|---|
| | | | | RDX | HMX | TNT | | |
| Live-Fire | | | | | | | | |
| Mortars: 60-mm | | | | | | | | |
| Fort Drum, NY/2000 | 2 | 373 | 80 | 0.210 | 0.008 | 0 | 99.99994 | 5.8E-05 |
| Ethan Allen, VT/2001 | 5 | 373 | 21 | 0.074 | 0.019 | 0.014 | 99.99997 | 2.9E-05 |
| Fort Richardson, AK/2006 | 7 | 373 | 214 | 0.073 | 0 | 0 | 99.99998 | 2.0E-05 |
| *Average* | | | | *0.093* | *0.008* | *0.005* | *99.99997* | *2.8E-05* |
| Mortars: 81-mm | | | | | | | | |
| Fort Richardson, AK/2002 | 14 | 953 | 128 | 8.5 | 0 | 1.1 | 99.99899 | 1.03E-03 |
| Mortars: 120-mm | | | | | | | | |
| Ethan Allen, VT/2001 | 7 | 2,990 | 720 | 4.2 | 0.28 | 0.33 | 99.99984 | 1.6E-04 |
| Fort Richardson, AK/2005 | 10 | 2,990 | 409 | 17 | 1.3 | 2.6 | 99.99930 | 7.0E-04 |
| *Average* | | | *537* | *12* | *0.9* | *1.7* | *99.99952* | *4.8E-04* |
| Artillery: 105-mm | | | | | | | | |
| Fort Richardson, AK/2002 | 13 | 2,086 | 480 | 0.095 | 0 | 0.17 | 99.99999 | 1.3E-05 |
| Artillery: 155-mm | | | | | | | | |
| Donnelly, AK/2005[2] | 7 | 6,622 | 757 | 0 | 0 | 0 | 100.00000 | 0.0E+00 |
| Donnelly, AK/2005 | 7 | 6,985 | 938 | 0.3 | 0 | 0.009 | 99.999996 | 4.4E-06 |
| *Average* | | | *848* | *0.15* | *0* | *0.00* | *100.00000* | *2.2E-06* |
| Blow-in-Place | | | | | | | | |
| Mortars: 81-mm | | | | | | | | |
| Ethan Allen, VT/2000 | 3 | 1,523 | 104 | 42 | 6.8 | 0.3 | 99.99678 | 3.2E-03 |
| Ethan Allen, VT/2001 | 1 | 1,523 | 295 | 14 | 3.4 | 0.081 | 99.99885 | 1.1E-03 |
| Fort Richardson, AK/2004 | 7 | 1,523 | 820 | 130 | 23 | 0 | 99.98995 | 1.0E-02 |
| *Average* | | *1,523* | *577* | *95* | *17* | *0.089* | *99.99262* | *7.4E-03* |

| Location/year | Number of Detonations | Explosives Load, g[1] | Mean Plume Area, $m^2$ | Average Estimated Residue, mg | | | Detonation Efficiency, % | Residue Remaining, % |
|---|---|---|---|---|---|---|---|---|
| | | | | RDX | HMX | TNT | | |
| Blow-in-Place (cont) | | | | | | | | |
| Artillery: 105-mm | | | | | | | | |
| Fort Richardson, AK/2004 | 7 | 2,656 | 860 | 41 | 8.8 | 0 | 99.99813 | 1.9E-03 |
| Artillery: 155-mm | | | | | | | | |
| Ethan Allen, VT/2002[2, 3] | 7 | 7,192 | 381 | 0 | 0 | 20,000 | 99.72191 | 2.8E-01 |
| Fort Richardson, AK/2004 | 7 | 7,555 | 1620 | 15 | 1.0 | 0 | 99.99979 | 2.1E-04 |
| Fort Richardson, AK/2004[2, 4] | 7 | 7,192 | 1970 | 4.7 | 0.21 | 14 | 99.99974 | 2.6E-04 |
| Fort Richardson, AK/2004[5] | 7 | 7,555 | 1010 | 19 | 4.1 | 0 | 99.99969 | 3.1E-04 |
| *Average*[6] | | | *1533* | *13* | *1.8* | *4.7* | *99.99974* | *2.6E-04* |
| *Average, Artillery*[6] | | | | | | | *99.99934* | *6.6E-04* |
| *Average, All BIP*[6] | | | | | | | *99.99750* | *2.5E-03* |
| Demolition (Donor) Charges | | | | | | | | |
| C4 | | | | | | | | |
| Ethan Allen, VT/2001 | 1 | 570 | 150 | 61 | 26 | 0 | 99.98474 | 1.5E-02 |
| Ethan Allen, VT/2002 | 4 | 570 | 151 | 12 | 4.3 | 0 | 99.99714 | 2.9E-03 |
| Ethan Allen, VT/2002 | 3 | 570 | 152 | 4.5 | 2.6 | 0 | 99.99875 | 1.2E-03 |
| Fort Richardson, AK/2004[7] | 3 | 570 | 103 | 4.8 | 10 | 0 | 99.99740 | 2.6E-03 |
| *Average* | | | *138* | *12* | *7.4* | | *99.99652* | *3.5E-03* |

[1] Explosives loads include donor charge for BIPs.

[2] Explosive load was TNT.

[3] Non-fuzed projectiles suspended nose-down above ground surface; stiff wind conditions.

[4] Includes outside-the-plume area sampled, about 30 percent of total area.

[5] Projectiles detonated in various configurations: three were detonated vertically with one donor change, three were detonated horizontally with two donor charges, and one was detonated horizontally without fuze with C4 in fuze well.

[6] Does not include Ethan Allen data for 155-mm rounds.

[7] One C4 charge was accompanied by a 140-g supplementary TNT charge.

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**14. ABSTRACT**

Access to live-fire training ranges is vital in maintaining the readiness of our Armed Forces. Understanding the nature of residue deposition and fate is critical to ensuring sound management of ranges. The objective of this project was to characterize residues of high explosives on training ranges. Residues were evaluated by sampling on various types of ranges across the U.S. and Canada. Deposition from high-order and low-order detonations, demolition, including blow-in-place, was characterized. Environmental transport parameters were developed to support estimates of site-specific source terms for risk assessment and groundwater models. Protocols were developed for characterizing soils containing the highly distributed solid formulations typical of ranges. Results demonstrated that residues are specific to range activities. Demolition areas, low-order detonations sites, and firing positions have great potential for accumulation of residues. Demolition typically generates small areas of relatively high concentrations. Low-order detonations generate primarily large solid particles reflecting the predetonation composition. Artillery impact areas tend to have widely distributed, low concentrations. Firing positions may exhibit high concentrations of propellants. This project defines the characteristics, distribution, and potential environment transport of explosives residues on training ranges and provides a scientific basis for development of reasonable control measures.

**15. SUBJECT TERMS**
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Fate and transport of explosives
High-order detonations
HMX
Low-order detonations
Propellants
RDX
Test ranges
TNT
Training ranges