

Distribution and Fate of Energetics on DoD Test and Training Ranges

Interim Report 4

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Interim report

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ABSTRACT:

The DoD has a mandate of environmental stewardship as well as military readiness. Therefore, the concern that training with live munitions potentially generates undesirable residual constituents is of interest. The objective of this study is to develop techniques for assessing the potential for environmental contamination from energetic materials on testing and training ranges. The project defines the physical and chemical properties, concentrations, and distribution of residues in soils, and the potential for transport of these residues to groundwater.

Surface soils associated with impact craters, targets areas, and firing points were characterized on 18 military installations in the United States and Canada. Residues from high-order, low-order, unconfined charge, and blow-in-place detonations were collected on witness plates, snow, and/or tarps for constituent analyses. Results of these analyses were used to characterize residue composition and spatial distribution in relationship to the types of training activities conducted. Results also contributed to development of surface soil sampling strategies for live-fire ranges. Transport parameters of contaminants of potential concern for which data are lacking were determined by leveraging this project with other funding sources.

The characteristics of constituent residues on training ranges, both chemical composition and aerial distribution, vary with the type of range activity and the specific munitions fired. Residues tend to be localized in highly distributed point sources in the vicinity of targets and fixed firing positions. Characterizing these sites requires careful consideration of soil sampling strategies based on site activities and will typically include multi-increment composite sampling. Special care must be taken in laboratory subsampling since residues occur as solid particles of various sizes that are highly heterogeneously dispersed in the soil. For the types of ranges studied, e.g., heavy artillery and hand grenade ranges, RDX is a significant contaminant of concern. TNT, which is typically restricted to surface soil, poses less threat to groundwater than RDX. At firing points, propellant residues can be significant.

High-order detonations, which constitute most of the explosions executed during training, generate undetectable to barely detectable, diffuse surface residuals; however, low-order detonations, the incidences of which are much lower than high-order detonations and which tend to be munitions-specific, are a potentially significant source of residues. Another issue with potential to generate significant residues is clearance of unexploded ordnance by blowing in place. Rendering safe does not always result in complete consumption of explosive charge. Therefore, care must be exercised to achieve complete detonations with secondary changes that do not contribute munitions constituents, especially RDX, to the soil.

Results of fate and transport studies indicate that initial release of energetics from compositions, such as Composition B, into soils tends to be locally very high, approaching temperature-dependent aqueous phase saturation, even though the compositions dissolve more slowly than the solubilities of the individual components would suggest. Furthermore, soil adsorption from solution phase, which is governed to some extent by soil properties, will not significantly limit transport. Therefore, RDX is readily transportable to groundwater. TNT transforms readily to mono-amino products, the transport of which is limited by covalent bonding of these transformation products to soils components.

Results of this study provide a technical basis for development of range-specific soil characterization approaches. Results also provide process descriptors for fate and transport of constituent residues and for assessing the exposure component of environmental risk assessments. The relationships emerging between various training activities and constituent residues provide a sound scientific basis for development of management practices for sustainment of training range activities while maintaining environmental stewardship.

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Abbreviations and Acronyms

Conversion Factors

Non-SI* units of measurement used in this report can be converted to SI units as follows:

l

^{*}*Système International d'Unités* ("International System of Measurement"), commonly known as the "metric system."

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 the Defence Research and Development Canada – Valcartier (DRDC-Val), Quebec, Canada, and AMEC Earth and Environmental, Inc. (AMEC), Westford, MA. 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 CP1155. The principal investigator was Dr. Judith C. Pennington, Research Biologist, Environmental Processes and Engineering Division (EPED), ERDC-EL. Co-principal investigators were Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch (ESB), CRREL; Dr. James M. Brannon, Geochemist, EPED, ERDC-EL; Drs. Guy Ampleman and Sonia Thiboutot, DRDC-Val; and Jay Clausen, AMEC Earth and Environment, Inc., Westford, MA.

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Chapter 1, "Introduction," was prepared by Dr. Pennington. Chapter 2 "Update on Massachusetts Military Reservation" was prepared by Mr. Clausen. Range soil characterization research reported in Chapter 3 "Characterization of Energetic Residues at Military Firing Ranges: Scholfield Barracks and Pohakuloa Training Area," was conducted by Alan D. Hewitt, Research Physical Scientist and Dr. Jenkins, ESB, ERDC-CRREL; Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Lebanon, NH; Dennis J. Lambert, Research Physical Scientist, ERB, ERDC-CRREL; Nancy Perron, Physical Science Technician, Snow and Ice Branch, ERDC-CRREL. Chapter 3 was previously reviewed by Dr. Clarence L. Grant, Professor Emeritus, University of New Hampshire, and Marianne Walsh, Chemical Engineer, ERDC-CRREL. Studies reported in Chapter 4, "Environmental Conditions of Surface Soils and Biomass Prevailing in the Training Area at CFB Gagetown, New Brunswick,"

were conducted by Drs. Thiboutot and Ampleman; Jeff Lewis, doctoral degree candidate at the Institut de National de la Recherches Scientifiques (INRS), Ste-Foy, Quebec; D. Faucher, André Marois, DRDC-Val; Dr. Richard Martel, Jean-Marc Ballard, hydrogeologists with INRS; Sheldon Downe, Canadian Forces Base Gagetown, New Brunswick; Dr. Jenkins and Mr. Hewitt. Tests for Chapter 5, "Evaluation of the Contamination by Explosives in Soils, Biomass and Surface Water at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase I Report" were conducted by Drs. Ampleman and Thiboutot, Mr. Lewis, Mr. Marois, Annie Gagnon, Mélanie Bouchard, Stéphane Jean, DRDC-Val, Dr. Jenkins, Mr. Hewitt, Dr. Pennington, and Mr. Ranney. Chapter 6, "Estimates for Explosives Residues from the Detonation of Army Munitions," was prepared by Mr. Hewitt, Dr. Jenkins, Mr. Ranney, Jeffrey A. Stark, Marianne E. Walsh, Dr. Susan Taylor, Michael R. Walsh, Dennis J. Lambert, Nancy M. Perron, Nicholas H. Collins, ERDC-CRREL, and Dr. Richard Karn, ERDC-EL. Chapter 7 "Estimation of the Quantity of Explosive Residues Resulting from the Detonation of Unconfined Explosives Charges," was prepared by Dr. Sylvie Brochu, BCR Polysyntech, Inc., Dr. Thiboutot, Mr. Lewis, Dr. Ampleman, and Patrick Brousseau, DRDC-Val. Chapter 8 "Study of the Environmental Impacts of the Blow-in-Place Procedure of Various Explosives, Munitions and Charges," was prepared by Pascal Dubé and Dr. Sylvie Brochu, BCR Polysyntech, Inc., Mr. Brousseau, Drs. Thiboutot and Ampleman, Mr. Lewis, Ms Bouchard, Ms. Gagnon, and Mr. Marois, DRDC-Val. Chapter 9 "Fate and Transport Parameters for Firing Range Residues," was prepared by Dr. Brannon, Cynthia B. Price, Sally Yost, Dr. June E. Mirecki, and Beth Porter, ERDC-EL. Chapter 10 "Summary and Conclusions," was prepared by Dr. Pennington.

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Chapter 7:

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1 Introduction

Background

The readiness of the Armed Forces of the United States and Canada is predicated on well-trained troops and continuous enhancements of our 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. The state of knowledge concerning the nature, extent, and fate of residual munitions constituents is inadequate to ensure environmental stewardship on testing and training ranges. These issues must be addressed if we are to continue range use while maintaining environmental quality. Project CP1155 was designed to characterize the distribution and fate of energetic residuals from various uses of live-fire munitions testing and soldier training ranges.

Scope of Project CP1155

This project is designed to develop techniques for assessing the potential for environmental contamination from energetic materials on testing and training ranges. Techniques are being developed to define the physical and chemical properties, concentration, 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.

Surface soils associated with impact craters, target areas, and firing points have been characterized on U.S. and Canadian sites. Residues from high-order detonations have been determined by initiating blasts on snow and collecting the visible residue for chemical analysis. Residues from high-order, low-order, unconfined charges, and blow-in-place detonations were collected on witness plates, snow, and tarps. Residue analyses permit characterization of spatial distribution of residues. "Ground truthing" consisted of intensive soil sampling on additional active ranges. These data contribute to refinements in the soil sampling strategies for live-fire ranges. Transport parameters (desorption kinetics, partitioning coefficients, and transformation and/or degradation rates)

for 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were determined using field soils from the sites. These site-specific parameters were related to soil properties and compared to values at other sites. Transport parameters of contaminants of potential concern for which data are lacking were determined by leveraging funds from the Strategic Environmental Research and Development Program (SERDP) with other funding sources.

Tests were conducted to reliably generate low-order detonations with low energy yields. Residues from such blasts were assayed to develop a source term for use in fate and transport and risk assessment models. The source term details the mass of explosive residue and, when appropriate, its distribution, particle size and surface area.

As additional sites are characterized, the database will be expanded to determine whether certain munitions consistently contribute more contamination than others. The database of climatic and geological data will also be related to contamination to determine whether these variables affect potential for contamination. Pertinent data from Massachusetts Military Reservation (MMR) will be reviewed and compared to the database annually to determine whether MMR residues are typical of other installations.

Objectives

The primary objective of the study is to provide the Department of Defense (DoD) with techniques to assess the potential for groundwater contamination from residues of high explosives (TNT, pentaerythritol tetranitrate (PETN), RDX, and HMX) at testing and training ranges. Results of the project will facilitate informed decision-making, minimize environmental impacts of testing and training, and contribute to continued operation of ranges.

Specific objectives include the following:

a. To develop a protocol that can be used to determine the nature and extent of surface soil contamination around impact areas. The protocol will include sampling strategies and analytical methods best suited to this application.

b. To provide source-term estimates for post-blast residues based on the extent of surface soil contamination and the attributes of dissolution and release to fate and transport processes.

c. To provide data for the relevant environmental processes controlling the fate and transport of residues of high explosives on ranges.

Regulatory Precedent: Massachusetts Military Reservation

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 Ranges and Central Impact Area (USEPA 1997). In January 2000, USEPA Region I issued Administrative Order No. 3 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, 42U.S.C.§ 300i(a) (USEPA 2000). The purpose of the Order was to require the respondents to "undertake Rapid Response Actions and Feasibility Studies, Design and Remedial Actions to abate the threat to public health presented by contamination from past and present activities and sources at and emanating from the Massachusetts Military Reservation (MMR) Training Range and Impact Area."

The MMR is a 21,000-acre installation on Cape Cod, MA. The Training Ranges and Central Impact Area consist of approximately 14,000 acres located on the Camp Edwards portion of the installation. The Central Impact Area, approximately 2,200 acres, has artillery and mortar targets and is surrounded by firing positions and training areas (AMEC 2001). The Cape Cod Aquifer, a sole source aquifer for western Cape Cod, lies directly beneath the Training Ranges and Central Impact Area. Based on the findings of lead, explosives, explosivesrelated compounds, pesticides and other organic contaminants in soils, and RDX, TNT, HMX, and some organics in groundwater, the USEPA ordered the respondents to conduct a remedial investigation and feasibility studies at several MMR areas including the Central Impact Area (USEPA 2000). The order also required rapid response actions for contaminated soils at several gun positions, target positions, and for contaminated sediments at a wetland site. Administrative Order No. 4 was issued January 4, 2001 under the Resource Conservation and Recovery Act (RCRA) to the National Guard Bureau. This order requires that munitions found subsurface or in burial pits be properly stored and disposed of in a Contained Detonation Chamber (CDC), or by other means which prevent the release of explosives, metals, and other contaminants into the environment. As of October 2002, the CDC has been used to destroy 2,802 items, with additional items awaiting disposal (USEPA 2001).

Although no new contaminants have been detected at MMR since the last update (Pennington et al. 2003), perchlorate has emerged as a contaminant of concern. Perchlorate predominated over other detections in MMR groundwater, representing 45.9 percent of the propellant, explosive, and pyrotechnics (PEP) compounds observed from 1 October 2002 to 30 August 2003. Also significant in frequency of detections were RDX, HMX, and aDNTs. See Chapter 2 "Update on Massachusetts Military Reservation" in this report for specific information.

Related Ongoing and Leveraged Studies

To meet the challenge of sustained training while protecting groundwater and other environmental resources, the DoD is funding a broad spectrum of research and development efforts. These efforts are funded under multiple programs and through installations with aims focused on specific aspects of range sustainability or on specific ranges. Examples of programs funding research and development

(R&D) efforts related to range sustainment and environmental stewardship follow. Collaboration and leveraging of these projects is indicated where appropriate.

Strategic Environmental Research and Development Program. The SERDP identifies, develops, and transitions environmental technologies that relate directly to defense mission accomplishment. It is 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 we have 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 is to demonstrate a methodology for measuring emissions of toxic release inventory (TRI) chemicals from DoD munitions activities and to apply the method to determine emission factors from munitions activities at DoD facilities. Research conducted under this project has not identified the presence of propellant-related chemicals in the air samples from controlled firing experiments. In our CP1155 research, however, we find residues of propellant compounds such as 2,4-dinitrotoluene (2,4-DNT) and nitroglycerin (NG) in surface soils at firing points for howitzers, mortars, and rockets. The analytical procedures for the two projects are different, however. For soils analysis, we extract the soil with acetonitrile, which captures 2,4-DNT and NG that is present, whether it is still imbibed within the propellant matrix or is present outside the propellant fibers. The procedure used to determine air emission factors will capture only gaseous 2,4-DNT or NG, and will not detect these compounds if they are still within the polymer matrix because the particulate portion of the emission is not analyzed for these compounds.

To investigate these procedures, we conducted an experiment at the Donnelly Training Area, AK, in an area with measurable residues of single-based propellant containing 2,4-DNT. We deployed Solid Phase Micro Extraction sampling devices in a manner developed to detect chemical signatures from buried landmines in which 2,4-DNT is the major signature chemical. While 2,4- DNT was readily detected in the soil, it was not detected in the air above the soil using the protocol that was successful in the landmine detection work conducted for the Defense Advanced Research Projects Agency (DARPA). Thus it appears that the 2,4-DNT deposited in the soil is tied up within the propellant matrix and would not be detectable using the analytical procedures used in the air sampling studies.

b. CP1226 "UXO Corrosion – Potential Contamination Source" (Bonnie Packer, Army Environmental Center (AEC)). The objective of this study is to identify the type, character, and rate of perforations in casings of unexploded

ordnance (UXO) underlying soil at U.S. military installations. The goal of the corrosion project was to examine approximately 200 pieces of ordnance during the study. Soils collected in proximity to UXO were analyzed at the U.S. Army Engineer Research and Development Center's Environmental Laboratory (ERDC-EL). A report of results is in review.

c. CP-1227 "Measurement and Modeling of Energetic Material Mass Transfer to Pore Water" (Jim Phelan, Sandia National Laboratories). This project seeks to describe and model the mass transfer of solid phase energetic materials to a solute in soil pore water. Because of our fate and transport process descriptor efforts, we have followed the progress of this project closely.

d. CP-1305 "Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges" (Eric Foote, Battelle Columbus). When this project was granted access to an Eglin Air Force Base (AFB) range, we were invited to conduct the initial soil characterization and share the data with both projects. Therefore, we used protocols developed in CP1155 to sample surface soils on the range that is currently being used to determine the impacts of prescribed burning on residual energetics.

e. 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 is to develop a low-cost, fieldable process for the rapid decontamination of energetic material from range scrap. We have provided debris from low-order detonation tests at Blossom Point, MD to facilitate trials of the techniques under development.

f. 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 are to define and model gaseous and particulate species formed by detonations. We have followed the progress of this project since it is directly relevant to ultimate development of the potential source term of energetic residues on ranges.

g. Remediation/CleanUp (CU)-CU-1230 "Topical Lime Treatment for Containment of Source Zone Energetic Contamination" (Jeff Davis, ERDC-EL). We have been interested in the potential for in situ remediation offered by this project. We have shared test site access with this project at Redstone Arsenal.

Defence Research and Development Canada – Valcartier. The Director, Land Environment (DLE) from the Canadian Headquarters has tasked DRDC-Valcartier scientists to perform research characterization of their main Army training area, to assess the impacts of live-fire training. Part of the work conducted within CP1155 is strongly linked with this objective. CP1155 includes partial funding for CFB Shilo and Gagetown and for Cold Lake Air Weapons Range (CLAWR) 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. All the data generated for these other analytes will be shared with the CP1155 project. The DLE

mandate included other training areas such as the one located at Canadian Forces Base (CFB) Valcartier and results obtained at this training area will be added to CP1155 database. Future work at other Canadian training areas such as Petawawa or Suffield will still be supported partly by DLE. In FY2003 Canadian studies leveraged with SERDP funds also included "Explosives Residues Resulting from the Detonation of Unconfined Explosives Charges," and "Study of the Environmental Impacts of the Blow-in-Place Procedure of Various Explosives, Munitions and Charges." On a yearly basis, approximately 30 percent of the fund is contributed by the SERDP project. Finally, another directorate, Directorate General Environment (DGE), sponsors DRDC-Valcatier for a small-scale UXO corrosion study. The scientific leader of this study has liaised with the Principal Investigator of SERDP CP1226 to discuss the data that will be acquired and link the studies. DGE also sponsors work on the study of the ecotoxicological properties of explosives, work that is closely linked with CP1155.

Army Environmental Quality Technology Program Focus Area on Characterization, Evaluation, and Remediation of Distributed Sources (UXO-C) on Army Ranges. This program, initiated in FY2003, contains 25 to 30 work units of which several are related to project CP1155. The following work units are specifically relevant to project CP1155:

a. Large-scale characterization of major contamination sources on military training ranges (Tom Jenkins, ERDC-CRREL). The objective of this work unit is to develop methods at the landscape scale for determining the types, numbers, physical dimensions, and distribution of large point sources at various types of ranges.

b. Minimization of explosive residues in blow-in-place procedures (Judy Pennington, ERDC-EL). The objective of this work unit is to optimize blow-inplace procedures while minimizing constituent contamination without compromising effectiveness and implementation ease.

c. Range and landscape level characterization methodology (Rose Kress, ERDC-EL). The objective of this work unit is to develop methods using geospatial tools for predicting patterns of contaminant distribution at the landscape level.

d. Surface runoff of distributed source contaminants from soils: A laboratory simulation study (Terry Sobecki and June Mirecki, ERDC-EL). The objectives of this work unit are 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.

e. Development of a distributed source contaminant transport model for ARAMS (Billy Johnson, ERDC-CHL). The objective of this work unit is to develop a model to simulate transport in the watersheds, rivers, streams, and groundwater linking a geographical information system (GIS) interface and best management plans to ARAMS.

f. 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 material on the soil surface through dissolution, degradation and transport by developing process descriptors suitable for use in groundwater and transport models.

U.S. Army Alaska Directorate of Public Works. ERDC's Cold Regions Research and Engineering Laboratory (CRREL) is working for the U.S. Army Alaska Directorate of Public Works at Fort Wainwright and the Donnelly Training Area (formerly Fort Greely). This work is an outcome of the environmental impact statement (EIS) in support of the lease renewal for 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 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 through the subsampling step of analysis.

U.S. Army Environmental Center Range Sustainment Program. The AEC (John Buck) with the Center for Health Promotion and Preventive Medicine (CHPPM, Barrett Borry) is also conducting a "Range Sustainment Program" to proactively ensure sustained training on ranges and to protect drinking water sources on active ranges. Project CP1155 has been coordinated with this project and has shared site access with this project whenever possible to benefit both efforts. In FY03 AEC extended joint access at Jefferson Proving Ground, IN and Fort Polk, LA.

Army Environmental Quality Technology Program. Two work units in this program are important to project CP1155.

a. Fate and Transport of Explosives Contaminants (A835/309E/RE004) is developing screening level and comprehensive fate and transport models and process descriptors for UXO in soil, aquifer, and aquatic environments for evaluating the exposure component of risk assessments.

b. Fate and Transport of Propellants, Smokes, and Illuminants (AF25/309F/HF201) is developing fate and transport process descriptors for propellants, smokes, and illuminants. These work units are concerned with explosives and other components from UXO rather than from the more diffuse and diverse explosives residues that exist at firing ranges. However, transport parameters developed under these work units will be used in the CP1155 study to ensure a comprehensive and unified database. Approximately 10 percent of the funds for defining fate and transport parameters are contributed by SERDP project CP1155.

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-EL to

determine toxicological and geochemical interactions of ordnance and explosives in marine environments. Geochemical studies will determine dissolution, adsorption, and transformation rates of explosives in marine environments. Process descriptors determined in fresh water will be compared with those determined in salt water to determine what descriptors are affected by salinity. The toxicology studies will focus on toxicity, bioaccumulation, trophic transfer, and tissue concentrations of explosives in marine organisms, and the toxic effects of mixtures of explosives.

Summary of Results to Date

Since the inception of project CP1155 in FY2000, extensive range characterization sampling has been conducted to determine the extent and nature of explosives contamination resulting from various types of live-fire training. To date ranges at 18 military installations in the United States and Canada have been sampled. Live-fire and blow-in-place testing has been conducted at three additional sites. Results demonstrate that characteristics of energetics contamination on ranges vary with the type of range activity and the specific munitions fired, and that the distribution of residues is extremely heterogeneous. Surface soil sampling techniques were developed to address the various sources of variability in range characterization data. Results of analyses of deposition from low- and high-order detonation tests conducted on snow and with witness plates provided an indication of the aerial extent and range in particle sizes associated with explosives residues. These results were used to estimate and source terms for specific munitions.

Specific results suggest the following:

- *a.* RDX is a significant contaminant of concern on live-fire ranges.
- *b.* TNT poses less threat to groundwater than RDX.
- *c.* Propellant residues at firing points can be significant.

d. High-order detonations, which constitute most of the explosions executed during training, generate undetectable to barely detectable, diffuse surface residuals.

e. Low-order detonations, the incidences of which are munitions-specific, are a potentially significant source of residues.

f. Current practices for clearance of unexploded ordnance on ranges generate significant explosives contamination.

g. Specific results indicate that initial release of energetics from compositions into soils tends to be locally very high, approaching temperaturedependent saturation.

h. Soil adsorption will not significantly limit transport.

i. Explosives compositions dissolve more slowly than individual components.

j. Transformation rate depends on soil properties.

k. TNT transforms readily to mono amino products in soils; TNT transport is limited by covalent bonding of transformation products to soils.

l. Explosives residues are resistant to microbial degradation under conditions typical of ranges.

m. RDX is readily transported to groundwater.

Range management practices recommended on the basis of the finding of this study include the following:

a. Tracking of duds and low-order detonations and removing/remediating any residues observed.

b. Tracking firing positions for characterization and remediation of propellant residues.

c. Improving blow-in-place procedures.

FY03 Execution

During FY03 three U.S. and two Canadian sites were characterized for explosives residues resulting from live-fire soldier training: Jefferson Proving Ground, IN; Eglin AFB, FL; Fort Polk, LA; CFB Gagetown, New Brunswick; and CLAWR, Alberta. CFB Gagetown and CLAWR were sampled in previous years of this study. However, CFB Gagetown was sampled again in FY03 to delineate more precisely the extent of contamination of specific ranges by munition-related contaminants. New patterns of sampling were studied that will allow a better statistical analysis of the dispersion of explosives in an antitank range. Cold Lake was revisited (CLAWR Phase 2) to confirm the results obtained in the first phase and delineate more precisely the extent of soil contamination. A third phase was also sponsored by Canadian DND to execute a groundwater monitoring program. Sample and data analyses for all of these sites are ongoing. Results will be reported in FY04. This report contains data from Scholfield Barracks and Pohakuloa Training Area, HI; CFB Gagetown previous sampling; and CLAWR Phase 1. Results of tests to determine residues from detonations on snow, residues from unconfined explosives charges, and blow-inplace studies are also reported here. All FY03 execution of fate and transport process descriptors are reported here.

Accomplishments to date of SERDP Project CP1155 include the following:

a. Data acquisition for estimating firing range source terms for various munitions and range usages including high-order detonations, low-order detonations, and munitions firing points.

b. Protocol for characterizing soil contamination on various types of ranges having high spatial and concentration variability, e.g., heavy artillery, antitank, hand grenade, and air fighter training.

c. Definition of the residues generated by various UXO demolition procedures (blow-in-place).
d. Process descriptors for range-specific energetic residues, including dissolution rates, partition coefficients, and transformation rates.

A bibliography of technical reports and presentations generated during execution of project CP1155 is included (Appendix A). Web sites where reports may be available include the following:

- CP1155 (*<http://www.wes.army.mil/el/serdp/index.html>*)
- ERDC EL (*<http://www.wes.army.mil/el/t2info.html>*)
- ERDC CRREL (*<http://www.crrel.usace.army.mil/products/products.html>*)
- Défense R & D Canada-Valcartier (*<http://www.valcartier.drdc-rddc.gc.ca>*)

• MMR Impact Area Groundwater Study (*[http://www.groundwaterprogram.](http://www.groundwaterprogram.org/index.htm) [org/index.htm](http://www.groundwaterprogram.org/index.htm)* and *<http://www.mmr-edms.net>*)

The following chapters appearing in this report were previously published as individual technical reports:

Chapter 4. Thiboutot, S., Ampleman, G., Hamel, A., Ballard, J.M., Martel, R., Lefebvre, R. and Downe, S. (2003). "Research on the environmental conditions prevailing in the training area at Canadian Force Base Gagetown, New Brunswick," DRDC-Val TR 2003-016, Defence Research and Development Canada - Valcartier, Val-Bélair, Quebec.

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Chapter 6. Hewitt, A. D., Jenkins, T. F., Ranney, T. A., Stark, J. A., Walsh, M. E., Taylor, S., Walsh, M. R., Lambert, D. J., Perron, N. M., Collins, N.H., and Karn, R. (2003). "Estimates of explosives residue from the detonation of army munitions," US ERDC/CRREL Technical Report 03-16, U.S. Army Engineer Cold Regions Research and Engineering Laboratory, Hanover, NH.

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2 Update on Massachusetts Military Reservation

Introduction

From 1 October 2002 through 30 September 2003, investigations continued at Camp Edwards, which is on the northern portion of the Massachusetts Military Reservation (MMR) near Falmouth, MA, on Cape Cod. A comprehensive site assessment has been underway since 1997. The Training Ranges and Impact Area at Camp Edwards encompass approximately 14,000 acres. The approximately 2,200-acre Impact Area contains artillery and mortar targets that have been used for training activities since 1911. The highest frequency of use occurred during and after World War II. The firing of high explosive (HE) artillery rounds was discontinued in 1989. Low-intensity training rounds (LITR) and inert and HE mortar rounds were fired until 1997, when a moratorium on artillery and mortar firing was established by the U.S. Environmental Protection Agency (USEPA). Surrounding the Impact Area are numerous firing ranges, artillery and mortar positions, and training areas (Figure 2-1). Site investigations, therefore, have addressed various types of firing ranges, open burn/open detonation (OB/OD) sites, and firing positions.

More than 40 summary reports and work plans have been prepared over the last year covering the activities at Camp Edwards (Appendix A). In addition, one paper has been accepted for publication (Clausen et al. in press) with another in review as well as six papers presented at conferences. Three significant reports are in development: a Central Impact Area Soil Report, an Impact Area Supplemental Groundwater Report, and a Surface to Groundwater Link Report.

Figure 2-1. Training range locations at Camp Edwards, Massachusetts

Site Overview

The 21,000-acre MMR is situated on soils consisting of fine to coarsegrained sands overlying very coarse sands and gravels that reside at the top of the saturated zone. Silts and clays compose the base of the saturated zone, which overlies relatively impermeable bedrock located 285 to 365 ft below ground surface (bgs). Depth-to-water over most of the site is approximately 100 ft. Camp Edwards Training Ranges and Impact Area lie directly over the Sagamore Lens, a major groundwater recharge area and the most productive portion of the Cape Cod Aquifer. The apex of the Sagamore Lens is at the southeast corner of the Impact Area from which groundwater flows radially in all directions. The ocean bounds the aquifer on three sides. Except on extreme slopes, surface water runoff at Camp Edwards is virtually nonexistent due to the highly permeable nature of the soils and aquifer material.

Since the last update (Pennington et al. 2003) several thousand soil and groundwater samples have been collected at Camp Edwards. Table 2-1 lists the number of samples, by media and site, collected from 1 October 2002 to 30 August 2003.

The data from these studies are summarized for soil and groundwater in Tables 2-2 and 2-3. No new explosive compounds have been detected since the last update. The distribution has changed with the inclusion of perchlorate as a standard analyte. Prior to 2001, perchlorate was not a contaminant of concern at Camp Edwards. Upon analysis for perchlorate in 2002, its presence became apparent after numerous soil and groundwater samples indicated detectable levels. The frequency of detection of perchlorate is on par with the RDX frequency of detection. Figure 2-2 is the distribution of propellant, explosive, and pyrotechnic (PEP) compounds observed in soil at Camp Edwards. The largest proportion of PEPs observed is 2,4,6=trinitrotoluene (TNT) and the amino-D initrotoluenes (aDNTs) followed by the "Other" category (perchlorate, DNTs, and RDX) in decreasing order of frequency. The "Other" category includes di-n-butyl phthalate, N-nitrosodiphenylamine, and white phosphorous (WP). Di-n-butyl phthalate and N-nitrosodiphenylamine (oxidation product of diphenylamine) are propellant compounds, whereas WP is used in some munition warheads.

Figure 2-2. Distribution of PEP compounds in soil at Camp Edwards for the dataset running from 1 October 2002 to 30 August 2003

The soil PEP compound findings are consistent with known activities at Camp Edwards such as the firing of munitions containing mixtures of TNT, RDX, HMX, and WP in the warheads, and propellants with nitroglycerin (NG), DNT, di-n-butyl phthalate, and N-nitrosodiphenylamine. The presence of the aDNTs is strongly suggestive of the aerobic degradation of TNT.

In contrast, the distribution of PEP compounds in groundwater (Figure 2-3) differs from that in soil but is consistent with previous groundwater findings as reported in Pennington et al. (2003), except for perchlorate. Perchlorate was added in 2002 to the standard analyte list for Camp Edwards. The predominant PEP compound observed in Camp Edwards groundwater is perchlorate followed by RDX, HMX, and aDNTs in decreasing order of frequency. The greater preponderance of perchlorate in groundwater can be explained by its high mobility relative to the other contaminants. As a consequence of perchlorate's high solubility, low to non-existent partitioning to soil, and recalcitrant nature, it is not expected to persist in soil for any significant length of time. Rather, once in contact with precipitation, perchlorate rapidly dissolves and is then transported down through the vadose zone to the groundwater. The significant decrease in TNT and aDNTs in groundwater relative to soil is a function of their susceptibility to degradation processes and sorption onto shallow surface soils. Even when the TNT and aDNTs overwhelm the natural microorganisms in the soil, these compounds are rapidly degraded within several hundred feet of where they are introduced into the aquifer.

Figure 2-3. Distribution of PEP compounds in groundwater at Camp Edwards for the dataset running from 1 October 2002 to 30 August 2003

Another interesting observation is that the majority of DNT observed in soil is the 2,4 isomer whereas in groundwater it is the 2,6 isomer. However, the distribution of DNT isomers should be similar for soil and groundwater since these isomers have similar fate-and-transport properties. Therefore, some other process must explain the discrepancy between soil and groundwater results. The Impact Area Groundwater Study has found that false positives of 2,6-DNT occur in the groundwater samples, especially when interferences are present. It is possible that the infrequent and sporadic 2,6-DNT detections, which are not reproducible between different sampling events, observed in groundwater samples are false positives.

The other important observation is the significant decrease of "Other" compounds and the lack of NG in groundwater relative to soil. N-nitrosodiphenylamine and WP are two of the "Other" compounds that have not been detected in any groundwater samples. The absence of N-nitrosodiphenylamine, NG, and WP is consistent with their fate-and-transport properties (i.e., rapid and strong sorption to soil, low solubility, and high degradation potential). Di-n-butyl phthalate is the "Other" compound detected in groundwater. Di-n-butyl phthalate would not be expected to be mobile due to its affinity to sorb onto soil and thus would not be expected in groundwater. The detection of di-n-butyl phthalate in groundwater has been spatially sporadic and nonreproducible between sampling rounds for the same monitoring well. Since di-n-butyl phthalate is a common laboratory contaminant, it is believed the detections in groundwater represent false positives. Di-n-butyl phthalate is found in propellants and thus its presence is expected in soil at locations where propellant was handled and fired such as the mortar, artillery, and rocket firing positions. The presence of di-n-butyl phthalate at other sites such as the Impact Area where propellants are not likely to be present is viewed with some uncertainty. Since DNTs and diphenylamine, which

oxidizes to N-nitrosodiphenylamine, are major constituents in the propellants that contain di-n-butyl phthalate, the detection of di-n-butyl phthalate in the absence of the DNTs and N-nitrosodiphenylamine is believed to be a false positive. A concerted effort has been focused over the past year on the presence of the PEP compound perchlorate (AMEC 2002a and b). As will be discussed later, perchlorate has been sporadically detected in soil and consistently in groundwater. Groundwater perchlorate plumes have been mapped for the Impact Area, Demolition Area 1, and Southeast Ranges (Figure 2-4). In addition, new perchlorate plumes have been found in the Bourne Public Water Supply (BPWS) area as well as an offsite area located to the northwest of MMR (AMEC 2002a and Figure 2- 4). To date, the sources of the Bourne and Northwest Corner groundwater plumes have not been identified.

In addition to activities specific to an operable unit, several studies have been conducted over the last year germane to the entire Impact Area Groundwater Study Program at Camp Edwards. The first such study was an explosive method comparability study (AMEC 2003j). This method comparability study discusses the findings from the analyses of seven previously characterized and homogenized soil samples. Matrix duplicates of these samples were analyzed by five different analytical methods: USEPA Method 8330 (USEPA 1994); a low level modification of method 8330 (USEPA 1994); USEPA Method 8321A (USEPA 1996b), a modification to USEPA 8270 (USEPA 1996a); and modification to USEPA Method 8095 (USEPA 1999). The results of this study show that High Pressure Liquid Chromatography (HPLC)-based methods (8330, 8330 low level, and 8321A) have acceptable precision and accuracy. Gas chromatography (GC) based methods (GC/mass spectrometry (MS) and 8095) show a higher frequency of false negatives, false positives, and lower precision and accuracy.

A second important report was a summary of all saturated flow and transport groundwater modeling conducted through 2002 (AMEC 2003l). The report covers the development of the regional groundwater model and discusses the processes used to develop subregional models focused on the Impact Area, Demo 1, SE Ranges, and Bourne Public Water Supply. These models are currently being used to locate monitoring wells and select appropriate screen intervals. In the case of Demo 1, the groundwater model is being used to design the pump-andtreat system.

Impact Area

The Impact Area is in the central portion of Camp Edwards and covers 2,200 acres. Within the Impact Area is the 330-acre Central Impact Area, the major source of groundwater contamination. Surrounding the Impact Area are a number of ranges and firing positions from which artillery and mortar rounds were fired.

Figure 2-4. Groundwater areas of investigation and treatment at MMR

Characterization of the nature and extent of the PEP compounds in the Central Impact Area is almost complete. In addition, extensive geophysical surveys have been conducted. The results of an aerial magnetometry (AIRMAG) survey of the Impact Area indicate that the overall geophysical conditions at MMR are not optimal for the detection of unexploded ordnance (UXO) (Tetra Tech (TT) 2002). In addition to AIRMAG, ground-based geophysical methods (e.g., EM-61 and cesium-vapor magnetometry (CVM)) have been used within the Impact Area (TT 2003a, k and 2002). The High Use Training Area (HUTA) study used geophysical and other methods to evaluate the nature and extent of explosive chemicals and ordnance items within the Impact Area (TT 2003a and 2002). The sites evaluated included six transects in HUTA 1, the five transects of HUTA II, the Eastern Test Site, and the sub-caliber air to ground rocket (SCAR) site. Eightyseven percent of the UXO items found in the HUTA investigations were in the first 0.76 m of soil. The deepest item was at 2.11 m, with everything below 1.0 m being a "forced" item such as a fuse or a debris piece that had been ballistically injected. Explosive compounds were detected in only 13 of 408 samples.

Currently, AMEC is preparing a Soil Report discussing all characterization efforts to date. A preliminary assessment of the data indicates that the source term for groundwater is confined to an area of approximately 330 acres. A total of 58 targets have been investigated in the Central Impact Area. To date, more than 3,500 soil samples have been collected (AMEC 2001a, Clausen et al. 2002a) and analyzed for some or all of the following parameters: explosives, metals, semivolatile organic compounds (SVOCs), herbicides, pesticides, volatile organic compounds (VOCs), cyanide, phosphate, nitrate, ammonia, perchlorate, polychlorinated naphthalenes (PCNs), and polychlorinated biphenyls (PCBs). The compounds 2-amino-4,6-dinitrotoluene (2a-DNT), 4-amino-2,6-dinitrotoluene (4a-DNT), TNT, and RDX have been identified as soil contaminants of concern (COCs) for the Central Impact Area based on a human health risk assessment (AMEC 2001a).

Two target areas will be investigated in greater detail through the installation of lysimeters and the collection of soil samples in the first quarter of FY04 (AMEC 2003d). The objective of this work is to determine the extent of explosive residues from the target as well as the density distribution of UXO. Following the detailed characterization activities, surface soil will be removed from around the two targets. The lysimeters will be monitored to assess the effectiveness of the soil removal (i.e., determine if energetic compounds remain trapped in soil pore water or sorb to soil, and then desorb, below the excavated soil).

Groundwater

A total of 319 monitoring wells at 126 locations have been installed within and downgradient of the Impact Area. In excess of 1,000 groundwater profile, grab samples, and 1,500 groundwater monitoring well samples have been collected and analyzed for explosives and VOCs.

Soil

The compounds RDX, 2,4-dinitrotoluene (2,4-DNT), and 4a-DNT have been identified as groundwater COCs for the Impact Area based on human risk characterization (AMEC 2001b). RDX concentrations found in groundwater samples are generally less than 10 µg/L, with an average of 3.43 µg/L. The USEPA health advisory limit is $2 \mu g/L$; 184 samples exceeded this limit. Reverse particle backtracks using a site groundwater model indicated that nonpoint source areas are located primarily in the vicinity of the targets along and east of Turpentine Road. High melting explosive (HMX) and perchlorate groundwater contamination was generally co-located with the RDX. HMX and perchlorate concentrations in groundwater samples averaged 1.06 and 1.26 µg/L, respectively. The highest perchlorate concentrations occurred along Turpentine Alley and peaked at 5 µg/L. TNT has been detected twice with a maximum concentration of 0.59 µg/L. The maximum detected concentrations of 2a-DNT and 4a-DNT are 0.76 and 1.2 µg/L, respectively.

The Impact Area groundwater plume covers an area approximately 16,000 ft long by 5,000 ft wide (Figure 2-4). Approximately 880 million to 1.3 billion gallons of water have been contaminated encompassing an area of 621 acres. The mass of RDX dissolved in this volume of contamination is approximately 30 to 80 lb (AMEC 2001b). Within the center of the Impact Area, RDX is present from the water table to a depth of approximately 87 ft below water table (bwt). Along the western (downgradient) boundary of the Impact Area, RDX is present from approximately 22 to 96 ft bwt. No explosive compounds have been detected in groundwater beyond the western perimeter of the MMR property boundary, although the propellant compound, perchlorate, has been detected offpost.

An aquifer test was conducted in the summer of 2002 (AMEC 2003k) to determine the transmissivity of the aquifer system, which then could be used to estimate the hydraulic conductivity and groundwater flow velocities for modeling and remedial design purposes. Results indicated that the drawdown in each of the observation wells during the 72-hr test was consistent with typical aquifers. Estimates of transmissivity ranged from less than 100,000 to over 300,000 gal/day/ft. The recommended transmissivity value for future modeling efforts based on evaluation of drawdown and recovery data is 227,000 gal/day/ft. Estimates of specific yield varied widely from 0.04 to 0.20 and the median value was 0.12. Estimates of the ratio of vertical to horizontal conductivity ranged from 0.98 to 1.13. The aquifer test revealed that estimated average groundwater flow velocities were lower than expected, 0.48 ft/day versus a presumed 1 ft/day based on soil lithology.

Currently, AMEC is preparing a supplemental groundwater report to assess any changes in groundwater contaminant distribution. Since January 2001, 89 monitoring wells have been installed at 42 locations per direction of the USEPA to complete the delineation of the RDX and perchlorate groundwater plumes. Once the supplemental groundwater report is complete, a Feasibility Study will be conducted in FY04/05 to evaluate appropriate remediation technologies for groundwater.

Demolition Area 1 (Demo 1)

Demo 1 is south of the Impact Area at Camp Edwards in a 1-acre kettle hole, with the bottom 45 ft below the surrounding grade. Demolition and Explosive Ordnance Disposal (EOD) training at Demo 1 as well as OB/OD operations began sometime in the mid-1970s and included the destruction of various types of ordnance using explosive charges of Composition 4 (C4, a mixture of RDX and plasticizers), TNT, and detonation cord. As part of a comprehensive site reconnaissance, chunks of C4 and other residual munitions were found on the ground surface and removed in accordance with approved procedures, which typically consisted of detonation in the Closed Detonation Chamber located on site.

Soil

Over 600 soil samples have been collected at Demo 1. The following explosive and propellant compounds have been repeatedly detected in soil and groundwater at Demo 1: perchlorate, RDX, HMX, 2a-DNT, 4a-DNT, TNT, and 2,4-DNT (AMEC 2001c). RDX (22 percent) and HMX (13 percent) were the most frequently detected explosive compounds. A maximum concentration of 14,000 mg/kg of RDX was measured in the soil below the C4, indicating that particulates were present in this sample. The average concentration of RDX in soil, using one-half the detection limit for nondetects and excluding three sample locations collected beneath C4 residuals, is 0.576 mg/kg. TNT was also heavily used in demolition training. The low frequency of TNT detection (2 percent) in soil is most likely due to the rapid degradation of TNT to the daughter products 2a-DNT (7 percent) and 4a-DNT (5 percent). The principal degradation products of TNT are 2a-DNT, 4a-DNT, and 2,6-DANT. 2,4-DNT and 2,6-DNT are not degradation products, but are components of propellants and impurities in TNT manufacturing.

Groundwater

A total of six explosives (RDX, HMX, 4a-DNT, 2a-DNT, TNT, and 2,4- DNT) and the propellant perchlorate have been detected in groundwater sampled from monitoring wells at Demo 1 (AMEC 2003e, 2001d). The identified COCs based on human health risk characterization are HMX, RDX, TNT, 2,4-DNT, 2a-DNT and 4a-DNT (AMEC 2001d). The highest observed concentrations of RDX and perchlorate in groundwater at Demo 1 were 370 and 300 µg/L, respectively. The Demo 1 perchlorate plume extends approximately 9,000 ft downgradient of the source, while the RDX plume extends approximately 5,000 ft (Figure 2-4).

Currently, a groundwater extraction system is being designed for remediation of the Demo 1 groundwater plume. The technology to be used for treatment of perchlorate is granular activated carbon for removal of the explosives and perchlorate. The current schedule calls for the hydraulic containment system to become operational in late FY04.

Demolition Area 2 (Demo 2)

Demo 2 was used from the late 1970s to the late 1980s for light demolition training. Records indicate that explosive charges including C-4 and TNT (in quantities of less than 10 lb), and claymore mines were used there. A subsurface geophysical survey was conducted at Demo 2 in September 2001. The area investigated was 190 m long and 60 m wide (approximately 3 acres), and was surface-cleared of any metal or other objects. Materials recovered from the surveyed areas consisted of scrap metal and barbed wire. No ordnance or ordnance-related materials were discovered.

Soil

Results for soils collected from the perimeter berm revealed the presence of four explosive compounds: RDX, HMX, 2A-DNT, and 4A-DNT. Nearly all of the compounds were detected in nine samples collected from Trenches 2 and 4 and associated spoils piles. Trench 1 samples exhibited a single detection of RDX. The maximum concentrations of RDX and HMX $(3,000 \text{ and } 300 \text{ J})$ ug/kg, respectively) were reported in samples collected from Trench 2, and the maximum concentrations of the TNT degradation products 2A-DNT and 4A-DNT (42 and 28 µg/kg, respectively) were reported in samples obtained from Trench 4.

Groundwater

Seven monitoring well locations have been installed in Demo 2. RDX and HMX have been detected in groundwater and the initial assessment is that at least 2,000 ft of downgradient migration has occurred (Figure 4). RDX concentrations ranged from 0.74 to $2.3 \mu g/L$.

Southeast Ranges

The Southeast (SE) Ranges are four ranges used by defense contractors for munitions testing including research and development activities. The J-1 Range was used primarily as an anti-tank and training range from the mid-1930s through the 1950s. The J-1 Range was subsequently used for weapons testing by a variety of military contractors until the 1980s.

The original J-2 Range was established in the late 1940s in an area currently designated as N Range. The J-2 Range was used historically as a musketry range (1935 to 1940s), transition range (1940s to 1950s), rifle range (1960s to 1980s), and a contractor test range (1953 to 1980). Examples of activities conducted by various contractors included: propellant and fuse testing, penetration testing for various munitions, fragmentation testing, obscuration testing, infrared testing of tank heat signatures, propellant and waste burning, munitions disposal, and loading of munitions with explosives.

The J-3 Range was used for mortar and machine gun practice from 1935 through the 1950s. Textron, Inc., under various military contracts, used the range from 1968 to the 1990s for the loading and testing of various munitions and fuses, and a wide variety of other munitions-related tests.

Based on historical use and recent ordnance discoveries, all deactivated ranges with the "L" designation were used for small arms with the exception of the current L Range. The current L Range, which is on the western side of Greenway Road just north of the J-3 Range, has documented ordnance and explosive (OE) use (AMEC 2003b).

Investigations in the SE Ranges have included installation of 61 monitoring wells, collection and analyses of over 3,400 soil and 2,600 groundwater samples, and biweekly sampling of Snake Pond surface water. Soil samples were analyzed using the standard analyte list plus dioxin/furans and PCNs. Groundwater was analyzed for the standard analyte list plus perchlorate.

Soil

Soil results indicate the presence of HMX at various locations throughout these areas. At the J-3 Range, HMX and various propellants were identified in the following areas: Melt/Pour facility, where melting of explosives and loading of munitions occurred; the northeast portion of the artillery range; a munitions detonation pit and burn area; and a drywell associated with an onsite workshop (AMEC 2003f). At the J-1 Range, RDX was detected in ash samples collected from a former burn kettle and from mixed soil and debris from a steel-lined pit which contained discarded munitions (AMEC 2003a and i). Explosive residues are present in the Ammunition Storage Magazine and the Melt/Pour building on the J-2 Range (AMEC 2003o). PCNs were also detected in many of the soil samples, as were low levels of dioxin and furans.

Groundwater

Groundwater contaminants identified at the SE Ranges include RDX, HMX, TNT, and perchlorate. Two regions of groundwater contamination have been identified at the J-1, J-3, and L Ranges (AMEC 2003c and m). One area is immediately downgradient (northwest) of the J-1 Range 1,000- and 150-meter berms, where RDX, HMX, and other miscellaneous explosives have been detected in groundwater (Figure 2-4). RDX has been detected at concentrations up to 150 µg/L in this area. The highest HMX concentration observed in this area was 62 µg/L. Computer modeling of groundwater flow suggests that the contaminants reached the water table near the 1,000-meter berm. There are various activities known or reported to have occurred in the area that could have provided a source for the detected contaminants. These activities include firing and detonation of munitions, cook-off tests, burning of excess munitions in the steel-lined pit and popper kettle, disposal by burning of lead azide on the range road, disposal of J-3 Range Melt/Pour wastewater, and burial of vehicles and pails of various waste materials. Nevertheless, soil analytical results available to date do not confirm a

clear and obvious source for the explosives detected in groundwater from this area, but the Melt/Pour building remains suspect.

The other potential source includes the area from the center of the J-3 Range downgradient to Snake Pond, where RDX and HMX have been detected in groundwater (Figure 2-4). RDX was also detected in a water sample from a septic tank at the J-3 Range (AMEC 2003c). The highest RDX concentration observed was 5.4 µg/L, while the maximum HMX concentration was 18 µg/L. Distribution in groundwater, groundwater modeling, and soil data suggest that multiple source areas may exist, including a detonation pit, the Melt/Pour building and drywell, as well as unidentified areas on the L Range or J-1 Range. Contaminants in groundwater are migrating south from the J-3 and L Ranges. Most of the contaminated groundwater discharges to or migrates beneath Snake Pond or is captured by the Installation Restoration Program (IRP) FS-12 groundwater extraction and treatment system.

Perchlorate, a propellant, has been detected at numerous widely distributed wells on the J-1, J-2, J-3, and L Ranges (AMEC 2003c, m, and n). The highest concentration (75 μ g/L) was detected in a sample from the center of the J-3 Range near a detonation pit. PCNs and dioxin/furans were not detected in groundwater.

Gun and Mortar Firing Positions

The 37 identified gun and mortar firing positions are located outside of the Impact Area in the Training Ranges at Camp Edwards and were used to fire artillery and mortars at targets established within the Impact Area. Burning of excess propellant bags and cleaning of artillery were reported to have been conducted at the gun and mortar firing positions. The average size of the firing positions is 2.2 acres. The gun and mortar positions were used to fire 75-, 105-, and 155-mm and 8-in. artillery rounds, and 60- and 81-mm, 3- and 4.2-in. HE, illumination, smoke and WP artillery and mortar rounds into the Impact Area (AMEC 2001e). The 105- or 155-mm artillery rounds were used most frequently. The type of propellant (M1, M2, M3, etc.) used depends on the type of munition. Double-base propellants contain mixtures of NC as the primary constituent, with various amounts of NG (0 to 43 percent by weight) as a secondary component. Other secondary compounds used in propellants include DNT, di-n-butyl phthalate, diphenylamine, and ethyl centralite, each ranging from 0 to 10 percent depending on the mixture specifications. Diphenylamine is not persistent in the environment and during combustion is transformed to N-nitrosodiphenylamine. Barium nitrate, potassium nitrate, potassium sulfate, and graphite, at 0 to 1.5 percent, are also present in propellant mixtures. The compound 2,4-DNT is used as a plasticizer in single-based propellants used for some mortars and artillery munitions. 2,4-DNT comprises 10 percent of single-based propellants. The overall mass of 2,4-DNT in the explosives filler in the projectile is less than 1 percent. The propellant for some munition types is not attached to the ordnance itself but rather is enclosed within bags, which are consumed within the gun with some residual fallout in and around the gun.

Over 1,300 soil samples were collected and analyzed for DNT with over 500 samples analyzed for the standard analyte list discussed earlier. The propellantrelated compounds, 2,4-DNT and 2,6-DNT, were detected at the gun and mortar firing positions, but not in the control samples. Overall, 2,4-DNT was detected in 4 percent of the gun and mortar position samples, approximately four times more often than 2,6-DNT. There were detections of 2,4-DNT in 38 separate sampling locations at 15 different gun and mortar positions. The majority (29) of the detections were in samples collected 0 to 1 ft in depth. There were detections of 2,6-DNT in 11 separate sample locations at eight positions, all at which 2,4-DNT was also detected. NG and pentaerythritol tetranitrate (PETN) were detected at two locations. The two detections of PETN occurred very early in the field investigation (March 1998), prior to the use of photo diode array (PDA) spectral analysis with explosive Method 8330, and are likely false positives (Clausen et al. 2002a).

Soil

Diethyl phthalate and N-nitrosodiphenylamine were detected at low frequencies of 3 and 6 percent, respectively (AMEC 2001c). Di-n-butyl phthalate was detected at a higher frequency of 17 percent and was present in the control grid samples, but at a much lower frequency (5 percent). There were 38 detections at 13 positions of N-nitrosodiphenylamine. These same 13 positions also were characterized by 2,4-DNT detections. The concentrations of all constituents were low, less than 10 mg/kg.

Soil sampling was conducted at four positions at 17 sample locations to evaluate the potential for perchlorate contamination. Perchlorate was detected at two positions in 11 of 39 (28 percent) soil samples collected, in concentrations up to 0.00746 mg/kg. A specific source or release mechanism of perchlorate at the gun and mortar firing positions has not been determined. Lead and aluminum were the only metals in gun and mortar soils where the mean concentration (calculated using one-half the detection limit for nondetects) exceeded the background concentration.

Groundwater

Twenty monitoring wells at eight locations were installed downgradient of four gun positions and four mortar positions. The groundwater data indicated that military training activities at the gun and mortar positions have not impacted the sole source aquifer (AMEC 2001e).

Known Distance (KD) Rocket Range

The KD Rocket Range comprises approximately 98 acres of land to the southeast of the Impact Area. The range consists of a 25-m rifle range with 55 firing points, a 365-m distance rifle range with 20 firing points, 2 firing points for Dragon missiles, and 90-mm recoilless rifle training, and a firing point for TOW missiles (Ogden 2000). A portion of the range has also been used for helicopter

gunship, machine gun, and grenade launcher training. Information from an interview indicates live tank gunnery was also performed in this area.

An armored personnel carrier target is located approximately midway downrange of the KD Range cleared area. Based on damage to the target and the amount of ordnance debris in the immediate vicinity, it is presumed to be the primary range target. Visible debris from fired rockets and missiles includes portions of housings, fins, and electronic circuitry. NG and nitrocellulose (NC) are the primary propellants used in anti-tank rockets. At the rocket firing positions, NG can be expected as a result of the rocket back-blast.

Soil

For the KD Range, more than 300 soil samples were collected at firing points and targets. NG was the most widespread explosive/propellant compound detected. Detected concentrations ranged from an estimated high of 130 mg/kg in a discrete sample collected at the surface within the easternmost current rocket firing point, to an estimated 2.9 mg/kg in the composite sample collected from the back-blast grid at the former 90-mm rocket firing point (Ogden 2000). NG was not observed in soils collected from the background grid. NG was detected in 22 of 215 samples collected between 0 and 2 ft in depth, but in none of the six samples collected below the 2-ft depth. NG was likely deposited on the surface as residue along with other propellant compounds from the ejected gasses and particles contained in the smoke produced by the detonation of the propellant during rocket and missile launching. Its distribution in soil (highest concentrations at or near the surface and decreasing with depth) at the firing points is consistent with the presumed airborne deposition of propellant compounds.

Other explosive compounds such as HMX, RDX, and TNT were discovered only in the primary target grids. These compounds, which were found in the grids positioned south and east of the target, are consistent with the known use of explosive ordnance at the range. HMX was observed at a maximum concentration of 10 mg/kg, RDX at 43 mg/kg, and TNT at 2.1 mg/kg. All were detected in the surface (0 to 3 in.) composite sample (Ogden 2000). RDX was also present within this grid in the 3- to 6-in. composite sample and the 6- to 12-in. discrete sample at concentrations of 0.18 mg/kg and 0.28 mg/kg, respectively. Again, the higher concentrations were found in the upper 6 in. of soil, consistent with the presumed surface deposition.

Groundwater

Monitoring wells placed immediately downgradient of the primary and secondary targets and TOW firing position do not indicate that any contaminants are present in groundwater. Each well was analyzed following the standard analyte list discussed earlier. No explosive compounds were verified by PDA in the 40 plus groundwater profile samples collected. The absence of NG is consistent with the physical and chemical properties of NG.

Phase IIB and Munition Survey Project Sites

The 12 sites identified in the original Phase IIB Field Sampling Plans were among several training areas, ranges, and other locations identified by the USEPA to be investigated. The Phase IIB areas consist of waste oil sites (3), latrines (63), an ammunition supply point (1), cleared areas (12), general training sites (25), engineering training/demolition sites (5), and ranges (36). The breakdown of ranges includes small arms (22), machine gun (7), anti-tank (2), skeet (1), battle assault course (1), and grenade courts (3). Many of the Phase IIB sites are in the process of being investigated. The initial results suggest very limited detections of PEP compounds (AMEC 2003e). In some cases the U.S. Army/National Guard Bureau decided that limited additional sampling was necessary. The most surprising finding was the lack of explosives in soils at the former grenade courts. These grenade courts had not been used since WWII, however, and it seems likely that the grenades from this era used TNT as the primary explosive. Given TNT's susceptibility to degradation processes, it is not too surprising that no explosive compounds were found.

In addition to reconnaissance and soil sampling at these sites a number of sites had geophysical surveys performed (TT 2003b through l). Although, geophysical anomalies were found at a number of locations, upon subsequent excavation no HE rounds were found. In most cases, metal debris was found, small arms ammunition, or inert projectiles, which would explain the anomalous geophysical signature, although in a number of instances nothing was found.

A total of 25 small arms ranges were evaluated as part of Phase IIb activities (AMEC 2003h). The investigation consisted of review of historical activity, reconnaissance of the sites, and soil sampling. Four propellant-related SVOCs were detected at some of the ranges and included 1,3-diethyl-1,3-diphenyl urea, di-n-butyl phthalate, N-nitrosodiphenylamine, and 2-nitrodiphenylamine. Five metals, antimony, barium, copper, lead, and zinc, were detected at concentrations sometimes exceeding established site background values.

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Table 2-2 Summary of Camp Edwards Validated Soil Data from 1 October 2002 through 30 August 2003

Table 2-3 Summary of Camp Edwards Validated Groundwater Data from 1 October 2002 through 30 August 2003

3 Characterization of Energetic Residues at Military Firing Ranges: Schofield Barracks and Pohakuloa Training Area

Abstract

The Department of Defense (DoD) tasked the U.S. Army Corps of Engineers, Sacramento District, with development of an Environmental Impact Statement (EIS) for two Army installations in Hawaii — Schofield Barracks and Pohakuloa Training Area. The objective of the EIS was to establish the extent, distribution, and fate of heavy metals, selected semi-volatile organic compounds, and residues of energetic compounds on two live-fire-training ranges. The U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) collaborated in this effort to further develop sampling strategies and sample processing protocols for explosives residues. Sampling was performed using professional judgment, focusing on locations where energetic residues had previously been detected on other military training installations, e.g., fixed firing points, and impact areas on anti-tank ranges, hand grenade, artillery and mortar ranges, etc. Composite soil samples were collected to enhance the probability of detecting energetic residues. Overall, the concentrations of energetic residues established were consistent with several previous studies of military training installations.

Introduction

Background

Hawaii is a strategic geographical location for housing and training Interim Brigade Combat Teams (IBCTs). DoD requested information about the concentrations of potential contaminants, including energetic compounds, at Schofield Barracks and the Pohakuloa Training Area (PTA) to aid DoD in the selection of a training facility for IBCTs. The two primary receptors of concern stated in the Environmental Impact Statement (EIS) were human exposure through ingestion or dermal contact and off-site migration via surface runoff or groundwater. Our role was to assist the Sacramento District in selecting the surface soil sampling locations, collection procedures, and sampling designs. Moreover, this activity provided the opportunity to evaluate current laboratory sample preparation protocol with that recommended in Method 8330 (USEPA 1996).

U.S. Army ERDC is investigating sources and pathways of energetic materials under the Strategic Environmental Research and Development Program (SERDP) CP1155, "Distribution and Fate of Energetics on DoD Test and Training Ranges." One of the tasks that has been under investigation for several years is how to properly characterize the major sources of energetic residues on military facilities (Jenkins et al. 1997a, 1997b, 1998, 1999, 2000, 2001; Walsh et al. 2001; Pennington et al. 2001, 2002, 2003; Hewitt et al. 2003; Walsh et al. 2003). An important finding from this body of work is the role of partial (loworder) detonations in dispersing energetic residues onto training ranges. A round that partially detonates often leaves visible quantities (chunks) of the high explosive charge remaining within the ruptured casing and nearby on the ground. The data indicate that as many as 100,000 high-order detonations are required to generate as much residue as deposited by one partial detonation in which only half of the explosive fill is consumed. Therefore, it is critical to the Army's training range sustainment program to quantify the magnitude, distribution, and fate of energetic residues resulting from the partial detonation of munitions.

Rationale

The ranges chosen for investigation included artillery, mortar, antitank weapon, rocket, hand grenade, small arms, and demolition. Previous studies have shown that residues of energetic compounds tend to accumulate near fixed targets, at firing points, and where partial (low-order) detonations or blow-inplace operations have occurred. Understanding the physical and chemical characteristics of these spatially distributed zones of energetic residues is necessary to properly define the current conditions and to assess the potential for off-site migration. Moreover, a clear understanding of the distribution and characteristics of these residues and the potential for areas to serve as source regions will enable range managers to prioritize and customize sustainment programs.

Objective

The Sacramento District's objective was to establish the extent, distribution, and fate of heavy metals, selected semi-volatile organic compounds, and residues of energetic compounds on two live-fire-training ranges in Hawaii. Our objective was to conduct research on sampling strategies and analytical protocols to adequately represent the distribution of energetic compounds in the surface soil at various training ranges. This chapter presents the findings associated with energetic residues.

Site description

Schofield Barracks, located on an 18,000-acre site in central Oahu, has existed since 1909. The impact ranges encompass 4,695 acres, almost half of which are on the eastern slope of the Waianae Mountain range. PTA, in operation since 1956, is located between Mauna Loa, Mauna Kea, and Hualalai volcanic mountains on the island of Hawaii. PTA covers 108,863 acres and is the largest training area in Hawaii. Approximately 51,000 acres of PTA are used as an impact area, which is more than ten times larger than the impact area at Schofield Barracks. Heavily wooded areas and open grasslands dominate the surface cover at Schofield Barracks, and rough ('a'a) and smooth (pahoehoe) lava flows cover most of PTA. The ranges at Schofield Barracks and PTA are used for troop maneuvers and live-fire training with artillery, mortars, grenades, anti-tank weapons, machine-guns, and other small arms.

Experimental Description

Collection, on-site splitting, and shipment of samples

One of the overall objectives was to establish representative average energetic residue concentrations at locations where munitions are either fired or detonated during military training activities. To achieve this objective, composite samples composed of 10 or more separate increments (portions of the surface soil/vegetation) were collected. Each increment consisted of surface material, and the depth was limited to 5 cm or less (depending on surface hardness). Previously, Jenkins et al. (1997a) showed that often two or three orders of magnitude difference exist between energetic residue concentrations in discrete samples collected within a meter of one another. Both in the Jenkins study and in Thiboutot et al. (1998), results from the analysis of composite samples were determined to be equivalent to the mean of the individual increments that made up the composite. Another benefit of using a composite sampling strategy is that it is more efficient with respect to analytical costs and time, and the likelihood of missing a hot spot is greatly reduced. The surface of training ranges is particularly important because both propellants and high explosives residues are distributed as particles during projectile firing and ordnance detonation. Because particles of energetic residues may become trapped in vegetated surfaces, leaf litter, moss, and grasses should be considered as part of the sample. These various forms of vegetation have traditionally been scraped away prior to the collection of soil samples when performing environmental investigations.

The number of increments that should be collected to build a representative composite sample for the different activities that occur on military training ranges has yet to be experimentally derived. Work is currently underway to address this issue, however, and to help provide some guidance on the limits of uncertainty for establishing mean concentrations for different range activities. The processing of a large composite sample that may or may not include vegetation requires that much more attention be given to laboratory protocols to ensure that the subsamples removed for analysis continue to be representative of these large field samples. This is a particularly difficult problem for energetic residues that reside

on vegetated surfaces or that are imbibed into fibrous materials (i.e., propellants, Walsh et al. 2003; Hewitt and Walsh 2003).

For this study, multiple composite samples with 10-30 increments were collected within identified areas of concern. These multi-increment samples were obtained within a 5-m-diameter circle, on the perimeter of a larger circle, or along a 15- to 30-m linear transect. The collection of increments to build a composite sample was random for a circular area and systematic (every 0.5- to 2-m interval) along the perimeter of a circle or along a linear transect, depending on the size or length, respectively. Surface soils to a depth of 5 cm or less were obtained with a short stainless steel scoop or a specially designed coring tool (similar in design to a bulb planter) with a 4.44-cm I.D. The metal scoop was used for non-vegetated loose materials (arid soils) and cobbled surfaces, and a manual coring tool (e.g., bulb planter) was used for cohesive soils and vegetated surfaces. In particular, the coring tool is useful for the unbiased collection of surface materials in vegetated areas. When vegetation is dense the proper depth is obtained by over coring (greater depth than necessary), then breaking or cutting the top section off after the soil core is removed from the barrel.

Sample increments were combined in an ultra-clean polyethylene bag $(30 \times$ 38 cm, 6-mil thickness). These composite samples ranged from 1.5 to 2.5 kg in total field moist weight (most samples appeared to be dry, i.e., <1 percent moisture content). At each sampling location, the Sacramento (CA) District sampling team mixed a composite sample and split it into equal subsamples. To mix the bulk sample in the field prior to splitting, the soil was hand massaged and any clumps present were broken apart with a hard object. Soon after acquiring the split samples, the Sacramento District field sampling team removed subsamples for the analysis of explosives, metals, and semi-volatile organic compounds. At several locations, field duplicates were collected to evaluate the representativeness of the sample collection strategy. With the exception of one location, ERDC-CRREL was the only laboratory processing and analyzing field duplicates.

Between sampling locations, the sampling tools were cleaned by repeated rinses with potable water or by rinsing with potable water followed by acetone. After rinsing, the sampling tools were wiped dry with a clean paper towel. While collecting and handling samples (i.e., sample splitting) the sampling team wore clean Latex gloves. Samples were packed with ice and shipped to a contract laboratory and to ERDC-CRREL for further processing and analysis.

Sample processing and analysis

The soil samples sent to a contract laboratory for energetic residue analysis were processed following the guidelines provided in EPA Method 8330 (U.S. EPA 1996). This method requires that soil samples be air-dried, ground using a mortar and pestle, and passed through a $\# 30 (0.6$ -mm) sieve. The sieved fraction is mixed, and a 2-g subsample is removed and extracted with 10-mL of acetonitrile in a water-cooled sonic bath for 18 hours. Following this protocol, the analysis dilution factor is 5 (10-mL / 2-g).

A modified version of EPA Method 8330 was used in the laboratory. Modifications included use of a different sized sieve to remove oversized debris, mechanical grinding of composite samples and removing larger subsamples for analysis (Walsh et al. 2002). These changes to sample processing and subsampling were instituted to address subsampling error. For this study, the samples were air dried and passed through a #10 (2-mm) sieve to separate pebbles, metal debris, and sticks (large pieces of vegetation). The less than 2-mm fraction was mechanically ground on a ring mill. Nonvegetated samples were ground for 60 seconds and vegetated samples for 90 seconds. Most of the ground sample passes through a $#200 (75-µm)$ sieve. The ground sample was thoroughly mixed, then spread over a flat surface. Twenty to thirty randomly located increments were removed to build a 10-g subsample. The 10-g subsample was extracted with 20 mL of acetonitrile in a water-cooled sonic bath for 18 hours. To assess subsampling error, laboratory duplicates were taken every tenth composite sample. This method of sample processing and subsampling was determined to provide representative laboratory subsamples for 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in samples from hand grenade, mortar, and anti-tank impact ranges (Walsh et al. 2002). An additional benefit of this approach is lower detection limits (dilution factor reduced from 5 to 2) for the analysis of energetic residues in soil samples.

The contract laboratory analyzed the soil sample extracts by highperformance liquid chromatography (HPLC) Methods 8330 and 8332 (U.S. EPA 1996) and by gas chromatography (GC) Method 8270C (U.S. EPA 1996). The practical quantitation limits (PQL, i.e., method detection limits "MDL" \times 3) that have been reported for Methods 8330 and 8332 are 0.2 mg/kg for each analyte. For Method 8270C, the PQL is 0.33 mg/kg.

Both HPLC and GC analysis were performed in the laboratory; however, the GC method used was Method 8095, which is a gas chromatography-electron capture detector (GC-ECD) technique that specifically addresses the analysis of energetic compounds (U.S. EPA 1999). Method 8270C is a GC-mass selective detector technique used to identify and quantify a host of semi-volatile organic compounds. Few of the energetic compounds are target analytes for Method 8270C. The HPLC analyses were performed on an instrument (Spectra System®, Thermo Finnigan, San Jose, CA) that can execute both Method 8330 and 8332 analyses by having a dual wavelength detector. The reduced solvent-tosubsample ratio allows the PQL to be lowered to 0.08 mg/kg for each of the analytes with the exception of the nitrotoluenes. Method 8095 produced PQLs between 0.0014 and 0.075 mg/kg for the explosives detected in the samples analyzed during this study (Table 3-1) (Walsh and Ranney 1999). As a general rule, all samples were initially analyzed by HPLC, and then those samples with concentrations less than 0.40 mg/kg were reanalyzed by GC-ECD. For this reason, the PQLs applied to the data set are those associated with GC-ECD analysis, i.e., Method 8095.

Tables 3-2 and 3-3 show the five energetic compounds determined by both laboratories for the split samples. These two tables show concentrations reported for nitroglycerin (NG), 2,4-dinitrotoluene (2,4-DNT), TNT, RDX, and HMX. Because of lower detection capabilities, the presence of 1,3,5-trinitrobenzene (TNB), 2,6-dinitrotoluene (2,6-DNT), 2-amino-4,6-dinitrotoluene (2-ADNT), and 4-amino-2,6-dinitrotoluene (4-ADNT) was also determined, in some of the samples. Appendix A lists the concentration estimates for these additional energetic compounds.

Table 3-2

Energetic Residue Concentration (mg/kg) Results from Both Laboratories for Split Sample from Schofield Barracks

a Values reported by ERDC/CRREL for split sample.

b Values reported by laboratory contracted by the Sacramento District for split sample.

c (<d) below PQL.

d Values qualified by the contract laboratory or during the data review process.

e (na) not analyzed.

f Profile sample (sample depth).

g Laboratory control sample was spiked at 1.0 mg/kg.

Table 3-3

Energetic Residue Concentration (mg/kg) Results from Both Laboratories for Split Sample from Pohakuloa Training Area

Table 3-3 (Concluded)

c (<d) below PQL.

d Values qualified by the contract laboratory or during the data review process.

e Laboratory control sample was spiked at 1.0 mg/kg.

f (na) not analyzed.

Locations sampled (chronological order)

Schofield Barracks

Engineering Demolition Range / Firing Point (FP 308) / Impact Range. The first excursion onto the training range at Schofield Barracks included a visit to a demolition range, a firing point, and an area just inside the boundary of the main artillery and mortar impact range. A total of nine composite samples were collected during this initial trip. Each sample was collected with the coring tool and contained 10 increments from the top 0 to 5 cm.

Four composite samples were collected on the engineer demolition (Eng-Demo) range. The first sample (SC-1) was collected in an area that had been burned within the last year, and the second (SC-2) was from a location along an access road that was unlikely to have been burned for a couple of years. Samples SC-3 and SC-4 were collected within an area where mortar fin fragments were on the surface. The next two samples (SC-5 and SC-6) were collected at FP 308 used for 105- and 155-mm howitzer training. Lastly, on the edge of the impact area just off of the North Fire Break Road (NFB 11), three samples (SC-7 through SC-9) were collected in an area where 60- and 81-mm mortar fins were found.

Anti Armor Range (KR 8). Range KR 8 is used for training with 40-mm rifle grenades, heat rounds, and Light Antitank Weapon (LAW) rockets. Soil samples were collected near two wooden targets about 150 m downrange. Near these targets, pieces of 40-mm rifle grenades and LAW rockets were observed. The presence of markings from spotting charges and intact LAW rocket motors and the condition of the target indicated that the fragments were from practice rounds. Duplicate 30-increment composite samples were collected along a 16-m linear transect between the two targets (SC-10 and SC-10fd; fd-field duplicate) and at distances of 5, 10, and 15 m in front of the target (toward the firing point, SC-11 through SC-13fd). Two sets of field duplicates (SC-14 through SC-15fd) were also collected at 10 and 20 m behind the firing point along the same 16-m

linear transect. All of the sample increments were obtained with a metal scoop and were from the top 0 to 2.5 cm of the ground surface. A dense growth of tall grass prevented access to targets further downrange. This vegetation limited visibility of the surface and a clear path could not be found that assured avoidance of unexploded ordnance (UXO).

Mount Assault Course (MAC). The MAC range is used for small arms and 40-mm rifle grenade training. Among the fixed firing points on this range was a wooden structure with a window that had recently been used for a 40-mm rifle grenade training exercise. At this range all of the targets were among tall grasses that inhibited access for sampling. For this reason, all of the samples were collected near the firing point. Thirty-increment composite samples (SC-16 through SC-18) were collected along 10-m transects that were parallel to the wooden structure, at distances of 1, 5, and 10 m downrange. A field duplicate was collected at 1 m (SC-16 and SC-16fd). Lastly, a fifth composite sample (SC-19) was taken directly in front (0.1 m) of this firing position and was extended on each side to complete the same 10-m transect as the other composite samples collected at this facility. All of the sample increments were obtained with a metal scoop and were from the top 0 to 2.5 cm of ground surface.

Infantry Demo Range (SR 5). Range SR 5 is used for training with hand grenades and Claymore mines. The main impact area for the hand grenade range is a 20-m-long trough with a small puddle of water in the middle, located some 30 m from a throwing bunker. At the end of a mound of soil that separated the hand grenade range from three sand pits used for detonating Claymore mines, an M67 hand grenade that had partially detonated was found. The presence of Composition B (60 percent RDX, 39 percent TNT, and 1 percent wax) residues on the inside surface of this hand grenade were qualitatively identified using an Expray kit (Plexus Scientific, Silver Spring, MD). Thirty increment duplicate composite samples were collected on either side of the puddle (SC-20 and SC-20fd "right side" and SC-21 and SC-21fd "left side"), in the bottom of the trough, and a single composite sample was taken across the top of the trough (SC-22) on the side closest to the throwing position. All five of these surface soil samples were taken from the top 0 to 2.5 cm using metal scoops. A composite profile sample was also obtained at this site. This composite sample was composed of ten increments collected in the bottom of the trough near the puddle using the core sampler. Each soil core was separated into the following depth increments: 0 to 2.5 cm (SC-23), 2.5 to 5 cm (SC-24), and 5 to approximately 8 cm (SC-25).

Firing Points South Range (SR 1 and SR 2B). At two separate 105- and 155-mm howitzer-firing positions, 15-increment composite samples were collected with the coring tool within 5-m-diameter areas. Two samples (SC-26 and SC-17) were collected at SR1, and five samples (SC-28 through SC-32) were collected at SR2B. The samples were taken from the top 0-5 cm of the ground surface at locations downrange from tracks of vehicles that may have been used to transport these guns.

Water Tank. This location was selected for the collection of background soil samples. Three 15-increment composite samples (SC-33 through SC-35) were collected using the soil-coring tool within three 5-m-diameter areas. All

three composite samples were taken from the top 0-5 cm of the ground surface, behind a large water storage tank.

Artillery Impact Range. A second trip into the artillery impact area started at a location where samples SC-7 through SC-9 had been collected, off the North Fire Break Road (NFB 10). Numerous craters and targets were encountered during this excursion, and fragments from the following munitions were observed: 60- and 81-mm mortars, 105- and 155-mm howitzer projectiles, TOWmissile wires, 2.75-in. rockets, and 40-mm grenades. Eleven 30-increment composite samples of the top 0-2.5 cm of ground surface were collected with stainless steel scoops. At the farthest point of penetration into the impact range, a sample (SC-36) was collected in a circular pattern, 0 to 2 m around a heavily impacted target (i.e., impact craters surrounded the target, and the surface was covered with debris). Also at this location, a set of field duplicates were collected (SC-37 and SC-37fd) in a circular area of 5-m diameter that encompassed several craters. Likewise, two sets of field duplicates were taken in an area of several craters between a second set of targets (SC-38 and SC-38fd), and just to the right of one of these targets (SC-39 and SC-39fd), moving back to the boundary of the impact range. In addition, near the second set of targets, a single composite sample (SC-40) was taken within and around the rim of a crater that appeared fresh (no vegetation) and was probably from the detonation of a 155-mm howitzer projectile. Moving away from the targets to an area of no impact craters, a sample (SC-41) was collected in an undisturbed location. The last few samples were collected near a third target, a relatively undamaged armored personnel carrier (APC). A sample was taken within a large crater (SC-42) and at a distance of 0 to 2 m around the APC (SC-43).

Pohakuloa Training Area

Firing Position 311. The first area sampled at PTA was a 105- and 155-mm howitzer firing position. Four sets of duplicate 30-increment composite samples (PTA-1 through PTA-4fd) were collected from the top 0 to 2.5 cm of ground surface within 5-m-diameter areas with the stainless steel scoop. At this firing point, no evidence of recent activity was observed.

Impact Range (R 11). Sampling performed on an active impact range at PTA was limited to an excursion along the boundary of Range R 11 because of the presence of sub-mission duds. Fragments from Dragon rockets, TOW missiles, 2.75-in. rockets, 60-mm mortars and 50-caliber armor-piercing munitions were observed. Around a tank target located about 200 m into the range, three sets of duplicate samples (PTA-5 through PTA-7fd) were collected at distances of 0 to 2 m (band), and 5 and 10 m (rings). At a second location some 50 m west of the tank, a single composite sample (PTA-8) was obtained within a 5-m-diameter area. Next to this sampling location, a partially detonated TOW missile was found. The engine compartment had broken open, and several propellant tubes were exposed. Sampling (wiping) the inside surfaces of the motor stage with a Q-tip produced a positive response when tested with the Expray kit for nitramines or nitrate esters. In this case, the compounds detected were likely either NG or nitrocellulose (NC) or both. The same soil sampling protocol (random sampling within 5-m-diameter area) was repeated six more

times moving in a westerly direction along the border between each sampling location (PTA-9 through PTA-14). The only sampling location that was different from the others was PTA-11, which was located near a crater that appeared to have been the result of a demolition exercise (blow-in-place). All of the surface samples were composed of cinder ash (0 to \leq 2.5 cm depth, often just 0–1 cm) and were collected with a stainless steel scoop.

Assault Hill (R 10). Hill R 10 is currently a troop maneuver area; however, prior to 2000 this range had served as an impact range for AT4s and 105-mm howitzers. Composite samples were collected along three 15-m parallel transects, positioned 5 m apart (PTA-15 through PTA-17) on the side of the hill that faced the impact area. Surface samples were from the top 0 to 2.5 cm and were collected with a stainless steel scoop. This sampling location was selected because it was heavily littered with shell casings from M60 machine guns and M14 rifles.

Engineer Demolition Range (R 9). During the initial survey of Range R 9 by explosive ordnance disposal (EOD) personnel, a baseball-size chunk of C4 (qualitatively identified with an Expray kit) was found on a wall of one of two man-made demolition pits. The surfaces of these $25 - \times 25$ -m demolition pits were covered with metallic debris, and in some areas the surface was discolored. Two samples were collected from each pit, one from each half. Each sample was a 30 increment composite surface sample (0 to 5 cm) collected with a stainless steel scoop (PTA-18 through PTA-21).

FP 802 and FP 804. Both of these firing positions had been used recently by troops training with 60- and 81-mm mortars; the tube firing positions (anchor points) were still visible. Four field duplicates were collected within 5-mdiameter areas that included the base plate imprints (PTA-22 through PTA-25fd) at FP 802. Likewise, four individual composite samples were collected at FP 804 (PTA-26 through PTA-29). All soil samples were collected with stainless steel scoops from the top 0-2.5 cm. Cartridges from small caliber arms, slap flares, and an assortment of other items were also present at these two firing positions.

Hand Grenade Range (R 5). At this hand grenade training facility, three bays were separated by piles of rocks. Each bay was approximately 30 m wide, had a concrete throwing bunker, and was open (no rock pile) downrange. EOD personnel surveyed all three bays looking for signs of recent activity prior to selecting one for sampling. The middle bay (Bay #2) was selected for sampling after the discovery of a large fragment of an M67 hand grenade. Thirty-increment composite samples were collected along linear transects. Transects extended the entire width of the bay, starting 15 m from the throwing pit and repeating at 5-m intervals to a distance of 40 m (PTA-30 through PTA-35). An additional 30 increment composite sample was collected at 41 m (PTA-36). All soil samples were collected with a stainless steel scoop from the top 0 to 5 cm.

FP 309 and FP 420. At these two artillery-firing points, 105- and 155-mm howitzers are fired. Four 30-increment composite samples (PTA-37 through PTA-40 and PTA-41 through PTA-44) were collected within 5-m-diameter areas at both firing points in locations where wire straps, fuse wrenches, small caliber

bullet casings, and glow sticks' wire straps were found. Soil samples were taken from the top 0-2.5 cm using stainless steel scoops.

Range Control. Two 15-increment composite samples (PTA-45 and PTA-46) were collected with a stainless steel scoop from the top 0–5 cm at the base of the puu (cinder cone) located just north of the Range Control building at PTA. This location was selected for background.

Results

Data review

The laboratory control sample (LCS) values in Tables 3-2 and 3-3 show that 75 percent or more (mean and standard deviation 96±7 percent) of the 2,4-DNT, TNT, RDX, and HMX that was spiked onto a known soil matrix was recovered. Although not reported here, in a subsequent study, NG was included in the spiking solution, and recoveries were better than 97 percent from this same soil matrix. In addition, very good recoveries of the four analytes listed in Appendix A were achieved. The LCS values established by the contract laboratory had an acceptable percent recovery range of 65-135 percent (U.S. Army Corps of Engineers, Sacramento District, 2002). Likewise, the matrix spikes (MS) and matrix spike duplicates (MSD) performed by the contract laboratory had an acceptable percent recovery range of 45-140 percent (U.S. Army Corps of Engineers, Sacramento District, 2002).

Nine of the soil samples processed and analyzed at ERDC-CRREL had laboratory duplicate subsamples removed for analysis (Table 3-4). Among the nine laboratory duplicates, there were 18 possible pairs of residue concentrations above our PQLs (Table 3-1). Two of the 18 possible pairs of values failed to have reportable concentrations in both replicates (Table 3-4). In both cases, the concentrations that were established were very close to the respective PQL. For PTA-13, RDX was detected at 0.013 mg/kg (PQL for RDX is 0.008 mg/kg) and for SC-32, 2,4-DNT was detected at 0.003 mg/kg (PQL for 2,4-DNT is 0.002 mg 2,4-DNT/kg). At trace levels $(<0.02$ mg/kg), it is not unusual to have large relative percent differences (RPDs) between laboratory duplicates. The median RPD of the remaining 16 sets of duplicates was 11 percent, and the range was 0.0–126 percent. In the majority of cases (10 of 18), NG and 2,4-DNT were the energetic compounds detected in the laboratory duplicates. NG, which degrades very rapidly in soil (Jenkins et al. 2003), is an ingredient in double- and triplebased propellants. 2,4-DNT is present in single-based propellants. All of these propellants contain NC. Moreover, the authors believe that NG and 2,4-DNT are retained within (imbibed by) the NC, which is a polymer that has proven to be very difficult to grind into particles that can be mixed throughout a bulk soil sample. This confounds efforts to homogenize samples for reproducible subsampling (Hewitt and Walsh 2003; C. Ramsey, personal communication). Efforts are underway to better understand the physical characteristics of propellant fibers and to improve laboratory processing of samples containing propellant residues (Marianne Walsh, personal communication). No replicate laboratory subsamples were analyzed for energetic residues by the contract laboratory.

 <d below PQL. — No value.

At 26 locations, duplicate field samples were collected for analysis. In only one instance was a duplicate field sample processed and analyzed by both laboratories. Neither laboratory detected any energetic compound concentrations above their respective PQLs for these samples. Of the 26 field duplicates, 20 contained one or more of the following analytes above their PQL: NG, 2,4-DNT, TNT, RDX, or HMX (values in Appendix A, which were all very low, were not included in this assessment). In all, there were 39 pairs of values that could be evaluated to assess the reproducibility of the field sampling protocol (Table 3-5). For 14 pairs (36 percent), energetic residues were found only in one of the field sample replicates. For the remaining 25 pairs, the median RPD was about 50 percent, and the RPD range was 0–187 percent. This comparison of analyte concentrations from duplicate field samples indicates that the distribution of energetic residues was very heterogeneous. Moreover, our sampling strategies were frequently not capable of controlling this source of sampling error. This finding is consistent with the theory that energetic residues are dispersed as particulates, therefore, the ability to collect representative (reproducible) samples on an active range is often confounded by the nugget effect (Radtke et al. 2001). For example, this would explain the large discrepancy between SC-20 and SC-20fd. These duplicate field samples were collected in an area where a partially detonated hand grenade was found. The RPDs for TNT, RDX, and HMX were among the highest established for this study (>168 percent), which could be

explained by the collection of a nugget of Composition B in one of the field duplicates from the partial detonation of the M67 hand grenade (Table 3-5).

Among the split samples analyzed by both laboratories, there were 93 instances where at least one laboratory determined that one of the five energetic compounds listed in Tables 3-2 and 3-3 was above 0.20 mg/kg. Of the 93 potential pairs of values, the presence of at least one of the energetic compounds was detected in 32 cases, whereas the contract laboratory failed to report concentrations above the 0.20-mg/kg threshold (Tables 3-2 and 3-3). In 11 other cases, the presence of an energetic compound above 0.20 mg/kg was detected, but the value reported by the contract laboratory was qualified ("j" value). In contrast, the contract laboratory reported only a single value for an energetic compound above 0.20 mg/kg that we did not concur with at or above this threshold concentration (Table 3-3, PTA-38). One possible explanation for the less frequent detection of energetic residues by the contract laboratory is that their sample preparation protocol (Method 8330) was biased low for energetic residues in samples from military training ranges as compared to the authors' laboratory protocol.

To determine if the sample preparation procedure in the 8330 Method can potentially be biased for energetic residue concentrations as compared to our protocol, a quick experiment was performed. Three composite samples (2 to 3 kg), which had been collected at a 105-mm howitzer firing position, were sieved separating the bulk sample into three size fractions. These samples, which were from a sparsely vegetated area (mostly sand and silty soil), were air-dried and then $\#10$ sieved (2 mm). The >2 -mm fraction was placed into a large glass bottle, while the material that passed through the 2-mm sieve was ground with a mortar and pestle and then passed through a $# 30 (0.6$ -mm) sieve. The fraction between \leq 2-mm and \geq 0.6-mm, and the \leq 0.6 mm fraction were also placed into separate large glass bottles. Each fraction (whole sample) was extracted with acetonitrile. The results of this experiment (Table 3-6) showed that the >2-mm fraction contained no detectable energetic residues, but the middle fraction (<2-mm to >0.6-mm) had a concentration (and mass) of 2,4-DNT that was greater than the smallest fraction. Likewise, in fractionation studies (>2 mm, $<$ 2 mm but >0.6 mm, and <0.6 mm) for a hand grenade range and an artillery/mortar impact range, the middle fraction often had the highest TNT concentrations, and in some cases also had the highest RDX and HMX concentrations. The presence of small particles of high explosives and propellants that are larger than 0.6 mm but smaller than 2 mm could explain the differences in the results from the two

laboratories. Our protocol required sieving through a # 10 (2-mm) sieve, while the contract laboratory used a $\# 30$ (0.6-mm) sieve. Thus particles of energetic compounds greater in size than 0.6 mm but less than 2 mm would be present in the portion of samples extracted by us, but not by the contract laboratory.

When Method 8330 was developed, most sampling activities were occurring at manufacturing, load and pack, and demilitarization facilities. These facilities used large quantities of water daily to help keep the equipment safe for operation. Therefore, energetic compounds were often dissolved before they came in contact with the environment, i.e., drainage ditches, holding ponds, etc. Typically, in a dissolved state, residues would tend to accumulate on soil particles with the greatest surface area (i.e., smaller size). This mechanism of distribution is very different from what occurs on a firing range. On firing ranges, residues of energetic compounds are dispersed as particles of various sizes. Based on the results of this study, and a couple of preliminary experiments, some of the energetic residues in samples from training ranges that fall into the generally accepted size classification for soil (i.e., < 2 mm), can go unaccounted for when samples are passed through a $# 30 (0.6$ -mm) sieve as recommended in the Method 8330 protocol.

Accumulation of explosives residues on training ranges

Howitzer and mortar impact areas. The only active artillery and mortar impact areas sampled in this study were on Schofield Barracks. Access to impact areas on PTA was limited because of the presence of sub-munitions. Samples were collected at PTA along the border of the impact range (R 11) and in a former artillery and rocket impact area (R 10) that is currently a troop maneuver area.

Composition B and TNT are the two high explosive fillers in mortar and howitzer rounds. Our laboratory determined very low levels of RDX (<0.06) mg/kg) in some samples collected in the impact range at Schofield Barracks (Table 3-2). In addition, the two-biotransformation products of TNT (2-ADNT and 4-ADNT) were present in some of the samples (Appendix A). Most of the samples containing explosives residues were collected in areas surrounded by craters and littered with mortar fins and artillery shrapnel. The low levels $(< 0.1$ mg/kg) of explosives residues in the soil on this impact range are consistent with the findings at several other ranges (USACHPPM 2000; U.S. EPA 2000; Ogden

Environmental and Energy Services 2000; Jenkins et al. 2001; Walsh et al. 2001; Pennington et al. 2001, 2002, 2003).

Along the border of the active PTA impact range (R 11), several 2.75-in. rockets and TOW missiles were observed; however, mortar or artillery rounds were not evident. Both laboratories detected NG and 2,4-DNT in soil samples from this range. Adjacent to a tank (target) and extending out to a 10-m radius, the concentrations of NG were between 1.0 and 10 mg/kg (Table 3-3). NG or 2,4-DNT, or both, were detected in several of the samples taken farther away from this fixed target; however, the concentrations were typically lower ≤ 1.0 mg/kg) than found near the tank (Table 3-3). Both of these analytes are present in propellants; therefore, the presence of NG and 2,4-DNT on this range is most likely attributable to the use of rockets. Rocket fuel that is not consumed during flight is dispersed as particles upon detonation.

In the samples from assault hill (R 10), both laboratories found NG and HMX in low mg/kg concentrations (Table 3-3). Low concentrations of 2,4-DNT, TNT, and TNB ([<0.2 mg/kg] Table 3-3 and Appendix A) were also detected. Because this range has served as both an impact and troop maneuver area, these residues could result from several different activities.

Howitzer and mortar firing points. A total of eight howitzer or mortar firing points were sampled on these two bases. NG and 2,4-DNT were detected in the samples collected at the Schofield Barracks firing points (Table 3-2). Both laboratories detected NG and 2,4-DNT in the samples collected at firing points on PTA (Table 3-3). Overall, either NG or 2,4-DNT, or both, were detected in about 40 percent of the samples collected at the howitzer or mortar firing points. In addition, 2,6-DNT was detected at very low concentrations in a couple of the firing point samples collected at PTA (Appendix A). With the exception of the samples collected at firing points FP 802 and 804 on PTA, the concentrations of NG and 2,4-DNT were usually below 0.2 mg/kg. Both FP 802 and 804 had been used in a training exercise within a week of our sampling. Indeed the imprints for the mortar's base plates were still visible. The concentrations of NG were estimated to be between 1.0 and 10 mg/kg in the samples from these two firing points (Table 3-3). NG is present in double- and triple-based propellants and 2,4- DNT is in single-based propellants. The detection of these energetic residues at howitzer and mortar firing points is consistent with several previous studies (USACHPPM 2000; Ogden Environmental and Energy Services 2000; Jenkins et al. 2001; Hewitt and Walsh 2003; Walsh et al. 2003).

Both NG and 2,4-DNT are imbibed into NC during the manufacturing process. They seem to remain in this condition after firing and being dispersed as particles (smoke) from the barrel and gun breach (Walsh et al. 2003). The particles of NC that were collected during the firing of 105-mm howitzer projectiles were a couple of millimeters in length with an aspect ratio greater than 20 to 1 (length to width; Susan Taylor, personal communication 2002). Preliminary findings suggest that these particles can become windborne unless trapped by vegetation (Walsh et al. in press). Moreover, with no evidence that these particles break down rapidly, NG and 2,4-DNT are anticipated to remain trapped within the NC matrix.

Rifle-grenade and anti-tank rocket training ranges. Two of the ranges sampled at Schofield Barracks were designed for troops to shoot at fixed targets that were placed from 150 to 2,000 m downrange. This type of range was not sampled at PTA because all of the targets were located on rough ('a'a) lava flows. Furthermore, the firing point at the PTA anti-tank range was not sampled because it also served as a parking lot. At both facilities on Schofield Barracks (KR 8 and MAC), 40-mm rifle grenades were fired. In addition, LAW rockets and heat rounds were also fired at KR 8, for which both laboratories detected HMX downrange, and NG behind the firing position (Table 3-2). TNT, RDX, and TNB were also detected on this range (Table 2 and Appendix A). No distinct pattern of explosives residue concentrations was observed next to and in front of the targets (Table 3-2, SC-10 through SC-13); however, a distinct gradient was observed behind the firing points. The NG concentration in the sample collected 20 m behind the firing positions was about two orders of magnitude below the sample collected 10 m behind the firing point (Table 3-2, SC-15 and SC-14, respectively).

The concentrations of 100–1,000 mg/kg for NG and 1–100 mg/kg for HMX on this LAW rocket range are consistent with previous findings (Jenkins et al. 1997b; Thiboutot et al. 1998, 2003; Jenkins, in preparation). NG is present in the double-based propellant used to drive these rockets into their intended target, while HMX is the primary high explosive in Octol (70 percent HMX and 30 percent TNT), which serves as the main charge. The back blast of propellant that occurs when a LAW rocket is fired leaves residues of unconsumed propellant behind the firing position. In addition, chunks of propellant often exist around the targets, since any unconsumed fuel is dispersed on detonation. The LAW rocket is a point-activated round and frequently fails to detonate when the target is missed or when the rocket hits the ground before reaching the target. In both instances, the casing can rupture, dispersing the high explosive filler. Based on findings in other reports, even higher concentrations of energetic residues are likely to exist further down range, but that area was not accessible for sampling because of safety concerns.

At the MAC training facility, a firing point that had recently been used for a 40-mm rifle grenade training exercise was sampled. Both laboratories detected NG in the samples collected around the firing position (Table 3-2), and low levels of 2,4-DNT and TNT were also detected. NG was present because the propellant for this type of round is double-based (Walsh et al. 2003). NG concentrations ranged from about 0.2 mg/kg at a distance of 0.1 m to about two orders of magnitude higher at distances of 1, 5, and 10 m in front of the firing point (Table 3-2, SC-19, SC-16 through 18, respectively). Walsh et al. (2003) also detected NG at a firing point used for 40-mm rifle grenade training.

Hand grenade ranges. The impact area on the hand grenade range at Schofield Barracks (SR 5) was trough shaped and contained a pool of water at the lowest point. All three impact bays at PTA had relatively flat surfaces. Both laboratories detected TNT, RDX, and HMX in the soil samples from these two hand grenade ranges, a finding that is consistent with the main charge of the M67 hand grenade, which is 183 g of Composition B (Tables 3-2 and 3-3). HMX was also present because it is an impurity in the RDX manufacturing process, typically comprising between 10 and 15 percent by weight of RDX (Urbanski

1967). The profile sample collected at Schofield Barracks established that there was an order of magnitude decrease in residue concentrations from the surface to a depth of 5 to 8 cm (Table 3-2, SC-23 through SC-25). In addition, TNB, 2- ADNT, and 4-ADNT were detected in the samples from the Schofield Barracks hand grenade range (Appendix A). These energetic residue concentrations and trends (profile) are consistent with earlier findings on active hand grenade ranges exhibiting evidence of partial detonations (Jenkins et al. 2001). Much lower residue concentrations have also been observed on some active ranges; however, in these cases, no large casing fragments were observed (Thiboutot et al. 2003).

Engineer demolition ranges. Samples were collected at both military training facilities on ranges that are used for the demolition of UXO and perhaps obsolete munitions (and other materials, i.e., fuels). At Schofield Barracks, a few pieces of mortar fins were found on the demolition range. The demolition range at PTA was heavily littered with debris (pieces of fuses, munitions, and other metallic items), and the surface was discolored in areas. Both laboratories detected energetic residue concentrations that ranged from 0.5- to 100-mg/kg in the samples collected where shell-casing fragments were present (Tables 3-2 and 3-3). At Schofield Barracks, both laboratories detected RDX and HMX; whereas NG, 2,4-DNT, TNT, RDX, and HMX were detected at PTA. TNB, 2-ADNT, and 4-ADNT were also detected at PTA (Appendix A). The high concentrations and variety of energetic residues are consistent with residues detected previously in samples from open burn and open detonation (OB/OD) ranges (Racine et al. 1992, Walsh et al. 1999) and after blow-in-place operations (Hewitt et al. 2003).

Conclusions

The collection and analysis of numerous composite surface samples from different military training ranges established the presence of NG, 2,4-DNT, TNT, RDX, and HMX. The values established can be used in models for predicting dermal exposure, ingestion, and migration into surface and subsurface water systems. The concentrations of energetic residues determined for the different training activities were consistent with concentrations found previously at other sites engaged in similar activities. The comparison of results established for field duplicates and for the split samples (two different sample preparation protocols) support the contention that energetic materials on active training ranges exist as particles. As particles, explosives residues on active training ranges can be underestimated if Method 8330 is used to establish soil concentrations $(< 2$ mm).

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Appendix A

Note: Only samples with a concentration of 2,6-DNT, TNB, 4-ADNT, and 2-ADNT above the PQL are reported in this table.

4 Environmental Conditions of Surface Soils and Biomass Prevailing in the Training Area at CFB Gagetown, New Brunswick

Introduction

Troop readiness involves intensive training in Canada. Moreover, many other countries use Canadian training ranges under international agreements. Testing and training ranges are therefore key elements in maintaining the capability, readiness, and interoperability of the Armed Forces. The current state of knowledge concerning the nature and extent of contamination of military testing and firing ranges is inadequate to ensure sound environmental management of these facilities as sustainable resources. Results of the ongoing environmental research program will contribute to the development of recommendations for sustaining range activities while ensuring environmental stewardship and regulatory compliance. The potential for environmental impacts, including contamination of drinking water supplies, mandates that installations demonstrate responsible management of these facilities in order to continue testing and training activities.

National defense departments need to be provided with techniques to assess the potential for groundwater contamination from residues of high explosives such as trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), RDX, and HMX, and other potential contaminants such as heavy metals or depleted uranium at testing and training ranges. Site characterization guidance should be developed and data gaps in fate and transport properties of high explosive residuals filled in. Additional research will increase the knowledge base supporting the credibility of guidance and recommendations for range sustainability. The most extensive study up to now was conducted at Canadian Forces Army Depot (CFAD) Dundurn where the impact of the open detonation of Canadian obsolete munitions was extensively studied [1]. The first actual training range visited was the Canadian Forces Base (CFB) Shilo training area where detailed research was achieved to assess the environmental impacts of many types of live fire training [2-3]. Anti-tank firing ranges across Canada were also the topic of another study [4-6]. Moreover, many papers were written in recent years concerning the fate and analysis of explosives in various types of sites [7-19].

This topic also is of very high interest and profile in the United States. The new Army slogan is "Protecting the Environment and our Country" and sustainable training is the highest priority in the Pentagon and Congress. Concern is growing over the potential for military training activities to lead to groundwater contamination on Department of Defense (DoD) ranges. An example of this situation exists at the Massachusetts Military Reservation (MMR). Military and law enforcement training has been conducted for more than 40 years in the Training Range and Impact Area, which encompass almost 14,000 acres at MMR. The Training Range and Impact Area lie directly over the Cape Cod Aquifer, which has been designated as the sole drinking water source for Cape Cod. This aquifer was contaminated by energetic compounds and other military-related compounds such as perchlorates. Training at MMR was consequently suspended by the U.S. Environmental Protection Agency (EPA). This situation, combined with other evidence, has led the Strategic Environmental Research and Development Program (SERDP), one of the most important corporate environmental research and development (R&D) programs (DoD, EPA, and Department of Energy), to request proposals in the area of environmental impacts from training. This program covers many aspects in which R&D has to be dedicated to better understanding the complex fate of contaminants from military activities, including the characterization of residuals from both high- and low-order detonations, the development of credible source term estimates for specific range activities, understanding of the complex environmental fate or targeted parameters in training ranges, and establishment of environmentally acceptable end-points. The second phase of this study was sponsored partly by SERDP.

This report presents the second characterization phase (phase II) carried out at CFB Gagetown training area in October 2002. The first phase (phase I) was conducted in the fall of 2001 and was dedicated to the drilling of wells on the northern half of the base to collect groundwater samples and to perform the hydrogeological characterization of the site [20]. Phase II of this work was a dual effort both on the surface and sub-surface where 26 wells were drilled and sampled in the southern half of the base and surface soils and biomass samples were collected. The information gained is of strategic value for CFB Gagetown and represents a detailed study on the characterization of such a huge and intensively used training area. The Gagetown study will be complementary to the CFB Shilo study based on its different geological context and based also on the nature of the training conducted there. This report presents the surface soil and biomass results while a second report will be published on the hydrogeological context of the training area. Field work was conducted in the fall of 2002 and data treatment followed in 2003.

Range History/Description

Geographical location

CFB Gagetown is 20 km southeast of Fredericton, New Brunswick, in the counties of Queens and Sunbury (Figure 4-1). The Base covers an approximate area of $1,100 \text{ km}^2$. The training area can be divided into two physiographic regions, the New Brunswick Lowlands in the north and the Ste-Croix Highlands in the south. The northern half of the territory is used by the military as the Static Range Impact Areas (SRIAs) and the southern half of the base is used as a general maneuver area, dismantled maneuver areas, and mountain impact area. The Garrison is located in the northwest portion of the base.

Figure 4-1. Gagetown Area map

History of activities

Army training activities at CFB Gagetown first took place in 1954. The base is still used today as one of the major training facilities by the Canadian Forces. Several military schools (i.e., Infantry, Field Artillery, Air Defence, Military Engineer, and Armoured) are actively training in the range and training areas (SRIAs). Such training activities represent potential contamination sources by energetic materials and metals for underlying soil and groundwater in most parts of the SRIA. Moreover, the CFB Gagetown training area is often used for foreign military training (U.S., U.K., and Australian troops). It is the main training area for other CF bases such as CFB Valcartier troops who often conduct training at CFB Gagetown due to its vast ranges for high caliber live-fire training.

Information sources

Most of the information needed to support the writing of the present report was taken from CFB Gagetown military personnel, mostly from the range control unit. The overview of the sensitive areas was also made possible with information and an area map from a preliminary initial study [14]. Fieldwork and planning of related activities were authorized by M. Sheldon Downe, Land Forces Atlantic Area Environment Officer for CFB Gagetown. Pertinent information was also obtained from Explosive Ordnance Disposal (EOD) military personnel who, for safety reasons, were always present when sampling in a danger zone.

Experimental

Field investigation

Fieldwork was conducted between 1 and 6 October 2002 on the northern sections of the training ranges of CFB Gagetown and around base limits. The surface sampling was concentrated in the live-fire impact areas located in the northern portion of the base (Figure 4-2). Sampling strategies were designed onsite, depending on the landscape, visual observation of the area, the information gathered from EOD unit personnel, and also based on the expertise gained in previous training area field work (Figure 4-3). The surface soils and biomass sampling was supervised and conducted by Dr. Sonia Thiboutot, Dr. Guy Ampleman, and André Marois from DRDC Valcartier, and by Dr. Thomas Jenkins and Alan Hewitt from CRREL (Figure 4-4). Jeff Lewis also participated in the surface soil sampling by collecting samples in rifle ranges after the departure of the surface sampling team.

Figure 4-2. Gagetown Training Area map

Figure 4-3. Establishment of the sampling strategy to be used in the AA firing range

Figure 4-4. Surface sampling team

Consultants and contractors

Hydrogeological work was done under the supervision of Institut national de la Recherche Scientifique Eau Terre et Environnement (INRS-ETE) personnel, which included Richard Martel, Jean-Marc Ballard, and Jeff Lewis. This team was responsible for the proofing of well locations with the help of electromagnetometers, drilling of wells, and groundwater and surface water sampling. Wells installed in the phase I study were resampled and many new wells were drilled in various locations in the training area. The Dillon consulting firm (based in Fredericton, NB) was retained by Defence Construction Canada (DCC) to assist in the collection of samples and data for the environmental site assessment. The services provided by Dillon also included the following: initial project coordination, borehole drilling and well installation supervision, purging and development of the well, groundwater sampling, and all other related logistics. DCC also hired contractors for the UXO proofing (Dillon), the borehole drilling (Dayes Well Drilling and Boart Longyear, Fredericton), and the global positioning system (GPS) surveys (Traynor Surveys Ltd. of Fredericton). The analytical work on water samples for metals, perchlorates, and general chemistry was performed by Research and Productivity Council (RPC) Laboratory, also located in Fredericton.

Chemical parameters and analytical methods

All groundwater and surface water samples were analyzed for metals, major anions, and energetic materials (RDX, HMX, TNT, 2,4-DNT, Tetryl and their main degradation byproducts). A sample of 500 ml of stabilized groundwater was passed through a Sep-Pak™ cartridge filter to absorb any explosive residues that may be present. Acetonitrile, 5 ml, was then passed through the Sep-Pak™ cartridges to extract the explosives residues. The extracts were treated according to EPA Method 8330 (USEPA 1994) [21]. Metals were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) by RPC Laboratory and all parameters available by this method were included in the study. Perchlorates were also analyzed by RPC on a portion of the groundwater samples selected based on the known use of perchlorates in ranges upgradient of the groundwater. Energetic Materials were analyzed by CRREL and DRDC Valcartier using HPLC and GC-ECD following EPA methods 8330 and 8095. [21].

Safety of the sampling teams

Many sampling teams were involved in the phase II campaign. They were split into six teams based on their roles and mandates in the campaign. A call sign (51 delta) was allocated by range control to the following six teams:

51 D1 – Surface sampling team

- Sonia Thiboutot (DRDC Valcartier)
- Guy Ampleman (DRDC Valcartier)
- André Marois (DRDC Valcartier)
- Jocelyn Trembaly (DRDC Valcartier)
- Tom Jenkins (CRREL)
- Alan Hewitt (CRREL)

51 D2 – Drilling team

- Jamie Wilson (Dillon Consulting)
- Don Daye (Daye's Well Drilling)
- David Daye (Daye's Well Drilling)
- Kevin Donald (Daye's Well Drilling)
- Larry Mason (Daye's Well Drilling)

51 D3 – Water sampling team 1

• Jamie Hunter (Dillon Consulting)

51 D4 – Water sampling team 2

• Steve Hartman (Dillon Consulting)

51 D5 – UXO clearance team

- Spencer Wilson (Dillon Consulting)
- Steve Borhese (Dillon Consulting)

51 D6 – INRS team

- Jean-Marc Ballard
- Jeff Lewis

The cellular telephone numbers of main points of contact were provided to all teams, including the range control command post, the EOD manager (Sgt Paul), Jean-Frédérique Lalonde and Ann Jones from DCC, the environmental officer of CFB Gagetown (Sheldon Downe) and range control scheduling responsible (Sgt Fronchak).

A schedule was established prior to the campaign in collaboration with Dr. Thiboutot from DRDC Valcartier, Jean-Marc Ballard from INRS Georessources, Ann Jones from DCC and range control command post. The schedule was established based on a previous visit to the training area (spring 2001) and an estimation of the time needed in each range to perform both surface and subsurface sampling. The schedule is included in the following table. Any modification to the accepted schedule had to be approved by Sgt Fronchak from range control. The schedule ensured that a safety template was applied at all times with no live firing conducted near teams while they were in the live-fire area.

3. One crew for each working simultaneouly.

4. May be able to work some GMA wells in between Oct 1 and Oct 19, 2002.

5. The GMAs will be busy with training activities in October, but available for drilling and surface soil sampling activities as required.

6. The GPS survey will take place on October 26 & 27, 2002.

7. Existing wells will be sampled/tested during these time slots.

A detailed safety briefing was given to all teams on 31 September. Capt. Melancon, the new Range Control Officer of the training area welcomed the sampling teams to CFB Gagetown. He stated that the range control and EOD staff would be dedicated to the success of the sampling campaign and that they would give full support to the study. The safety briefing included detailed information on the type of munitions that the teams might encounter on ranges and how to

minimize the danger associated with working in such an environment. Clear instructions were given on the liaison with range control either by cellular telephone or radio provided by range control. Motorola 100 radios were distributed to each subunit with instructions to use Channel 1 for internal communication at a frequency of 47.66. Each subunit was instructed to check on a daily basis for range availability, to ensure that they would be informed of any changes that could be made to the Daily Range Safety Orders, and to ensure that EOD requirements were addressed for every subunit. Each team was required to request permission at the gate to enter the danger red zones and to inform range control when exiting the red zone. A team contact list and sign allocation sheet were written and distributed to all teams with clear instructions on who to contact for each need at all times. More precisely, all subunits were clearly instructed to remain in constant communication with their main point of contact, and subunits had to use their call signs when addressing the main point of contact.

Eight EOD specialists were dedicated to the sampling teams and were always to be present with the team when entering a red zone. They drove and walked all day with teams to ensure their safety when in a red zone. They also provided useful and detailed information on each of the ranges sampled by identifying the highest impact area in each range.

Sample handling and treatment

Explosives are not volatile compounds and, therefore, no specific precautions (such as the use of sealed containers) have to be taken during sampling of media containing explosives. Composite soil samples (comprised of 20 to 30 randomly obtained increments) were collected. These bulk samples were stored in polyethylene bags. The biomass samples were stored in large commercially available polyethylene bags. The bags were labeled and immediately stored in coolers on ice, in the dark, to avoid the photodegradation of light-sensitive compounds. At the end of each day, the samples were transferred to a freezer. The use of polyethylene bags decreased the space needed for storing samples and reduced shipping costs. The samples were shipped frozen to DRDC Valcartier, who dried them in the dark for 24 hr, under a hood, then homogenized them by adding 50 ml of acetone and mixing the resulting slurry thoroughly. The dried and homogenized samples were sieved on a 25-mesh sieve and split into three subsamples. One set of samples was sent to CRREL for explosives analysis, another set was sent to RPC for metals analysis, and the remaining set was kept at DRDC Valcartier for explosives analysis. Biomass samples were collected in polyethylene bags, kept frozen in the dark, and sent directly to RPC laboratory for metals analysis. Digestions of the finely cut plant materials were done on all biomass samples for metals analysis. For explosives analysis, one biomass sample collected in a pond downgradient of a high impact area was lyophilised, extracted, and analyzed at DRDC Valcartier.

Sample labeling system

All of the collected samples were named according to the following five-part labeling system:

First part: Sample type

- S: Soils
- B: Biomass (Prairie Grass and other species)

Second part: Location by range

- AA: Anti-Armour Range
- AR: Argus Impact Area
- BG: Background samples collected outside of training area
- CGR: Castle Grenade Range
- GF: Greenfield Range
- H: Hersey Impact Area
- L: Lawfield Impact Area
- NCRGR: New Castle Rifle Grenade Range
- NCHGR: New Castle Hand Grenade Range
- WAT: Wellington Anti-Tank Rocket Range

Third part: Identification of the sample source

- Target number $(1, 2, \text{ and } 3)$
- Background location by GPS

• LS for linear sampling at XX percent of the range, where XX percent = percent of the overall range length

- FP (firing position), xm, x being the distance from the firing position
- Left, Mid, or Right when sampling only on these portion of ranges
- Core, when depth sampling was conducted with position specified

• Xm: In grenade range when only linear sampling was done perpendicular to the firing point, x being the distance from the firing point

• Crater: when sampling around or in craters with GPS position of the crater sampled

• HS: when hot spots were located on the range, followed by a GPS position

Fourth part: Identification of the sample

• A or B for the linear sample, A being in the eastern portion and B in the western portion from the middle of the range, starting point on the access road

• GPS position

Fifth part: Date of Collection

Range Description and Sampling Strategy

The surface sampling team collected 137 soil and 58 biomass samples in the following ranges: Anti-Armour range (AA), Old Castle Grenade range (CGR), New Castle Rifle and Hand Grenade ranges (NCRGR, NCHGR), Wellington Anti-Tank Rocket Range (WAT), Argus Impact Range (AR), and Lawfield, Hersey, and Greenfield impact areas (L, H, GF). These ranges were selected based on their intensive use by the troops and how they represented specific types of ranges. Later on, the small arms ranges were sampled by Jeff Lewis from DRDC Valcartier. Soils and biomass collected in these latter ranges were analyzed for metals only. The sample IDs, their GPS positions, and some pertinent information on each sample can be found in Tables 4-1 and 4-2.

Many sampling patterns were used in the present study, based on combined previous experiences and visual inspection, the presence or absence of targets, and the general settings of the ranges visited. In general, linear transects patterns (Figure 4-5) were used for the artillery ranges and large impact area. Circular sampling was used around targets (Figure 4-6), and linear sampling patterns were used for various distances from the firing position (Figure 4-7). Mostly surface soils (from 0 to 5 cm deep) were collected; however, some core samples were collected in specific areas of interest. The cores were collected with a manual corer designed by the CRREL team. The corer allowed easy sampling between 0 and 10 cm deep, with the possibility of discriminating at least three layers of subsamples (Figure 4-8).

Figure 4-5. Linear Transect Approach (A and B represent the half portion of the range for compositing)

Figure 4-6. Circular sampling around targets. Surface soil composite samples (30 increments) were collected around the target at 1 and 4 m

Figure 4-7. Linear sampling pattern used in firing position of AA range

Figure 4-8. Core sampling with manual augers

Background samples (BG)

Soil and biomass data were compared with accepted thresholds criteria for each of the specific analytes measured. When such criteria are either not available or not published, it is highly interesting to compare the results with mean results obtained on the largest amount of representative background samples. For this reason, 16 soils and 12 biomass samples were collected in a close distance outside the live-fire training area (in the dry zone, where no live firing is allowed). The limited number of representative background samples will not allow a statistically detailed comparison with actual live-fire range sample data. However, distinct trends would indicate the potential for metals to accumulate. Access roads were available in all directions around the training area, and it was relatively easy to drive and collect samples at regular intervals around the area. GPS positions of all samples are reported in Tables 4-1 and 4-2. The labeling was: S-BG-GPS position and B-BG-GPS position.

Anti-Armour Range (AA)

A total of 32 soil and 8 biomass samples were collected in the AA range. This range was used for 105- and 155-mm tank rounds toward three tank targets and also for the firing of smoke grenades. The AA range is in the northern part of the training area, approximately 1 km south of Shirley Road. It covers approximately 7 km^2 and is split in the middle by a trail that runs north to south. It is mainly flat and covered with prairie grass for the first 2 km from north to south with small hills in its southern portion (Figure 4-9). On the hilltops in the

southern portion are three target tanks located, respectively, at the following GPS positions: Target 1 (T1): 04673 76868, Target 2 (T2): 04519 76882, and Target 3 (T3): 04618 76204 (Figures 4-10 and 4-11). Firing position number 4 is located directly in the middle, at the northern entrance of the range at GPS position: 04805 78895. An Expray field test kit [21] was used to verify the content of a cracked 105-mm UXO found in the AA. The result was negative and the UXO was identified as inert (Figure 4-12).

Figure 4-9. Overview of the AA landscape with middle access road

Figure 4-10. Sampling near Target Tank 1, AA range

Figure 4-11. Surface sampling around Target Tank 2, AA range

Figure 4-12. Expray field testing on cracked UXO content, AA range

The following samples were collected:

a. Composite samples of surface soil and vegetation (20 increments each) were collected along linear transects (Figure 4-5) perpendicular to a center line at 20, 40, 70, and 100 percent of range, going from firing point to targets. Composite A included samples taken east of center; composite B included samples taken west of center. The labeling was S-AA-LS-x percent-A or B for soils and B-AA-LS-x percent-A or B for biomass.

b. Composite soil samples (30 increments) were collected at 1 m and 5 m around target tanks 1, 2, and 3 (Figure 4-6). The labeling was S-AA-Tx-Comp 1 or 5m.

c. Discrete soil cores were collected in front of targets T1 and T2, which appeared to have been the most used. One sample was collected 1.5 m in front of T1 and another 1 m in front of T2. Cores were split between 0-2 cm and 2-5 cm. The labeling was: S-AA-Tx-core-y cm front.

d. Two samples were collected around T3. Composite surface soil samples were collected at both 1- and 4-m distances from the target tank (Figure 4-6). The labeling was: S-AA-T3- 0-1, and 5m comp.

e. Composite soil samples (30 increments) were collected in front (avant/northern) and in the rear (arrière/southern) of the three targets. The labelling was S-AA-Tx-avant/arrière. The 30 subsamples were collected in a rectangular pattern of the same width as the target between 0 and 5 m from the target (Figure 4-13).

Figure 4-13. Sampling pattern in front and rear of targets, AA range. Surface soil composite samples (30 increments) were collected along a 5-m transect to the front and the rear of each of the three targets at AA range. Schematic diagram represents the sampling pattern for targets number 1 to 3 (T1 to T3)

f. A composite sample (20 increments) was collected in the dry drainage channel in front of target 2. The labeling was: S-AA-T2-runoff (Figure 4-14).

Figure 4-14. Dry runoff channel in front of Target 1, AA range

g. Composite samples (20 increments) were collected in 25-m-wide perpendicular lines at 0, 10, 20, 30, 40, 50, and 100 m from firing position 4 (Figure 4-7). The labeling was: S-AA-FP xm.

Wellington Anti-Tank Rocket Range

Eighteen soil samples and one biomass sample were collected in the Wellington Anti-Tank Rocket Range (WAT). The range is north of the Argus and Greenfield impact area and is approximately 5 km^2 . It is located in the northern part of the training area at the intersection of Shirley and Schanes Roads. The six target tanks (T1 to T6) on the range are at various distances from the firing position. Figure 4-15 illustrates the relative positions of the firing position and the target tanks. Targets 1 to 5 are respectively the nearest and the farthest from the firing position, while target 6 was on the other side of a small internal road within the range. Target 6 area was not sampled because of its lesser use by the troops. The WAT was covered with schrapnel and propellant residues (Figures 4-16 through 4-19).

Figure 4-15. Positions of Targets 1 through 5 at the WAT range. Surface soil concentrations of explosives and GPS coordinates are given for each target location and firing point

Figure 4-16. UXO schrapnel, WAT range

Figure 4-17. Target 5, WAT range

Figure 4-18. Target 1, WAT range

Figure 4-19. Sampling in front of Target 1, WAT range

The GPS positions of the five sampled targets (T) and firing position (F) were as follows:

- T1: 00998 77317
- T2: 01003 77311
- T3: 01042 77271
- T4: 01062 77245
- T5: 01084 77206
- FP: 00849 77364

The Expray field test kit was used on remains of material that appeared to be solid rocket fuel, found near targets 1 and 2. The test gave a positive response to the second reactive can, which is indicative of a double- or triple-based propellant.

The following samples were collected:

a. Composite surface soil samples (20 increments) were collected around five target tanks, at 1-4 m distance around targets (Figure 4-20). The labeling was: S-WAT-T1 to T5.

Figure 4-20. Sampling pattern around target tanks, WAT range. Surface soil composite samples (30 increments) were collected around the target at 1 and 3 m

b. Near-surface soil profile samples (at 0-2, 2-5, and 5-10 cm depths) were collected in front of T2. The labeling was S-WAT-depth (x-y).

c. At the firing point, composite surface soil samples were collected in front of and behind the firing position in a rectangular pattern of the same length as the firing line and with a width of approximately 2 m (Figure 4-21). The labeling was S-WAT-FP-Front or back.

d. Composite (10 increments) core samples were taken along transects at 10, 20, and 50 m from the firing position and soil between 0-2 and 2-5 cm were composited together (Figure 4-22). The labelling was S-WAT-FP-CORE- xm $(x-y)$.

Figure 4-22. Firing point core sampling, WAT range

e. One composite sample (30 increments) was collected in an OD pit adjacent to the firing range, used frequently for the OD of unexploded anti-tank rounds. This sample was labelled S-WAT- OD pit.

f. One composite biomass sample (30 increments) was collected in a circular pattern at 1 and 5 m from targets 1 and 2.

Old Castle Grenade Range

Seven soil and four biomass samples were collected in Old Castle Grenade range. The range was decommissioned 2 months before the sampling campaign. In the past, the range was used for both the firing of 40-mm rifle grenades and hand grenades. The surface of the range was graded after decommissioning and, therefore, the soil profiles were disturbed. It was decided, based on previous studies conducted both in Canada and the United States on similar ranges [2,3], to sample the range. For any further need, the GPS position of the middle of the old range was recorded as: 02761 79732.

The following samples were collected:

a. Three composite surface soil and biomass samples were collected within the impact area at the left, in the middle, and at the right-hand side of the range when facing it. The labeling was S-or B-CGR-left, mid, or right.

b. Six core samples were taken, compositing the sections between 0-2, 2-5, and 5-20 cm depths on the right side of the range where debris was found. The labeling was S-CGR-core x-y cm.

New Castle Rifle Grenade Range (NCRGR)

Two soil and one biomass samples were collected in NCRGR. This range had not been made operational as of this date. No hand grenades had even been used on the range; only 40-mm rifle grenades. In the past, this portion of land was part of the ricochet area of the Argus Impact Range (artillery). The NCRGR range is located at the entrance to the training area, north of AR. The soil behind the two wooden targets was sampled. The GPS positions of the two targets are 0178 7669 (T1) and 0221 76678 (T2).

The following samples were collected:

a. Two composite surface soil samples (20 increments) were collected behind targets. The labeling was S-NCRGR-T1 or T2 back.

b. One composite biomass sample (20 increments) was collected behind T1. The labeling was B-NCRGR-T1.

New Castle Hand Grenade Range (NCHGR)

Six soil and four biomass samples were collected in the NCHGR range. This range has been in operation for only 9 months. No rifle grenades have even been fired on the range, only hand grenades. Six soils were sampled following a pattern illustrated in Figure 4-23 by sampling linearly, parallel to the front wall of a recently built bunker at distances of 10, 20, 30, 40, and 50 m. Four biomass samples were collected including a field duplicate on the right and left side of the range when facing it, and in the rear of the range.

Figure 4-23. Linear sampling, NCHGR

The following samples were collected:

a. Composite surface soil (30 increments) in lines parallel to the bunker. The labeling was S-NCHGR-xM.

b. Composite vegetation samples (20 increments) were collected within the impact area. The labeling was B-NCHGR-Rear, Front, or LeFort

Hersey Impact Area

Fifteen soil and fourteen biomass samples were collected in the Hersey Impact Area, which is an artillery range used mostly in conjunction with Lawfield Impact Area for high explosives (HE) and illuminating rounds. It covers approximately 19 km^2 and is located northeast of the training area. A dirt road (Hersey Road) runs through its middle from northeast to southwest. It is relatively flat and highly covered with prairie grass and many craters from past detonation events. The sampling team chose to use the linear transect approach (Figure 4-5) for this huge range and chose the Hersey Road as the middle point of the transects. GPS positions were calculated to locate the 40-, 60-, 80-, and 100-percent transects. Moreover, the sampling team decided to sample in transects while sampling preferentially in and around craters in the transects. This technique was decided upon due to the high number of visible craters in all transects. This sampling approach would be considered new as it combined both the composite transect pattern and many discrete crater sampling in the same transect. The presence of a thick layer of prairie grass mandated the use of the manual auger tool for all sampling. After samples were collected in craters, the first layer of grass was removed to uncover the first centimeter of soils that were successfully collected. Various field duplicates were also collected.

The following samples were collected:

a. Composite surface soil and vegetation samples (20 increments) were collected along linear transects in and around craters on either side of Hersey Road at approximately 500-m distances downrange from the center line. Note: Several craters had an area that was covered with a whitish substance. The A subsamples were located east of Hersey Road, while the B samples were located west of Hersey Road. The labeling was S-H-x percent A or B and B-H-x percent A or B.

b. A very fresh crater area located at GPS position 08721 73805 was composite sampled (20 increments) with a circular pattern within a radius of 0- 5 m from the center of the crater. The labeling was: S-HS-GPS position.

Lawfield Impact Area

Nineteen soil and nine biomass samples were collected at Lawfield Impact Area, which covers approximately 12 km^2 and is located southeast of the Hersey Impact Area. A dirt road runs through it from west to east (Argus East Road). The sampling strategy selected for Lawfield was the preferential sampling of craters without the linear transect approach, except for the 25-percent transect. The 25-percent transect compared the results acquired in Lawfield with those from Hersey to refine the global approach. Results could lead to future directions in sampling artillery ranges (linear transects versus discrete locations at craters).

The following samples were collected:

a. Several composite surface soil and vegetation samples were collected around impact crater clusters (2-4) in the middle of the range. Note: Several UXOs and large pieces of casing were present on the surface and samples were collected around these potential contamination sources (Figures 4-24 and 4-25). The labeling was: S-or B-LS-HS-GPS position.

Figure 4-24. Hot spot sampled, Lawfield Impact Area, GPS location: 14016E 69427N, 105-mm artillery projectile

Figure 4-25. Hot spot sampled, Lawfield Impact Area, GPS location: 13973E 69357N, 155-mm artillery projectile

b. Cores were also taken in the middle of two fresh impact craters, separating 0- to 2-, 2- to 5-, and 2- to 10-cm increments. The labeling was S or B-L-25 percent A or B, A being north of the centerline; B south of the centerline.

c. Composite surface soil and vegetation (20 increments) samples were collected along linear transects on either side of the centerline at 25 percent of range. Note: Numerous impact craters were present at this distance; however, none appeared to be fresh.

Argus Impact Area (AR)

In Argus Wood, 18 soil samples and 1 biomass sample were collected. The AR is an HE live-fire range heavily used by artillery. Troops fire many types of rounds including: 66- and 84-mm rockets, simulated anti-tank mines, 60- and 81 mm mortar, 105- and 155-mm artillery projectiles, 500-lb bombs, white phosphorus munitions, 40-mm rifle grenades, C4 blocks (70-lb blocks for demolition trials), smoke rounds, M203 grenades, Trigran for creating craters (a cratering explosive based on granulated Tritonal (80 percent TNT, 20 percent aluminium), 2.75-in. rockets, and ADATS and TOW missiles. Two weeks prior to the sampling campaign, a major exercise named "Staunch Gladiator" was conducted on AR. This exercise involved the firing of all the types of munitions listed earlier in this paragraph. This exercise is an annual event in which live firing is conducted for a civilian and military audience to demonstrate the firing capabilities of the troops.

The range covers approximately 11 km^2 with many dirt roads that run through it in all directions to provide access to the various target areas. At the entrance to the range is a company defense position, which is an elevated area on which the main firing points are to be found. The two EOD staff personnel dedicated to the surface sampling team explained in great detail the Staunch Gladiator exercise and guided the team exactly to all target and crater locations for sampling. In the northern part of the range, all targets and craters formed by the use of C4 or Trigran were sampled (Figure 4-26). At the south end of the range, in a heavily cratered area located on the top of a small hill, various locations in and around the craters were sampled. One crater (crater $#4$) was of particular interest because it contained reddish water and a large piece of whitegrey residue, which suggested a low-order detonation of a 500-lb bomb (Figure 4-27). The grey-white solid gave a positive test for TNT with the Expray field test kit. The crater surface water was also sampled to verify if the reddish color was due to the presence of photo-degraded TNT.

Figure 4-26. Fresh Trigran crater, Argus Impact Area

Figure 4-27. Low-order crater, Arugs Impact Area (red coloration of water was indicative of TNT contamination)

A biomass sample was collected in a pond downgradient of the cratered area (Figure 4-28). This pond was formed by many rivulets coming from the cratered area. The biomass sample was analyzed for energetic materials.

Figure 4-28. Biomass collection, pond downgradient of a highly cratered area, Argus Impact Area

The following samples were collected:

a. Composite surface soil sample (20 increments) was collected inside and around the rim of a large impact crater created by the use of C4 and Trigran. The labeling was S-AR-Crater in and out.

b. A composite surface soil sample (20 increments) was taken in front and to the left of two cement block targets labeled T1 and T3. The labeling was S-AR-Tx-front or leFort.

c. A composite surface soil sample (20 increments) was taken in front of a target tank. Pieces of propellant were visible on the surface. The labeling was S-AR-T2- front.

d. Circular composite surface soil samples were taken around three 500-lb bomb craters at radii of 1, 2, and 5 m from the center of the crater (Figure 4-29). One sample was also collected within 0-1 m of the center of the crater when possible (if no standing water was in the crater). This was labeled "around." Crater 4 had standing water that was a red-orange color. A 2- to 4-lb piece of light grey material in the crater gave a positive response to the 1st Expray reagent, suggesting the presence of TNT. In addition, several large fragments of the 500-lb shell were present in and around Crater 4. This crater was believed to be from the partial detonation of a 500-lb bomb. The labeling was S-AR-crater 1 to 4, 1, 2, or 5 m or around).

Figure 4-29. Circular sampling pattern used around crater, Argus Impact Area. A composite sample (30 increments) was collected around each crater at each distance indicated

e. Samples were collected around two 2.75-in. rocket craters (5 and 6). The labeling was S-AR-crater 5 or 6 and GPS position.

f. Biomass was sampled for explosives analyses in a pond downgradient of the cratered area. The labeling was B-AR-GPS position.

Greenfield Impact Area

Four soil and four biomass samples were collected in Greenfield Impact Area, which is located south of the Anti-Armour Range, between Hersey and Argus Impact Areas. Greenfield is considered by military personnel as a "ricochet" zone, or bouncing zone for Argus, Hersey, and AA ranges. Greenfield covers approximately 12 km^2 and is highly grass-, bush-, and tree-covered. No trails cross the range; therefore, use of a vehicle within the range, even an allwheel-drive vehicle, is problematic. Sampling was limited to a total of four soil samples and four biomass samples in the two accessible transects, based on the limited use of the range for direct firing, on the absence of targets, and on the high vegetation present on the range. Only the 40- and 60-percent transects were

sampled, the 40-percent transect being near the north-south road coming from the AA range at a GPS position of 04650 75199. The GPS position of the 60 percent transect was 05498 74504. Composite A samples were collected south of the mid-section, while B samples were collected north.

The following samples were collected:

a. Composite surface soil and vegetation samples (20 increments) were collected along linear transects on either side of center line at 40 percent and 60 percent of range, going from firing point to targets. The labelling was: S or B-GR-LS-x percent A or B.

Small Arms Ranges and Burning Area

Small Arms Ranges. To verify their potential contamination by heavy metals, three representative small arms ranges were sampled according to a sampling pattern previously used in the Shilo training area [2,3]**.** The ranges were located in the same area and were named Batouche, Reichwald, and Vimy. Batouche and Vimy ranges presented 12 targets, while Reichwald presented 20. Composite surface soil samples were collected by combining subsamples collected in front of three targets. Some subsurface soils were also collected from 10 to 40 cm deep with the help of a manual auger to verify the vertical profile of contamination. The following samples were collected:

a. Five samples were collected in Batouche in front of targets 1 to 4, 5 to 8, 9 to 12; one duplicate and one deeper sample were collected in front of target 12 (Figure 4-30). The labeling was S-Batouche x-y or S-Batouche 12-Depth.

Figure 4-30. Sampling pattern, Batouche and Vimy Small Arms Ranges

b. Six samples were collected in Reichwald in front of targets 1 to 4, 5 to 8, 9 to 12, 13 to 16, and 17 to 20, and one depth sample was collected in front of target 1 (Figure 4-31). The labeling was s-Reichwald-x-y or S-Reichwald-1- Depth.

Figure 4-31. Sampling pattern, Reichwald Small Arms Range

c. Four samples were collected in Vimy in front of targets 1 to 4, 5 to 8, and 9 to 12. One depth sample was collected in front of target 1 (Figure 4-30). The labeling was S-Vimy x-y and S-Vimy-1 depth.

Burning Area. A decision was recently made at Gagetown training area to bring excess artillery propellant to two centralized locations for burning as opposed to burning in the field wherever the artillery guns happened to be firing. This decision was made to better control the burn procedure. Therefore, burn pads of concrete approximately 20-cm thick were installed at each burn location in order to prevent the burned residues from contaminating the soil. The burn pads are rough slabs approximately 2 m x 2 m located in the middle of a large flat area cleared of vegetation. The two burning pads and the surrounding areas were sampled to verify the localized impact of this activity. The two locations were identified as Airstrip-2 and Lawfield.

At both locations, despite the presence of the concrete pad, large amounts of propellant had obviously been burned on the adjacent ground. These burn marks were clearly evident visually as scorched and blackened strips approximately 30 cm wide by 3 to 5 m long, directly on the soil. The preference for burning excess propellant is to lay it out in long narrow piles of these dimensions, which the concrete pad cannot accommodate. Use of the pad greatly increases the amount of time required to dispose of the propellant as only relatively small amounts can be burned at any one time on the pads. This accounts for the propellant being burned on the ground very close to the burn pad. The burn marks were sampled by making a composite of a dozen discrete surface soil samples taken along the length of the burn mark. Almost every burn mark had small amounts of unburned propellant along its outer extremity. Some of this propellant was included in the composite sample.

The burn pads themselves were blackened and had clearly been used for their intended purpose. The concrete, being very rough and porous, could not be methodically sampled. Instead, the soil immediately beside the pads was sampled, in the water run-off channels caused by rain. The samples were composites of at least a dozen increments each.

Results and Discussion – Energetic Materials

Results of sample analyses by DRDC-Valcartier and CRREL were in excellent agreement. Plots of DRDC versus CRREL concentrations for HMX (Figure 4-32), RDX (Figure 4-33), and TNT (Figure 4-34) by GC-ECD, and TNT

(Figure 4-35) by HPLC are presented in Figures 4-32 to 4-35. Both CRREL and DRDC-Valcartier used either HPLC 8330 or GC 8095 methods depending on the concentrations detected for energetic materials.

Analysis for NG was conducted at CRREL only. Instead of complicating the discussion with results from both laboratories, the results from the analysis at CRREL will be presented in the text. Values from both laboratories are given in Tables 4-3 aa through kk.

Figure 4-32. Comparison of HMX concentrations determined by DRDC and CRREL using GC-ECD analysis

Figure 4-33. Comparison of RDX concentrations determined by DRDC and CRREL using GC-ECD analysis

Figure 4-34. Comparison of TNT concentrations determined by DRDC and CRREL using GC-ECD analysis

Figure 4-35. Comparison of TNT concentrations determined by DRDC and CRREL using HPLC analysis

Background samples

The results from analysis of the 16 BG soil samples are presented in Table 4-3 aa. TNT was detected in all 16 samples with concentrations ranging from 10.6 to 2,410 µg/kg. This result was totally unexpected and might indicate that either the areas chosen to collect these samples had been impacted by livefire activity, which is highly unlikely considering the remote locations chosen for BG sampling, or that TNT was cross-contaminated when samples were processed. Another possible explanation could be that there is a chromatographic interference that we were unable to separate from TNT. The possibility of interference is remote, however, because HPLC analysis also indicated the presence of TNT in some of these sample extracts. The two transformation products of TNT (2ADNT and 4ADNT) were detected in only one of these BG samples. In past studies, these transformation products were almost always present in samples where TNT was detected. If cross-contamination occurred during sample processing, no microbiological processes would be expected to take place because the soils were air dried at this point. Additional sampling at Gagetown was conducted in the fall of 2003 and the problem associated with TNT in these samples was investigated to resolve this issue.

Other target analytes were largely below detection limits for these BG soils, although NG was detected in one sample, 2,4-DNT in one sample, RDX in three samples (concentrations at or below 5 µg/kg), 2ADNT and 4ADNT in one sample, and HMX in one sample. If cross-contamination of TNT occurred for these samples, it apparently did not affect the other target analytes.

Because of the concern for TNT in the samples collected at Gagetown and a potential overestimation due to a co-elution interference, the reporting limit for TNT was raised to 100 µg/kg and values obtained below this value will be reported as <d for all data sets except the BG samples.

Anti-Armour Range

The results from the analysis of soil samples from the Gagetown AA range are presented in Table 4-3 bb. At the AA range, samples were collected at the firing point, at various distances downrange between the firing point and the targets, and at several tank targets within the impact area. The munitions fired at this range are predominantly 105- and 155-mm rounds.

At the firing point, concentrations of NG and 2,4-DNT were detected in all surface soil samples collected from the firing line out to 100 m from the firing line (Figure 4-7). For NG, the concentrations varied from 7,540 µg/kg at a distance of 10 m from the firing line to 210 μ g/kg, 40 m from the firing line. At 100 m, the concentration of NG was 624 µg/kg. For 2,4-DNT, concentrations declined from 4,520 at a distance of 20 m from the firing line to 14.2 μ g/kg 100 m from the firing line. The presence of 2, 4-DNT in these samples is consistent with firing point sampling for areas where 105-mm howitzers are fired using single-based propellant in which 2,4-DNT is present [22]. The presence of NG is due to the firing of the 155-mm rounds that use triple-based propellant containing NG. The locations and concentrations of NG and 2, 4-DNT at the Gagetown AA range firing area are similar to that found at the Yakima (Washington) Training Center Multipurpose Range Complex, where 120-mm tank guns are fired [23-27].

Results from the linear transect composites collected at various distances between the firing point and impact area also showed detectable concentrations of NG and 2,4-DNT. Except for NG, concentrations were generally below

100 μ g/kg. The concentrations of NG in these samples ranged from 24.7 μ g/kg at 70 percent of the distance downrange to 1,850 µg/kg, 20 percent downrange.

At the impact area, samples were collected around three tank targets. At target 1, RDX (58.6 µg/kg) was detected in the surface composite sample collected at distances of 1 m around the target, and TNT (37 µg/kg) was detected in the composite collected 5 m around the target. A much higher concentration of TNT (4,620 µg/kg) was detected in a discrete core sample (0-2-cm depth) collected 1 m from the target. At the 2- to 5-cm depth, the concentration of TNT was reduced to below the 100-ug/kg reporting limit.

At target 2, concentrations of RDX, HMX, and NG were detected in the 1-m surface composite at concentrations of 280, 166, and 28 μ g/kg, respectively. At 5 m, the concentration of RDX was 31 µg/kg, NG was 20 µg/kg, and the other analytes were below a reporting limit of 10 µg/kg. RDX was also detected in a surface composite collected in front of the tank target.

For the third target, the concentrations of RDX in the surface composite samples collected around the target were much higher than at the other two targets. Concentrations of RDX around the target at distances of 1 m and 5 m were 1,380 and 308 µg/kg, respectively. The concentration of RDX in the surface composite collected 1 m in front and back of the target were 4,220 and 112 µg/kg. Likewise, the HMX concentration in the two composites collected around the target were 320 and 44 µg/kg, respectively. The transformation products of TNT (2ADNT and 4ADNT) were not detected in any of these samples.

The concentrations of RDX and HMX near target 3 were much higher than observed previously near artillery targets at Camp Guernsey, WY and Fort Bliss, TX [23] or around artillery craters at Fort Lewis, WA [22] where 105-and 155-mm howitzers were fired. Because the concentrations of RDX and HMX were greater than TNT for these Gagetown samples, these residues are probably from 105-mm rounds that contain composition B, or from blow-in-place detonations of duds using C4, rather than TNT-filled 155-mm rounds. The reason for the much greater concentrations detected for target 3 compared to targets 1 and 2 is uncertain, but may be a reflection of the occurrence of a low-order (partial) detonation near target 3 at some time in the past.

Wellington Anti-Tank Rocket Range

Analytical results for soil samples collected at the WAT Rocket Range and analyzed at DRDC-Valcartier (RDDC) and CRREL are presented in Table 4-3 cc. NG was a target analyte for the analyses conducted at CRREL only.

At the firing point, concentrations of NG exceeded all other energetic compounds by several orders of magnitude. Values in the surface soil (0-2 cm) ranged from $424,000 \mu$ g/kg (ppb) 10 m in front of the firing line, to 14,100 μ g/kg at 50 m from the firing line (Figure 4-21). Because the antitank rockets used at this range (66-mm M72 LAW rocket) create a back blast, the NG concentration in the soil sample collected behind the firing line was enormous

 $(11,300,000 \mu g/kg)$ or 1.13 percent). Assuming that the NG in this sample is imbibed within a nitrocellulose (NC) matrix, the concentration of NC in the surface soil must be 3-5 percent. No analyses for NC were conducted with these samples since this polymeric material is particularly difficult to extract and quantify in a soil matrix.

The NG concentrations in the surface soil at Gagetown are much higher than found for surface soils at antitank firing ranges at the Yakima Training Center and Fort Bliss [23]. The results are similar, however, to samples collected at an antitank rocket range at Schofield Barracks, HI (Hewitt et al. in press). At Yakima, the highest NG concentration 5-10 m in front of the firing line was 3,600 µg/kg, and at Fort Bliss the highest concentrations in front and behind the firing line were 1,600 and 1,100 µg/kg, respectively. At Scholfield, NG concentrations behind the firing point were as high as 1,390,000µ g/kg [25]. Visually, the WAT Rocket Range appeared to be used to a much greater extent than those at Yakima and Fort Bliss, and it is this more intense usage that undoubtedly accounts for the higher concentrations observed here. At Scholfield, mostly subcaliber practice rounds are fired, thus the level of activity cannot be judged based on debris at the impact area. Thus it is difficult to visually assess the level of activity at the Scholfield range.

NG concentrations at the depth interval of 2-5 cm below ground surface were also determined at 10, 20, and 50 m in front of the firing line at the Wellington Anti-Tank Rocket Range (Figure 4-21). The concentrations ranged from 34,000 µg/kg at the 10-m location to 2,300 µg/kg at the 50-m location. The concentrations for these three shallow subsurface samples were about one order of magnitude lower than the surface samples collected at a 0- to 2-cm depth. No subsurface samples were collected at the firing point at Fort Bliss or at Yakima Training Center.

The relatively high NG concentrations in the shallow subsurface at WAT are surprising because the half-life of NG in soil has been estimated in previous experiments to be less than 1 day [26]. This half-life estimate refers to NG in equilibrium between soil moisture and sorption sites on the soil, but the NG present in the soil at Gagetown is probably still imbibed within an NC matrix and thus not subject to the degradative processes within the soil. Future studies at antitank ranges should collect deeper subsurface samples to see if the NG is penetrating into the soil profile. To the authors' knowledge, however, NG has not been reported in groundwater samples collected at training ranges in Canada or the United States.

Firing point samples at WAT also contained TNT, and occasionally HMX, but concentrations were much lower than for NG. The presence of TNT in firing point soil samples was unexpected; none was found in any of the soil samples from firing points at Yakima, Fort Bliss, or Schofield Barracks. In addition, the two transformation products of TNT were not detected in these samples. Thus these results, while higher than the elevated reporting limit for TNT, appear suspicious and more sampling will be conducted to attempt to verify these data.

The concentrations of HMX far exceeded those of any other energetic compound for samples from the impact area at the WAT Rocket Range.

Concentrations of HMX in surface soils (0-2 cm) collected around five tank targets ranged from 74,200 to 1,290,000 µg/kg (Figure 4-14). HMX accounts for 70 percent of the high explosive in octol, the explosive composition used in 66-mm M72 LAW rockets, which is the major munition fired at this range. The concentrations of TNT in these samples are generally about two orders of magnitude lower than HMX with values ranging from 330 to $22,800 \mu g/kg$. TNT is present in octol at 30 percent, but it has very different fate and transport properties that account for the much lower concentrations found relative to HMX. The two major transformation products of TNT (2-ADNT and 4-ADNT) were also found in surface soils in these samples. Concentrations ranged from 104 to 1,980 µg/kg and were always much lower than for TNT. Concentrations of RDX in soil samples from the impact range were even lower than for TNT. The maximum concentration of RDX in surface soil samples was 2,280 μ g/kg.

Concentrations obtained for surface soils near targets at antitank impact areas at the Arnhem range at Valcartier [17,18]and Fort Ord, CA [27] are in excellent agreement with the results at Gagetown. Concentrations of HMX are in the hundreds to low thousands of mg/kg (ppm) and the ratio of HMX to TNT is generally about 1:100. For samples collected at Yakima, the HMX concentrations were generally about an order of magnitude lower, but the ratio of HMX to TNT was similar to that found for antitank ranges at Gagetown, Valcartier, and Fort Ord.

The concentration of HMX in shallow subsurface soils was obtained for only one core sample at Gagetown. The concentrations were 846,000 gµ/kg for the 0 to 2-cm depth, $1,130,000 \mu g/kg$ for the 2- to 5-cm depth, and 932,000 g μ/kg for the 5- to 10-cm depth. The concentrations of TNT in these samples were 2,420 µg/kg for the 0- to 2-cm sample, 13,800 μg/kg for the 2- to 5-cm sample, and 9,300 µg/kg for the 5- to 10-cm sample. HMX and TNT seem to occur deeper in the soil profile at the Gagetown site than elsewhere [29]. Additional core samples to greater depths should be obtained to confirm this finding.

NG was also found in surface soils around these tank targets at concentrations ranging from 9,700 to 42,800 µg/kg. NG is present in the propellant for M72 LAW rockets and these rockets are propelled all the way to the target, unlike artillery rounds. Thus, all of the NG in these rockets is not expended when impact occurs. The presence of NG near the targets is, therefore, not unexpected. NG was also found in shallow subsurface samples at concentrations of 20, 400, 15,000, and 43,600 µg/kg for the 0- to 2-cm, 2- to 5-cm, and 5- to 10-cm samples, respectively. As found at the firing point, the penetration of NG into the soil profile was unexpected. Mixing of the soil profile from the explosions could account for this. More samples should be collected to verify this result.

Old Castle Grenade Range

The results for the soil samples collected at the Old Castle Grenade Range are presented in Table 4-3 dd. This range had been used for both hand grenades and rifle grenades, but had been closed and the surface soil had been graded
2 months prior to sampling. RDX was detected in all four surface composite samples at this range, and in the core samples as well. TNT was detected in several surface samples and in two subsurface samples as well. The concentration in the sample collected at the 2- to 5-cm depth was higher than at the surface probably because the soil had been graded prior to sampling, redistributing the residues. 2ADNT and 4ADNT were detected in the subsurface samples, as well, supporting the presence of TNT in these samples.

RDX was also detected in all of the samples collected from this range. Concentrations varied from 15 to 364 µg/kg. In the samples from the soil core, the highest concentration of RDX was found at the deepest depth (5-10 cm) and the lowest at the surface, again demonstrating that the soil had been reworked or that RDX leached through the soil profile. The only other residues detected in these samples were HMX, 2ADNT, and 4ADNT with concentrations generally less than 50 μ g/kg.

The residues detected at this range are indicative of the type of explosives used in hand grenades and 40-mm rifle grenades, namely Composition B. This formulation is composed of RDX/TNT at a ratio of 60/40. HMX is an impurity in RDX and tends to remain at the surface, relative to RDX, due to its lower solubility in water. The concentrations found at this range were generally lower than found for grenade ranges at Fort Lewis or Fort Richardson, AK, probably due to range closure and the soil grading that occurred. The distribution of residues at this range will be unpredictable because of the uncertainty of how the soils were moved during the grading process.

New Castle Rifle Grenade Range

Only two surface composite soil samples were collected at the New Castle 40-mm range. NG, 2,4-DNT, and TNT were detected in these samples; the concentrations ranged from 87 to 222 μ g/kg (Table 4-3 ee). The presence of both NG and 2,4-DNT was unexpected in the impact area because these two compounds are generally associated with propellants and not often found at impact areas in concentrations greater than those compounds associated with detonations. The TNT that was found is present in the 40-mm grenades, and it was not surprising to find it in the target area. The relatively low concentrations found at this range are probably due to the fact that it has only been in use for nine months and it is possible that no low-order hand grenade detonations occurred during this period.

New Castle Hand Grenade Range

The results from the linear surface composite samples are presented in Table 4-3 ff. Like the 40-mm range, this range has been in use for only 9 months and the concentrations of compounds present in the surface soil were quite low. M67 hand grenades contain Composition B and detectable concentrations of TNT and RDX were expected. RDX was detected in one sample analyzed at RDDC and HMX was detected at about 25 μ g/kg in the samples collected 50 m from the throwing area.

The concentrations of residues from Composition B were much lower at this range than at other hand grenade ranges sampled [22]. This is probably because this range is new and may not have had any low-order detonations. Only very low concentrations of residues result from high-order detonations of hand grenades [25].

Like the 40-mm range, however, concentrations of NG and 2,4-DNT were found in most of the soil samples collected at this range. For NG and 2,4-DNT, concentrations ranged from 43 to 200 μ g/kg, and from 6 to 61 μ g/kg, respectively. These compounds are normally found on ranges due to their use in various types of propellant formulations. Since no propellants were used at this range, the reason for their presence is unknown. Whether this site had been used for other purposes prior to being converted to a hand grenade range is unknown, but seems a likely possibility. Both NCRGR and NCHGR were included in the past in the rebounding area of Argus Impact Area. This would likely explain the presence of NG and 2-4 DNT.

Hersey Impact Area

The results for the soil samples collected at the Hersey range are presented in Table 4-3 gg. All but one of these samples were linear surface composites collected to the east and west of the road that runs down the length of the range. One sample had an NG concentration of 466 µg/kg and several had barely detectable levels of 2,4-DNT, but the compound found in the most samples was RDX. However, the highest concentration of RDX was only 22 μ g/kg. A few samples also had detectable concentrations of TNT and its transformation byproducts 2ADNT and 4ADNT. The detection of both TNT and RDX at low levels in these samples is indicative of the impacts of Composition B rounds (possibly 105 mm) at this range.

The concentrations of RDX residues obtained for samples from the Hersey range were below 25 µg/kg, indicating that the potential for RDX groundwater contamination from this area is very small. This agrees with most of the samples collected at artillery ranges where concentrations are in the low µg/kg range except near areas contaminated from low-order detonations [24].

Lawfield Impact Area

Concentrations of energetic compounds for soil samples from the Lawfield range were generally higher than for the Hersey range (Table 4-3 hh). The transect sample, collected from 25 percent of the downrange distance to the south of the centerline, had a TNT concentration of 426 µg/kg. Concentrations of 2,4-DNT, NG, 2ADNT, and 4ADNT were also detected in this sample, but at much lower concentrations.

Residues of energetic materials were also found near five cratered areas in the Lawfield range. For the first crater area, samples were collected at three depths below surface. For the 0- to 2-cm sample, concentrations of RDX and NG were detectable at 9.1 and 30.6 µg/kg, respectively. NG was not detectable in the samples from 2-5 cm and 5-10 cm, but RDX was detected at 10.7 and 5.6 μ g/kg, respectively, due to its greater mobility in soil.

Similar results were obtained for surface samples collected in a runoff area below a cratered area; NG was detected at $37 \mu g/kg$ and RDX at 11.3 $\mu g/kg$. 2,4-DNT was also detected at 31 μ g/kg in this sample.

Much higher TNT concentrations were found for composites collected inside a relatively new crater. The highest TNT concentration was 920 µg/kg, but this sample had no detectable RDX, 2ADNT, or 4ADNT, indicating that this area was recently contaminated by TNT rounds. Other samples in this area had detectable concentrations of TNT, RDX, 2ADNT, and 4ADNT with maximum values of 332, 140, 76.7, and 83.4 µg/kg, respectively. These areas were likely contaminated at an earlier date with residues from a round filled with Composition B.

Depth samples were also collected within another crater. In these samples, RDX was detected at 114, 23.2, and 10.3 μ g/kg for samples collected at 0-2, 2-5, and 5-10 cm, respectively. Concentrations of 2ADNT (11.5 µg/kg) and 4ADNT (10.4 µg/kg) were detected in the surface sample, but concentrations were below detection for the deeper samples.

In the final crater samples from Lawfield, TNT and RDX were again detected at maximum concentrations of 612 and 132 µg/kg, respectively. Overall, the concentrations of explosives residues within the Lawfield range are somewhat higher than found at other artillery ranges including Fort Lewis [22], Yakima Training Center [22], or other ranges at the Gagetown training area.

Finally, two samples were collected next to 105-mm UXO rounds at Lawfield. For one round, the sample contained an RDX concentration of 20.8 µg/kg, but we are unable to say whether this low RDX concentration was from the UXO round or from another source on the range. The lack of detectable TNT, 2ADNT, and 4ADNT implies that the contamination is not from recent leakage from a Composition B-filled 105-mm round.

Argus Impact Area

As mentioned earlier, the Argus Impact area had been the site for a major live-fire exercise 2 weeks before the sampling campaign. As a result of this and other firing events, TNT was detected in most samples collected from this range (Table 4-3 ii). RDX, on the other hand, was detectable only at a significant concentration in one sample, indicating that the most contaminating rounds fired at Argus are TNT-containing ordnance. Except for two samples collected near crater 2, concentrations of 2ADNT and 4ADNT were below detection limits, indicating that the TNT concentration found on this range must be relatively fresh or a greater portion would have transformed into these by-products.

The concentrations of TNT in surface soil samples around two targets and in a large open demolition crater were generally about 100 µg/kg. The concentrations around several bomb craters (craters 2-4), however, were much

greater, ranging from 17,600 to 4,220,00 µg/kg. As mentioned earlier, the standing water that had collected in crater 4 was reddish-orange in color, probably due to phototransformation of TNT. Upon analysis, the concentration of TNT in water collected from this crater was about $20,000 \mu g/L$.

Overall, the TNT concentrations in surface composite samples from the area around crater 4 averaged about 3,000,000 µg/kg, an order of magnitude greater than samples collected around crater 2, which had concentrations about an order of magnitude greater than the area around crater 3. Apparently, these bombs did not undergo a complete detonation, leaving substantial residues in and around the bomb craters.

Soil samples were also collected around two 2.75-inch rocket craters (craters 5 and 6). The concentration of TNT in one of these surface samples was 596 µg/kg. HMX was also detected in these two samples at 37.4 and 39.0 µg/kg, but RDX was below 5 μ g/kg in both samples.

Overall the concentrations of explosives residues at the Argus range are much higher than normally found on artillery ranges. The higher concentrations were generally for TNT and may be related to the use of this range for bombing as well as artillery when large combined fire exercises are conducted at Gagetown. With respect to the potential for groundwater contamination, RDX is the major compound of concern due to its much greater tendency to leach and its low regulatory limit in drinking water. The RDX concentrations for most of the samples from this range were below detection and hence no major groundwater contamination source for RDX was identified.

Greenfield Impact Area

Analyses of soil samples from the Greenfield range are presented in Table 4-3 jj. As pointed out above, the Greenfield range is located between the Hersey and Argus Impact Areas and serves as a "ricochet" range for rounds fired at the Hersey, Argus, and AA ranges.

Linear composite soil samples at 40 and 60 percent were analyzed. One sample had a TNT concentration of 134 µg/kg. RDX was detected in several of these samples, but concentrations were 25 µg/kg or below. HMX, NG, and 2,4- DNT were detected in one or more of these samples, but concentrations were generally below 60 µg/kg.

Burning Area

The results of analysis of samples collected at several burning areas are given in Table 4-3 kk. 2,4-DNT was detected in all of these samples with concentrations ranging from 148 to $31,600 \mu g/kg$. Apparently the majority of the burning activity was for single-based propellant bags. Other target analytes detected in these samples were 2,6-DNT, TNT, RDX, and tetryl. No NG was detected in any of these samples. This was the only set of samples collected at Gagetown in which tetryl was detected. It should be emphasized that several of

these samples contained visible amounts of unburned propellant, left over from the destruction process.

Results and Discussion – Metals

Background samples

Background soil and biomass samples were collected in order to assess the extent of the anthropogenic contribution of metals to the training ranges. For biomass, no guidelines are published in relation to metals contamination, so results are compared to the mean background (MBG). For soils, MBG is still considered as a good comparison tool, but the Canadian Council of Ministers of Environment (CCME) provides quality guidelines for agricultural soils (ASQG), which is the base of comparison for the results. All results discussed in the following section are presented in Table 4-4 for both soil and biomass.

Biomass background samples. Thirteen biomass BG samples were collected at various locations. One of those, identified by B-BG-17385-70972, was duplicated. The following parameters were analyzed in the biomass: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Te, Tl, U, V and Zn. The MBG level was calculated by adding the average concentration of the samples to twice the standard deviation, which ensures that results higher than the MBG are statistically relevant. In the BG samples, 21 values slightly exceeded the MBG, so those values contributed to an increase in the MBG level. The values are highlighted in red in the table. It is interesting to note that 10 out of those 21 values were found in the same sample, which is B-BG-03678-79720. This particular sample was collected downwind of the Old Castle grenade range, which may explain the higher levels encountered. However, the soil sample collected in the same area did not show any higher trends.

Soil BG samples. Fourteen soil samples, four of them duplicated, were collected at various locations around the training area and in almost the same locations as the biomass samples. The parameters analyzed for soil samples were the same as for biomass samples, with the addition of Hg. The MBG was calculated as for the biomass samples but, when available, the CCME ASQG was noted in the table. Values exceeding the MBG were highlighted in red. Sixteen values slightly exceeded the MBG, found mostly in samples S-BG-12879-78123 (five parameters), S-BG-03737-65708 (three parameters), S-BG-97286-74154 (two parameters), S-BG-MCALPINES-2SACS (three parameters) and S-BG-HARTS (three parameters). No values exceeded the ASQG in BG samples, since the level is more permissive and MBG is an average of all samples from the same area, which lowers the average and standard deviation, thus the MBG.

Anti-Armour Range

Four biomass samples (plus one duplicate) and 28 soil samples (plus one duplicate) from the AA range were analyzed. The details are presented in the next two paragraphs.

Biomass AA samples. The sampling method used for biomass samples was linear transects at 20 and 40 percent of the range. Two of the samples were collected on the eastern part of the centerline, whereas the other two were collected on the western part. Comparison was made with the MBG, and 13 values exceeded this level. They are highlighted in red in Table 4-4. The two most exceeding parameters were Bi (four of five samples exceeded) and Pb (all 5 samples exceeded). The other exceeding parameters were Cu, Sb, Sr and Te. Sample B-AA-LS-40 percent A contained 5 out of the 13 exceeding values.

Soil AA samples. Soil samples were collected according to all methods described in the AA section under Range Description and Sampling Strategy. Seven composite samples were taken in front of firing position 4, at 0, 10, 20, 30, 40, 50, and 100 m from the firing position. Eight composite samples were collected along linear transects at 20, 40, 70, and 100 percent of the range. The other 13 samples were collected around tank targets 1, 2, and 3. Results that exceeded MBG, but were less than ASQG, were highlighted in red, whereas values that strictly exceeded ASQG (and MBG implicitly), were highlighted in blue. A total of 192 values exceeded MBG. The greatest exceedance was by Ca, which exceeded the MBG by one order of magnitude. The main parameters that exceeded MBG were (numbers in parentheses are the numbers of samples) Ag (8), B (11), Ba (10), Ca (8), Cu (15), Mo (16), Pb (13), Sb (21), Sn (10), Tl (10), and Zn (8). Forty-three values exceeded not only MBG, but also ASQG. Principal parameters of concern were As (2) , Cd (7) , Cr (2) , Cu (12) , Ni (4) , Pb (12), and Zn (4). The following samples, which contained a significant number of parameters exceeding ASQG, are of particular concern: S-AA-T1-ARRIERE (5), S-AA-T2-AVANT (6), and S-AA-T2-ARRIERE (6). In general, the high levels of Cu, Mo, Pb, Sb, Sr, and Zn, are the characteristics of the AA range. Ten soil samples showed levels of Cu or Pb even higher than the CCME Industrial Soil Quality Guideline (ISQG). These metals can significantly affect the environment. Also, it seems obvious that the samples collected around the targets show more contamination than the others, due to the detonation of the munitions. The following parameters were detected over MBG in both soils and biomass: Pb, Cu, Sb, and Sr.

Wellington Anti-Tank Rocket Range samples

Only 1 composite biomass sample and 11 soil samples were analyzed for the Wellington Anti-Tank Rocket Range. The results demonstrated a trend in the contamination, however.

Biomass WAT sample. The only biomass sample collected was a composite created by mixing samples that were collected around targets 1 and 2. Of the 31 parameters analyzed, 19 exceeded the MBG (highlighted in red in the table). Bi and Cu exceeded MBGs by two orders of magnitude, and Ag, Cd, Cr, Pb, Sb, and Sn exceeded MBGs by one order of magnitude. Since only one biomass sample was taken, no comparison can be established with other parts of the range. However, the one sample is certainly contaminated by various metals at one or two orders of magnitude over the MBG.

Soil WAT samples. Soil samples were collected around targets 1 to 5, around the firing position, and at the open detonation (OD) pit. At first glance, samples collected around the targets showed more contamination than at the firing position, which is obviously caused by the detonation. In this series of samples (around targets), Cd, Cu, Pb, and Zn exceeded ASQG in all eight target samples, while Cr and Ni exceeded ASQG in five of the eight target samples. Cu, Pb, and Zn results were by far the most important, since the majority of them exceeded ASQG by at least one order of magnitude. Cu, Zn, and Pb results also exceeded the ISQG in all samples around target tanks. The other important parameters were Ag, Bi, Mo, Sb, Sn (all eight target samples exceeded MBG), Ba (seven out of the eight target samples exceeded MBG), B, Sr (five of the eight target samples exceeded MBG), Ca, Fe, K, Na, Tl, and U. For the other series of samples, which were around the firing position and at the OD pit, no major contamination was detected. The most contaminated firing position sample was S-WAT-FP-BACK, with 10 of the 32 parameters exceeding MBG. Two of those exceeding parameters, B and Sn, exceeded MBG by one order of magnitude. Those results indicated that EM was sprayed behind the gun after shooting the munitions. Parameters found both in soils and biomass were Ag, Bi, Cd, Cr, Cu, Fe, Ni, Pb, Sn, Tl, U, and Zn. Strangely, hits for uranium occurred in both soils and biomass, while no record of the use of uranium-based ammunitions were available for this range.

Old Castle Grenade Range samples

Five biomass samples and six soil samples were analyzed. Even with the previous decommissioning of the range and disturbing of the soil profile, some contamination was discovered.

Biomass CGR samples. All five samples analyzed showed results exceeding MBG. In total, 51 parameters exceeded the MBG level, the most important being Zn (all samples), Cd (four of the five samples), Bi, Mo, Na, Te (three of the five samples), Al, As, Be, Co, Cr, Cu, Fe, Li, Mg, Ni, Tl, U and V (two of the five samples). The most contaminated samples were B-CGR-MIDDLE and its duplicate, with 34 of 51 samples exceeding parameters. Those results indicated that most of the contaminants are found in the middle of the range, where the majority of the grenades were fired.

Soil CGR samples. Results for CGR soil samples were well distributed. First, the most important parameter was Zn again, where all samples exceeded ASQG. The other parameters that had to be taken into consideration were Cd and Cu (five of the six samples exceeded MBG, and the other sample also exceeded ASQG, along with Sr (all samples exceeded MBG), Sb, Sn (four out of the six samples exceeded MBG), and Ca, As, Ba, Ni, and Pb. The most contaminated sample was S-CGR-CORE-5-10 CM, with nine parameters exceeding MBG, including two parameters that also exceeded ASQG. (Zn exceeded ASQG by one order of magnitude.) These results showed that contaminants were found mainly in deeper layers of the soil. The further migration of these contaminants in the aquifer could lead to human adverse impacts. The following metal analytes were found in both soil and biomass: As, Cd, Cu, Ni, Sn, and Zn.

New Castle Rifle-Grenade Range samples

Two biomass and two soil samples were collected and analyzed. The NCRGR being very recent and less firing activities occurring there, no major contamination was detected with only two soil samples showing higher levels of Sr than MBG.

Biomass NCRGR samples. One biomass sample was taken at the left of the range, and another was collected behind target 1. In these two samples, a total of 14 parameters exceeded MBG, the most important being Bi, Cu, Pb, Sn, and Zn (both samples exceeded MBG), Ag, Cd, Mo, and Te. Sample B-NCRGR-LEFT showed more contamination, with results four times greater than the MBG for Cu and Zn.

Soil NCRGR samples. Only two parameters slightly exceeded MBG, both related to Sr. This result may be attributed to the presence of strontium in 40-mm rifle grenades.

New Castle Hand-Grenade Range samples

Three biomass and seven soil samples were analyzed for NCHGR. Again, the contaminants were very well distributed, which facilitated the interpretation of the results.

Biomass NCHGR samples. Twenty parameters exceeded the MBG levels. The greatest were Cd, Cu, Pb, Zn (all three samples), Na (two of the three samples), B, Bi, Mg, Rb, Sb, and Te. The most contaminated samples were B-NCHGR-RIGHT and its duplicate, which exhibited 16 of the 20 parameters. Again, Zn was the metal that seemed to accumulate the most in this area.

Soil NCHGR samples. In the seven samples analyzed, three parameters gave significant results. The first one was Zn with six samples exceeding ASQG and the other one exceeding MBG. The second important parameter was Cu, with six samples exceeding MBG and the other exceeding ASQG as well. The final parameter was Sb, with six samples slightly exceeding MBG. The most contaminated sample was S-NCHGR-10M, in which the concentration of Zn was exceeded at three times the ASQG. Such results are understandable, since this sample was collected close to the bunker wall, where most of the grenades are fired. Even if this range was recently built, many trends of metal accumulation could be measured.

Hersey Impact Area samples

Sixteen biomass and sixteen soil samples were analyzed. No significant contamination seemed to have occurred there, but some results are still highlighted.

Biomass H samples. Sixteen composite biomass samples were collected along linear transects to the left- and right-hand sides of Hersey Road, from 40 to 100 percent of the distance from this road. A total of 36 parameters exceeded MBG. No samples greatly exceeded the MBG level, except Al and Fe, where the concentration was more than twice the MBG. The most important parameters were Te (eight samples), Cd (four samples), Rb (three samples), Pb, Sn, Tl (two samples), Ag, As, B, Be, Bi, Co, Cr, Cu, Li, Mo, Sb, U, and V. The most contaminated sample was B-H-LS-80 percentB, with 15 out of the 36 parameters exceeding ASQG. This result could indicate that most of the detonations occur in this transect, leading to a measurable pattern for metal dispersion.

Soil H samples. In the 16 samples analyzed, only two parameters exceeded ASQG, one for Cd and one for Zn. Cd (11 samples), Cu (12 samples), Sr (six samples), Zn (five samples), Ag, K, Pb (three samples each), Ba, Ca, Mn, and Rb (two samples each) exceeded MBG only. In general, the concentrations did not greatly exceed MBG, so one can conclude that the area is not highly impacted.

Lawfield Impact Area samples

For the Lawfield Impact Area, 10 biomass and 14 soil samples were analyzed. Soil samples consisted of composite surface samples around impact crater clusters and composite surface samples at 25 percent of overall length of the range, either side of the centerline. Biomass samples were collected in the same manner.

Biomass L samples. A total of 62 parameters exceeded MBG, the two most important being Cd and Zn, where all samples exceeded the MBG levels. The other important parameters were Cu (exceeded MBG in seven out of the ten samples), Pb (six samples), Ag (five samples), Al, Bi, V (three samples each), Co, Cr, Fe, Li, Ni, Sn (two samples each), Be, Mo, and Tl. The most contaminated samples were B-L-HS-13930-69376 and its duplicate, which exceeded 28 of the 62 parameters. Those samples were collected around impact craters and close to UXOs, which indicate a localized impact of the UXO presence. The field duplicate showed similar results indicating good field reproducibility.

Soil L samples. Results of the soil sample analyses were very similar to those of the biomass sample analyses. First, almost no values exceeded ASQG; in fact, the only two values that exceeded ASQG were values for Cu, which barely exceeded ASQG (values were 64 and 67 ppm). As for the biomass samples, the most important parameters were Cd and Zn (exceeding MBG in 12 samples out of 14 samples), but also Cu, where all samples exceeded MBG. Besides that, only the following parameters exceeded the MBG values: Ba, Mo, Pb, Sb, Sn, Sr, and V. The most contaminated sample was S-L-HS-13952-69466, which contained the highest concentration of Cu (67 ppm) and Zn (170 ppm). This sample was also collected around impact craters and UXOs.

Argus Impact Area samples

For the Argus Impact Area, one biomass and 19 soil samples were analyzed. Despite the intense use of this training area, no major contamination was detected.

Biomass AR sample. In the sole biomass sample analyzed, 14 of the 31 parameters exceeded MBG. Those parameters were Al, As, Be, Bi, Co, Cr, Fe, Li, Ni, Pb, Sb, Tl, U, and V. The most critical ones were Pb, which exceeded MBG by one order of magnitude, and Al, which exceeded MBG by 2.5 times. The sample was collected to the left of target 1.

Soil AR samples. Fifteen soil samples, which were collected around six different craters, were analyzed, and the four other samples came from targets 1 to 3. In general, for the samples collected around craters, Cd was the most considerable parameter, with 11 out of the 15 values slightly exceeding MBG. Some other parameters presented exceeding values (e.g., B, Cu, K, Sn, Sr and Tl). More contamination was found in the four samples that were collected around targets 1 to 3. For example, two of the four samples presented values that exceeded ASQG for Cu. Also, Pb exceeded ASQG in three samples, while Cd, Tl, and Zn exceeded ASQG in one sample, which was S-AR-T2-FRONT. This sample was by far the most contaminated, since Cu and Zn exceeded ASQG by one order of magnitude, and lead exceeded ASQG by two orders of magnitude. Many other parameters exceeded only MBG: Ag, As, Ba, Be, Bi, Ca, Co, Cr, Fe, K, Mg, Mo, Ni, Sb, Sn, Sr, and Tl.

Greenfield Impact Area samples

Four soil and four biomass samples were collected along linear transects at 40 and 60 percent of the overall length of the range, on either side of the centerline. The results showed almost no contamination.

Biomass GF samples. Only three parameters slightly exceeded MBG Ag, Sb, and Sr. None of those parameters greatly exceeded the level, so one can conclude that contamination was minor. Sample B-GF-LS-60 percentB contains two of the three parameters.

Soil GF samples. Only four parameters, all part of the same sample (S-GF-LS-60 percentB), slightly exceeded MBG, Ag, B, Ba, and Pb. The most contaminated soil sample was co-located with the most contaminated biomass sample. Therefore, one can conclude that this area of the range was possibly more contaminated than elsewhere.

Small arms ranges and burning locations

Some samples were collected at small arms ranges such as Batouche, Reichwald, and Vimy and also in two gun propellant burning locations named Airstrip and Lawfield. Only soil samples were collected. Some high levels of contamination were found.

Batouche Range. Five composite soil samples were collected in Batouche Range, covering targets 1 through 12. All five samples presented exceeding values, in the following way: Cu and Pb (exceeding ASQG by one order of magnitude for Cu, two orders of magnitude for Pb, except in sample S-BATOUCHE-12 DEPTH, where Cu slightly exceeded ASQG and Pb exceeded ASQG by one order of magnitude), Sb, Sn, Sr, and Tl (all exceeding MBG by one or two orders of magnitude). Some other parameters exceeding MBG in all samples except S-BATOUCHE-12 DEPTH, were Ag, Bi, Te, and Zn. Other significant parameters were As (exceeding MBG in two samples), K (one sample), Mo (two samples), and Na (three samples). The most contaminated sample was S-BATOUCHE-5-8, with the highest values of Cu (818 ppm) and Pb (21,500 ppm).

Reichwald Range. Seven composite soil samples were collected for targets 1 to 20. The sample at target 1 was collected to a depth of 0-5 cm and was duplicated. Since no contamination was detected in the samples collected at depth, one can conclude that contaminants usually reside at the surface. For the five samples that were collected in the surface around targets 1 to 20, high levels of Cu and Pb were found (exceeding ASQG by one or two orders of magnitude). Also, values for Ag, Sb, Sn, and Tl exceeded MBG in those five samples. The other parameters were Bi (exceeding MBG in four samples), Sr (four samples), Te (four samples), and Zn (four samples, including a value that also exceeded ASQG). The most contaminated sample was S-REICHWALD-13-16, showing the highest concentrations of Cu (1,860 ppm), Pb (17,000 ppm) and Zn (218 ppm).

Vimy Range. Four composite soil samples were collected around targets 1 to 12 and in depth at target 1. All four samples exceeded ASQG in Pb, and two out of the four samples exceeded ASQG in Cu (the two other samples exceeded only MBG). The other parameters were Ag (exceeding MBG in one sample), As (one sample), Bi (one sample), Ca (two samples), K (one sample), Na (all four samples), Sb (all four samples), Sn (all four samples), Sr (three samples), Te (one sample), Tl (two samples), and Zn (one sample). The most contaminated sample was S-VIMY-9-12, with high concentrations of Cu (379 ppm) and Pb (13,500 ppm), along with 11 other parameters that exceeded MBG.

Airstrip burning location. Three soil samples were collected at burning location Airstrip 2. High levels of lead were found in all three samples, and all exceeded ASQG by an order of magnitude. Values for Cu, Sb, and Sr also exceeded MBG in all three samples. Other parameters were B, Bi, Sn, and Tl. Cu and Pb were the most common metals found in this burning location, which is in keeping with the Pb used in artillery propellants as a lubricating agent.

Lawfield burning location. Three soil samples were also collected in the Lawfield burning location. Again, Pb exceeded ASQG by one order of magnitude in one sample, and by two orders of magnitude in the other samples. Values for Sr also greatly exceeded the MBG in all three samples. Other parameters exceeding MBG or ASQG were Ba, Mn, Sb, Sn, Tl, and Zn.

Conclusions and Recommendations

Metals

The average and standard deviations were calculated for all background samples site wide. The MBG level was calculated by adding the mean value to twice the standard deviation. This served as the basic comparison level, when no other criteria were available, such as for metals concentrations in biomass and in most of the agricultural soils. Results that exceeded only these MBG levels were highlighted in red in all tables, while results that also exceeded ASQG were highlighted in blue. In this manner, no results were highlighted in blue for biomass, since no criteria exist. Although based on an insufficient number of background samples for statistical comparisons, these data are highly interesting for observing contaminant trends in the live-fire area.

The most common metals found in biomass were Cd, Pb, and Zn, especially in the grenade ranges and in Lawfield range. In soil samples, the most common metals were almost the same: Cd, Cu, Pb, and Zn. The areas of primary concern are AA Range, WAT Rocket Range (high levels of Cu, Pb, and Zn), all of the grenade ranges for their high Zn concentration, and all of the small arms ranges for their high concentrations of Cu and Pb.

More particularly for the AA Range, 21 parameters in soils exceeded MBG with Cu, Mo, Pb, Sb, Sr, and Zn being the most predominant. Four parameters were detected in both soil and biomass samples Pb, Cu, Sb, and Sr. Highest concentrations were found around targets. The following parameters were found in concentration over either the ASQG or the ISQG: Cd, Cr, Cu, and Pb.

In WAT Rocket Range, high levels of various metal analytes were detected in soils both at the target locations and to the front and rear of the firing position. Many parameters were detected in both soils and biomass including uranium, which might indicate a past use of this metal on the range. The following parameters were detected around targets at levels above the ASQG or the ISQG: Cd, Cu, Cr, Pb, and Zn.

In both the AA Range and WAT Rocket Range, high concentrations of heavy metals in the target areas and firing positions were observed. Greater levels of heavy metals and Ca, Na, and K are also found in the biomass samples. More biomass samples are needed in WAT to confirm the high results obtained.

The three grenade ranges sampled were impacted by various heavy metals. The oldest (Old Castle Grenade Range) was the most affected. Both soil and biomass showed a pattern of multiple contaminants and the greatest concentrations were detected for Cd, Cu, and Zn.

Metals were also detected in high concentrations at target areas or in craters in artillery impact areas. The contaminants of concerns in the artillery ranges are Cd, Cu, and Zn. The Argus Impact Area presented the most elevated concentrations of metals followed by Lawfield, Hersey, and Greenfield Impact Areas.

In small arms ranges, various analytes were found in high concentrations in the firing butt. Pb is the primary contaminant of concern with values as high as 21,500 ppm. High values of Pb were observed in all samples collected. High levels of Na, Ca, Mg, and K were found in the same samples. These salts might attract grazing wildlife. Other metal analytes that were found in high concentrations were Cu, Sb, Sn, Sr, Tl, and Zn.

The burning area presented high concentrations of Pb and Sr with levels as high as $7,060$ and $3,905$ ppm, respectively.

In general, trends that were identified for soil accumulation were correlated with biomasss results. This is caused by the phyto-accumulation of metals, since plants are known to have the potential to concentrate contaminants in their tissues. Results for biomass were obtained only on the stem and leaves, since no roots were collected. Roots are known to bioaccumulate metals to a greater extent than stems and leaves, so results may have been higher if roots had been sampled as well. The results for biomass in many of these ranges are of concern since Na, Ca, and K were detected at elevated concentrations combined with heavy metals. This trend was also observed in the Shilo training area. This may attract wildlife to preferentially graze on the contaminated biomass.

Energetic materials

Both the AA Range and WAT Rocket Range had concentrations of NG and 2,4-DNT to the front and rear of the firing positions, with concentrations up to percentage levels (up to 11 percent) in surface soils behind the firing position of Wellington. These residues are related to the use of single- and double-base propellants. Results found at the AA Range were similar to those found on a U.S. range (Yakima Training Center). The same contaminants were also found downrange at Wellington, probably as a result of rocket fuel (propellant) that is distributed at the detonation point, TNT and RDX were found near targets at the AA Range at various concentrations less than 5 ppm. Concentrations of RDX and HMX were higher near target 3. A possible explanation for the higher levels near target three is the blow-in-place of UXOs or a partial detonation of a munition filled with Comp B. At Wellington, concentrations of HMX far exceeded those of any other energetic compounds in the impact area near targets. The HMX likely originated with the use of Octol-based M72 shoulder anti-tank rockets on the anti-tank ranges. High concentrations of HMX and TNT were also detected in deeper soil samples, with HMX detected at concentrations up to 932,000 ppb for one core sample. This trend will be further investigated when more core samples are collected.

In the grenade ranges, a pattern of concurrent contamination by TNT, TNT derivatives, and RDX was found, with the oldest range (Old Castle Grenade Range) being the most concentrated. These residues are indicative of grenades filled with Comp B that are used on these ranges. Results obtained are similar to those found in other Canadian and U.S. grenade ranges. In both new ranges (NCHGR and NCRGR), NG and 2,4-DNT were also detected, which is somewhat unusual for a grenade range. These later compounds might be present because of unknown past use of the area or because of burning of excess

propellant at these locations. The two newest ranges were resampled in the fall of 2003 to assess the buildup of energetic residues. By knowing how many rounds were fired between each sampling, one might even be able to estimate a yearly source term for both ranges.

Results from the four artillery impact areas varied greatly in explosives residues. Hersey and Greenfield presented both low concentrations and spatially distributed contamination primarily by RDX, but with NG and 2,4 DNT. Lawfield presented higher concentrations of TNT, RDX, and amino-DNT near craters. The concentrations detected in Lawfield were somewhat higher than found in similar ranges in the United States. Argus had the greatest quantities of energetic residues. TNT was detected in all samples from this range, while RDX was detected in only one sample. Locations sampled on the Argus range, therefore, were more likely to have been impacted by detonations of munitions filled with TNT as compared to Comp B. One crater from a low-order air-toground bomb presented very high concentrations of TNT, both in the soil and in surface standing water. The high results found in Argus might be explained by the prior Staunch Gladiator exercise and also by dual use of Argus for artillery and air-to-ground bombing. The Staunch Gladiator exercise involved both surface-to-surface and air-to-surface artillery and bomb military capabilities from several nations.

2,4-DNT was detected at relatively high concentrations in all samples. Since no NG was found, mostly single-base propellant must have been burned there. Other target analytes such as 2,6-DNT, TNT, and RDX were also detected.

General conclusions are that the AA Range and WAT Rocket Range are impacted by various heavy metals and explosives residues, both at levels of concern. The most contaminated areas were found near targets, and to the front and rear of firing positions. Artillery ranges were mainly impacted by Cd, Cr, Zn, and Pb. Explosives residues were detected at lower concentrations on artillery ranges than on the AA Range and WAT Rocket Range. Grenade ranges also present mixed contamination by both metals and energetic materials with the oldest range being the most highly impacted area. The burning area presents high concentrations of Pb, Sr and 2-4, DNT as expected, since burning of propellants is known to be an incomplete process that leads to the accumulation of propellant residues in the environment. Finally, small arms ranges firing butts are heavily impacted by lead and other heavy metals as found in Shilo SARs.

Recommendations

More sampling was recommended for the fall of 2003 to complete the datasets and answer the question posed in this report. A relationship should be established between the surface soils-biomass and groundwater results to determine whether vertical and horizontal migration of the contaminants is occurring at the training area. Finally, a site risk assessment should be conducted when all results are obtained to identify any potential adverse effect on human health resulting from the anthropogenic contaminant contribution of the firing activity.

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List of Symbols/Abbreviations/Acronyms

Table 4-3 aa GC-ECD Analysis of Background Soil Samples Collected at Gagetown

Table 4-3 ff

Table 4-3 jj GC-ECD Analysis of Soil Samples Collected In an Area Between Hershey and Argus Impact Areas (Greenfield), Gagetown

Table 4-4

BLUE: Exceeds ASQG

5 Evaluation of the Contamination by Explosives in Soils, Biomass, and Surface Water at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase I Report

Abstract

This chapter describes the evaluation of the impacts of live-fire training activities at the Cold Lake Air Weapons Range (CLAWR) in Alberta, Canada, performed during August 2002 (Phase I). CLAWR is the largest air weapon range area in Canada and was the first Canadian Air Force Base (CFB) to be characterized for explosives and metals. This study was conducted by Defence R&D Canada-Valcartier (DRDC-Valcartier) in collaboration with the U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research Engineering Laboratory (CRREL), Hanover, NH, and Environmental Laboratory (EL), Vicksburg, MS.

The problem of Army ranges should be different from that of Air Force ranges because the air weapons are different even if they are filled with the same explosives. Reconnaissance of four ranges on the site was conducted during August 2002. Alpha, Bravo, Jimmy Lake, and Shaver River Ranges were sampled for explosives using different strategies. Particularly, efforts were most intensive at the Shaver River Range since it is used mainly for air bombing. A linear transect sampling strategy was used at the ranges to evaluate the progression in explosives concentrations across all of them. All the samples were composited using 20-30 subsamples. A new circular sampling strategy adapted to the air-bombing situation was achieved by collecting 26 samples around the targets at specific locations. Some soil samples were also collected at different depths in front of the targets. In total, 193 soil samples, 13 biomass samples, and 4 surface water samples were collected during this first phase of the evaluation.

Metal analyses were done using Inductively Coupled Plasma /Mass spectrometer (ICP/MS) and explosives concentrations were done using the Gas Chromatograph/Electron Capture Detector (GC/ECD) method developed at CRREL. This study demonstrated that the ranges have some accumulation of metals due to the firing activities, but the extent of contamination is very low, with the exception of Jimmy Lake where cadmium, copper, and zinc concentrations were higher than the industrial health risk criteria. The contamination by explosives is also minimal except in the Shaver River Range, where 2,4,6-trinitrotoluene (TNT) was found at concentrations up to 400 ppm.

Introduction

Energetic materials are prominent components of munitions and weapons that can be found in war zones, on training ranges, and on production sites. During the last decade, many needs have already emerged related to the identification, quantification, delimitation, and elimination of energetic contaminants dispersed by munitions, or present in explosives dumps, trial or destruction fields, firing areas, and production sites [1-25]. The international context of the end of the Cold War resulted in the closing of many military bases and a growing awareness of environmental issues. Within this context, the Director, Research and Development Branch, through DRDC-Valcartier, has directed some of its resources to assess and develop expertise related to the environmental risks associated with explosives compounds.

Many Canadian Forces sites used as impact areas, training ranges, demolition and open burning/open detonation (OB/OD) ranges, which were used to destroy out-of- specification materials, are suspected of being contaminated with energetic substances as described in the literature [1-14]. To evaluate the contamination of Department of National Defence (DND) sites, sampling and characterization of various ranges was performed over the last 10 years. A protocol describing the different methods of sampling and the analytical chemistry was developed [15]. This protocol was recently updated in collaboration with CRREL and is presently being reviewed under the auspices of The Technical Cooperation Program (TTCP) by the member nations in a key technical area (KTA 4-28) [16]. Research results to date have demonstrated that explosives are not common contaminants, since they exhibit limited aqueous solubility and are dispersed in a heterogeneous pattern of contamination. In the United States, much effort has been made to develop analytical chemistry, to establish the best sampling procedure, and to understand the complex fate of explosives in the environment [3, 4, 6-12, 17-25].

The selection of CLAWR in CFB Cold Lake, Canada, to conduct the first R&D efforts to assess the environmental aspects of live-fire activities on an Air Force training area was the result of a growing interest by 4 Wing following the contamination characterization of CFB Shilo and also because Cold Lake is the largest air base in Canada. Being the biggest and the most used area for air practice with live weapons, it is the area most representative and worthy of study among air bases. The problem of air bombing is completely different from problems encountered on Army ranges. The weapons used are different,

especially in size and content. In Army ranges, unexploded ordnance (UXO) buried in the ground may corrode and eventually leak explosives to the groundwater; however, many UXOs will be needed to generate an important plume to the groundwater. An air-bomb that did not explode may become a deeply buried UXO and, may corrode, perforate and leak, resulting in a bigger plume from the many kilograms of explosives released in one location such as when 500- or 1000-lb bombs are used. Even a low-order detonation with such large weapons may result in dramatic impacts to the environment as was seen at CFB Gagetown. At this base, a 500-lb bomb that underwent low-order detonation released its explosive content into a crater filled with water. The concentration of TNT was 35 ppm [26]. Also, many air weapons use rockets that contain ammonium perchlorate, a newly recognized contaminant that is extensively studied in the United States. When these rockets hit the ground, some of them do not completely burn and can break into pieces at impact spreading ammonium perchlorate at the surface. This contaminant is ionic, very water soluble, recalcitrant and goes directly to the groundwater. Even though the expertise of DRDC-Valcartier, ERDC-CRREL, and ERDC-EL is based mainly on Army ranges, it directly applies to air ranges for understanding this new problem that represents a new area of research.

The ultimate goal of this sampling campaign was to assess contamination related to explosives and heavy metals dispersed at the surface. The contamination patterns of surface soils around targets and across the ranges were evaluated. The extent of biomass contamination in the worst-case scenario locations was assessed, and, finally, the surface water quality was also evaluated to a limited extent due to limitations in time and funds available. In previous DRDC-Valcartier studies, both energetic materials and metals-contaminated surface soils have been found in training ranges [1, 2, 13-14].

To better understand and assess the contamination and characterize an area, an appropriate definition and understanding of the hydrogeological context of the site are required. Characterizing the groundwater quality, especially on such large ranges, is critical because metals and energetic materials are mobile in sandy environments and may migrate in groundwater, presenting a threat to human health and to the environment. Managers or site owners must ensure that no contamination migrates off site. Soil surface sampling may point out specific areas where the contamination occurs, but the final answers will be obtained following the hydrogeological study. Groundwater flow has to be carefully assessed by determining its velocity and direction. The quality of the groundwater also has to be evaluated. Groundwater is often used to supply drinking water to the base, to sustain aquatic ecosystems, and for irrigation on some occasions. Consequently, any contamination could impact human health and aquatic ecosystems. In fact, groundwater flowing under CLAWR discharges into Primrose and Jimmy Lakes and also into rivers such as Shaver River. All are highly sensitive areas for wildlife and humans receptors. Consequently, it is imperative that a hydrogeological study be conducted in Cold Lake to assess the impacts of the activities.

Biomass has also proven to bioaccumulate both metals and energetic materials [10]. Therefore, prairie grass or other flora could represent a high potential intake source of these compounds for wildlife like bears. Finally, since wildlife has access to the surface water, surface water quality has to be verified.

Approach

This chapter describes the work carried out during the preliminary phase in March 2002 and Phase I in August 2002. The preliminary phase consisted of collecting some samples in winter 2002, but most of the study was accomplished in August 2002. This chapter will concentrate on the results obtained during Phase I. The approach and the strategy were adapted to the new context of airdropping and the results obtained from this sampling campaign are described. The four ranges of Alpha, Bravo, Jimmy Lake, and Shaver River Ranges were sampled during the August 2002 event. Significant efforts were made to characterize the Shaver River range, which was the one most used for airdropping of live weapons. Background samples were also collected to compare and assess the natural and anthropogenic contribution. Biomass samples were collected in the four ranges. In total, 193 soils, 13 biomass, and 4 surface water samples were collected. A deficiency of this study was the low number of background samples collected during August 2002; this was corrected at the next sampling campaign in August 2003.

This study was performed under the work breakdown element 12NY01, "Characterization of DND Sites Contaminated with Energetic Materials," and was sponsored mainly by 4 Wing and by SERDP for the sampling of the surface soils. All work was done in collaboration with ERDC-CRREL and ERDC-EL under the umbrella of the Canada-United States Test and Evaluation Programme (CANUSTEP). This joint venture between Canada and the United States was initiated to evaluate the fate of explosives in live-firing ranges under the auspices of SERDP, a major funding program in the U.S. Department of Defense (DoD). Defence Construction Canada (DCC) was responsible for hiring the analytical laboratory, and providing manpower, logistics, and liaison with range control personnel.

Range history and description

Four Wing Cold Lake is in the remote northeastern corner of Alberta on the border with Saskatchewan. It was opened in 1954 as an air weapons training base and still performs that function today.

The Cold Lake area was settled in the early 1900s. The early community was largely composed of French Canadians and European immigrants drawn by the possibilities of the area's extensive natural resources. Prior to their arrival, the area was inhabited by the Chipewyan Indian Nation. There were exceptional possibilities for trapping, forestry, and fishing, and over time a considerable agricultural base was established.

Because of its remote location, Cold Lake was chosen following World War II as the site for Station Cold Lake, the first flying station to be built for Royal Canadian Air Force (R.C.A.F.) fighters. A spur line from the Canadian National

Railway was built in 1951 to bring in building materials, and in 1952 construction began on the base itself. The main runway and two hangars were useable by the spring of 1954. The entire infrastructure of the base, including water supply lines, sewage, housing, and roads, had to be constructed from scratch over a period of several years at an overall cost of \$30,000,000.

Imperial Oil began exploration of the extensive Cold Lake area oil sands in 1964. Production began in the 1980s. The Cold Lake production project accounts for half of Imperial Oil's annual production, averaging 40-45 million barrels per year. In 2002 Imperial proposed a \$1 billion expansion of its Cold Lake project. The injection of money from petroleum production has decreased the community's dependence on the military as a primary employer.

Over 3000 military personnel, 3200 dependents, and 470 civilian employees live at Cold Lake, making it both the biggest and the busiest fighter base in Canada. It is home to three tactical fighter squadrons flying the CF-18 aircraft: 410 "Cougar" Squadron, 416 "Lynx" Squadron, and 441 "Silver Fox" Squadron. In addition, Cold Lake has a tactical training squadron, 419 "Moose" Squadron, and the 417 combat support squadron. Cold Lake is also home to the Aerospace Engineering Test Establishment (AETE), which is responsible for flight-testing all aircraft, weapons, and avionics systems destined for use in military aircraft.

Four Wing also takes care of the nearby Cold Lake Air Weapons Range (CLAWR), one of the most sophisticated facilities of its type in the world. It is the only tactical bombing range in Canada, and incorporates over 100 target areas with over 700 individual targets ranging from disused vehicles to dummy surface-to-air missile sites and airfields. CLAWR has been designated a supersonic range, with pilots able to fly their aircraft at speed down to 30-m altitude. The CLAWR is used heavily during the annual Maple Flag exercise, which brings together several North Atlantic Treaty Organization (NATO) air forces for 6 weeks of intensive flying above the Cold Lake pine forests.

CLAWR covers an area of approximately 180 by 65 km and is approximately 54 km northeast of CFB Cold Lake at the junction with Saskatchewan, having Primrose Lake as a boundary. This beautiful lake is used for commercial fishing and as an approach to the ranges. CLAWR has four main ranges: Alpha and Bravo ranges that are part of the Primrose Lake Evaluation Range (PLER), and Jimmy Lake and Shaver River ranges. Alpha and Bravo ranges are located, respectively, from South to North following the southwest shoreline of Primrose Lake (see map Appendix A), while the Jimmy Lake range is located between Jimmy and Primrose Lakes. The Shaver River Range is remote to the lakes and close to the Shaver River. This range is the one most dedicated to aerial live firing of 500-lb bombs. All ranges in CLAWR contain several ground target complexes for bombing training. Both the Jimmy Lake and Shaver River Ranges are licensed for live weapons use up to 2,000 lb general purpose bombs and live firing missiles. The Primrose Lake water zones are called drop zones Charlie, Delta, and Echo and are used to analyse the performance of stores such as dispenser or cluster munitions.

Preliminary sampling at CLAWR was conducted in 1993 by D.A. Westwood & Associates. They reported some trends with metals such as cadmium, barium,

copper, vanadium, and lead. Defence Construction Canada (DCC) also performed a study of the soils, and of sediments in the lakes. They recommended a thorough investigation of the flora such as lichen, fish tissue, and water samples. No investigation prior to the current study examines the potential for explosives contamination. This was the main objective of this sampling campaign, to determine the explosives concentrations in soils in the different CLAWR ranges. A second objective was to evaluate the metal concentrations in the ranges.

Experimental Description

Contractors

DCC was responsible for collecting soils samples during the preliminary phase in March 2002. Appendix B is the DCC partial report for this activity. They were also responsible for hiring the analytical laboratory and supplying all of the analytical tools, solvents, bottles, etc., and the manpower to assist DRDC-Valcartier, CRREL, and EL for the sampling of soils, biomass, and surface water samples during Phase I in August 2002. The analytical work for metals was subcontracted to Enviro-Test Laboratory (ETL) in Edmonton, Alberta, for the analyses of the samples collected during the preliminary phase. For Phase I, the analytical chemistry for metals was performed on all samples by Maxxam Analytics, Inc. in Calgary, Alberta. All of the energetic materials analyses were performed for both phases by DRDC-Valcartier. Furthermore, the energetic materials analyses for the samples collected during Phase I were also performed by CRREL to evaluate the heterogeneity of the samples and to validate the methods of analysis in both laboratories. DCC was responsible for the shipment of all samples to the laboratories.

Sample handling and treatment

Explosives are not volatile compounds, and, therefore, no specific precautions, such as the use of sealed containers, had to be taken during sampling of media containing explosives. Soil samples were composites based on a minimum of 20 random subsamples and were stored in polyethylene bags. The bags were immediately stored on ice in coolers in the dark to avoid photodegradation of light-sensitive compounds. The use of polyethylene bags decreased the space needed for storing samples and reduced shipping costs. The soil samples were shipped frozen to Maxxam, where the samples were split into two subsamples after a thorough hand homogenization. One set of frozen samples was sent to DRDC-Valcartier for explosives analysis and the other was digested and analyzed for metals by Maxxam. Surface water samples for metals analyses were collected in standard 500-ml polyethylene bottles, and acidified to a pH of 2. These water samples were not filtered onsite because they are surface water and particles can be ingested by wildlife. Biomass samples were collected in polyethylene bags, kept frozen in the dark, and sent to Maxxam. The samples were then cut in small pieces, homogenized, digested, and analyzed for metals by Maxxam.

Parameters monitored and analytical methods

Soil, biomass, and surface water samples were analyzed for metals and energetic materials. Metals were analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) by ETL and Maxxam Analytics, Inc. All of the analytes available by this method were included in the study. For soils and surface water samples, energetic materials were analyzed by DRDC-Valcartier and CRREL using the Gas Chromatography/Electron Capture Detection (GC/ECD) SW 846 Method 8095, a method that can produce a 0.004-ppb detection limit for water. At DRDC-Valcartier, with the GC-ECD method, a quantification limit of 10 ppb for most of the analytes was obtained based on interference peaks in the chromatograms; at CRREL, the quantification limits varied from 2 to 50 ppb. When higher explosives concentrations were detected or suspected as in the Shaver River range, Reverse-Phase High Pressure Liquid Chromatography (RP-HPLC) SW 846 Method 8330 was used by both laboratories and quantification limits varied from 100 to 1000 ppb as shown in Table 5-5. See the Environmental Protection Agency method 8330 found on their Internet site (www.epa.gov) for a complete description of this method. No biomass samples were analyzed for energetic materials, since no explosives were detected in another study [27-28].

All samples were analyzed in duplicates (one replicate was extracted and analyzed at DRDC-Valcartier and the other at CRREL) to verify the sample homogenization efficiency. Means and standard deviations were calculated for all sets of replicate measurements. Suspect individual measurements were flagged on the basis of extreme values of the relative standard deviation (RSD) and inconsistencies in the overall pattern for that sample or analyte. More than 80 percent of the laboratory replicates showed an RSD of < 30 percent, which indicates that the approach taken for soil homogenization by adding acetone after the drying step was quite efficient. For some parameters, however, RSD values as high as 155 percent were still observed.

Soil samples were dried in the dark and homogenized by adding acetone to form a slurry, which was then evaporated. Soils were sieved through 25-mesh sieves and split into two portions. One portion was sent to CRREL for analysis and the other portion was extracted at DRDC-Valcartier for analysis. Soil samples were extracted at DRDC-Valcartier according to the following procedure. Four grams of soil were mixed in acetonitrile (10 mL) and a vortex was applied for 1 minute, followed by a sonication period of 18 hr, after which the samples were left to settle for 30 minutes. The mixture was then filtered on a 0.45-micron filter and these extracts were then analyzed using the following procedure:

Soil extracts were maintained at 4°C until analyzed by GC-ECD. Analyses were performed with a HP6890 GC equipped with an electron capture detector (GC-ECD), an auto-injector HP7683 at an injection temperature of 250 ºC. A capillary column based on phenylmethyl siloxane HP-5 (HP19095J-121) of 10.0 m x 0.53 mm was used under helium carrier gas. The temperature run used was as follows: 100 °C/ 2 minutes, ramp of 10° C/ minute until 200 °C, ramp of 15 ºC/minute until 280 ºC, and a pause of 4 minutes at 280 ºC. This method was based on recent work published in the U.S. [22-23].

At CRREL, the apparatuses and the analytical procedure were slightly different even if the same GC method was used. CRREL has a HP6890 GC equipped with a Ni63 cell micro-electron capture detector (GC-µECD) and the auto sampler vials containing the acetonitrile soil extracts were placed into GC auto sampler trays that were continuously refrigerated by circulating 0°C glycol/water through the trays. Results were obtained according to the general procedure outlined in EPA SW846 Method 8095 (Draft, *www.epa.gov*). A 1-µL sample of soil extract was directly injected into a purged packed inlet port, maintained at 250°C, that was equipped with a deactivated Uniliner from Restek Corporation, Bellefonte, PA. Primary analysis was conducted on a 7-m x 0.53 mm ID fused-silica column, with a 0.5-um film thickness of 5 percent-(phenyl)methylsiloxane (Rtx-5MS from Restek). The GC oven was temperature programmed as follows: 100°C for 2 min, 10°C/min ramp to 270°C, 2 min hold. The carrier gas was hydrogen at a constant flow of 10 mL/min (linear velocity approximately 95 cm/sec). The detector temperature was 300°C. The ECD makeup gas was nitrogen flowing at 45 mL/min.

If a peak was observed in the retention window for a specific signature compound, the extract was reanalyzed on a confirmation column, 6-m X 0.53 mm ID having a 1.0-µm film thickness of a proprietary phase (Rtx-TNT2 from Restek). The GC oven was temperature programmed as follows: 130°C for 1 min, 10°C/min ramp to 160°C, 30°C/min ramp to 270°C, 2 min hold. The carrier gas was hydrogen at a constant flow of 15 mL/min (linear velocity approximately 150 cm/sec). The detector temperature was 300°C. The ECD makeup gas was nitrogen flowing at 45 mL/min. Concentrations were estimated against commercial multianalyte standards (from Restek) from peak heights. Where analyte concentrations exceeded the highest standard, appropriate dilutions of the extract were made and the diluted extract was reanalyzed. If analyte concentrations were within the linear range of the ECD, concentrations reported were taken from the determination on the primary column, unless co-elution with another compound was evident. In such cases, reported concentrations were taken from the determination of the confirmation column. An important difference between the two labs is that at DRDC-Valcartier, no confirmation analyses were done using a second column system, since no second column was available.

Sample nomenclature

All samples were named according to the following four-part labelling system during Phase I:

- First part: sample type S: Soils SW: Surface Water B: Biomass (Prairie Grass and other species)
- Second part: Location by range AL: Alpha BR: Bravo JL: Jimmy Lake

SR: Shaver River RIF: Rifle Range BG: Background Sample

- Third part: Identification of the sample source Target number (1 and 2) or Firing Position (FP) or Background location (ex: North of target) or Background location by global positioning system (GPS) or LS for linear sampling at XX percent of the range where XX percent = percent of the overall range length or open detonation area (OD-1, 2 or 3)
- Fourth part: Identification of the sample Linear sampling at xx percent (A or B): A being the right side of the road access and B the left side; 0 percent is at the beginning of the road towards the target at 100 percent Systematic target sampling (A1, B2, C3, etc. according to Figure 5-1 (under Sampling Strategy) In rifle ranges: X-Y where X is the left target and Y the right target or the position of the firing position, ex. 100 or 200 m.

Quality assurance and quality control (QA/QC)

QA/QC programs were included in this study. Background soil and background biomass samples were collected away from the ranges. Analyses were done twice for energetic materials (laboratory replicates), but were done only once for the other parameters. Furthermore, each energetic analysis was repeated by CRREL for inter-laboratory study. Ten percent of field replicates were also sent for analysis. The contracted laboratory reported their QA/QC including surrogates and blanks, detection limits, and quantification limits. Trip blanks and field blanks were also included in the QA/QC plan.

Safety and emergency plan

The sampling of a UXO-contaminated area represents an increased level of risk for personnel. The Range Control Officers gave a safety briefing to people involved in the sampling program. This briefing explained the precautions to be taken to avoid contact with UXOs on the ranges and also described the various types of UXOs that may be found on ranges. A safety and emergency plan was also put in place for any incident that could have occurred while sampling water, soils, and biomass. This plan was under the responsibility of the CLAWR Range Control unit. When on site for sampling, personnel were always equipped with radios to contact range control in case of an emergency. Walkie-talkies were available to communicate between the teams. Range control personnel always accompanied the sampling team.

Sampling strategy

During the preliminary phase, DCC sampled in Alpha, Bravo, Jimmy Lake, and Shaver River Ranges to provide preliminary results for energetics and metals. The metals analyses are not included in this report. For the energetic materials, DCC used a circular pattern to collect soils around targets in the ranges. Appendix B provides a complete description of this work. During Phase I, soil, biomass and surface water sampling was conducted by DRDC-Valcartier, CRREL, EL, and DCC. A total of 193 soil, 16 biomass, and 4 surface water samples were collected during Phase I. The surface water samples were collected in Primrose Lake, Jimmy Lake, Shaver River, and a pond containing UXO on Shaver River Range. For statistical analyses and quality evaluation, 8 background samples and 18 field duplicates (9 percent) were collected for soil analyses. All samples were analyzed for metals (193), while a limited number were analyzed for energetic materials (131 soils - 12 field duplicates (9 percent)). All of the analyses for energetic materials were performed by both DRDC-Valcartier and CRREL following the drying, homogenization, sieving, and splitting of the samples. This was done to compare the results between laboratories and also to validate the results. Samples collected in Alpha, Bravo, and Jimmy Lake ranges were analyzed using the GC-ECD method, while most of the samples collected on Shaver River Range, which were suspected to have higher concentrations of explosives, were analyzed using the HPLC method EPA 8330. For biomass samples, only two background samples were collected; this was a deficiency that was corrected during Phase II in August 2003. Biomass samples were collected in all four ranges.

Background soil samples are critical for establishing the anthropogenic contribution versus the natural contribution for metals. The background composite samples were collected in a random manner, in a circular pattern of approximately 20 m in different locations inside and outside the base. A minimum of 30 subsamples was composited to form each background sample. A statistical analysis was conducted to quantify a mean background concentration and to define a limit for a value that can be considered abnormal. Samples located at the extremity of the lognormal curve were identified, and the limits were chosen for a probability of 97.72 percent (two times the standard deviation). The probability of finding a result with a value higher than this limit is 2.28 percent. When metals were not detected by the analytical laboratory, the authors chose to consider a value of half of the detection limit for the purpose of analysis.

The initial strategy planned for soil sampling was based on systematic sampling around a representative number of targets on ranges and also around hot spots (broken casings, UXOs or debris, etc.). Usually, surface soils are collected from the top 0-5 cm of soil. This strategy was successfully used in previous studies on antitank ranges, which showed very distinct patterns of contamination around targets [2]. However, the nature and type of firing exercises conducted in the Air Force ranges are different from those conducted in Army antitank ranges in the sense that the airplane, which is the firing point, is moving fast and represents a different situation compared to static firing positions or targets in Army ranges. Even if some air weapons are laser guided and, consequently, very precise, many air-dropped weapons are not guided and

precision around targets can be more difficult to achieve. For these reasons, two main sampling approaches were used, both based on the collection of composite samples, in order to decrease the high level of heterogeneity usually observed with explosives residues in such scenarios [2, 6].

The first sampling approach used a linear sampling pattern (Figure 5-1). This approach was used to evaluate whether the level of contamination by metals or energetic materials was following a pattern with distance from the target in the ranges. If firing activities led to the accumulation of contaminants in soils, higher concentrations should be found around targets, since most of the ammunitions fired or ordnances dropped were supposedly aimed at these targets. Therefore, composite samples were collected at distances of 20, 40, 60, 100, 120, and 140 percent of the distance from the entrance of the range to the target. Most of the time, there was an access road going directly to the targets in the middle of the ranges. This road was used for maintenance and cleanup so it was used to build transects (right and left of centerline) that were perpendicular to the road. Twenty or more increments were taken to build each composite. Transects were fixed with the help of the GPS. The GPS locations are reported in Table 5-1. The linear samples corresponded to the percent of the distance between the range entrance and the target. As an example, at 20 percent of the distance, samples were collected on each side of the road walking perpendicularly to the road using a GPS to keep on a straight line. A minimum of 20 surface sub samples taken from the top 0-2 cm of soil were collected to build each composite sample A and B corresponding to the right and left side of the road. The composites were built by walking 100-200 m. In some instances such as hot spots or other objects of interest, composite sampling was used that consisted of building the sample using discrete samples around the hot spot (20 minimum).

Figure 5-1. Linear soil sampling pattern used for composite sampling in ranges

The second sampling strategy is a new approach and consisted of sampling around targets by compositing samples taken in a circular pattern. This strategy, based on the circular sampling used at CFB Shilo, was used for specific target

evaluation. The strategy was modified to adapt to the specific context of air-toground targets and was designed to allow a comparison of the relative concentrations in front of and behind a target. A semi-circular pattern was used to collect composite samples at specific distances from the targets. This is illustrated in Figure 5-2. Twenty-six soil samples were collected around targets, one within each of the cells around the target. These cells are defined by three circles located at 10-, 30-, and 50-m radius of the target. Two composite samples (A1 and A2) were collected in hemispheres of the first 10-m-diameter ring (front and back of target). Eight equal-sized rectangles sampled between 10 and 30 m (B1-B8), and 16 between 30 and 50 m (C1-C16). Twenty or more increments were collected to build 800-g to 1.5-kg composite samples.

Figure 5-2. New circular soil sampling pattern designed for air-to-ground targets. The total number of samples around a target is 26

Wherever biomass samples were collected, the method consisted of building composite samples of indigenous living plants by randomly cutting various types of plants. A minimum of 20 to 30 subsamples of mixed biomass material were collected to build the different biomass samples, around targets, in transects or in rifle ranges. Only the upper part of the plants (without roots) was collected, since grazing animals rarely eat the roots of the plants as verified by consulting an expert from Environment Canada (Lucie Olivier, Environment Canada-Montréal). Metals could bioaccumulate either in the upper plant system or in the roots, depending on the solubility of the metals. Metals were evaluated by digesting the biomass samples using a standard procedure in nitric acid.

At the Jimmy Lake range, a practice target was used for the circular sampling and the linear sampling strategy was used for the 20-mm firing range. Composite soil samples were collected behind three targets in transects that were split into A and B (west and east) sections. Transects were perpendicular to targets at distances of 20, 40, 60, 80, and 100 percent of a 120-m range. In addition, samples of vegetation were taken just beyond the 120-m distance about 30 m in front of targets. The soil samples collected in this range were comprised of finegrained sand.

In Shaver River range, air dropping of 250-, 500-, and 1,000-lb high explosive (HE) bombs at stationary targets is done on a regular basis. Again, the circular strategy was applied. Also, duplicates taken within each of the three rings (one per ring) were collected. Downrange from the target, transects were made at 100, 200, 300, 400, and 500 m. Transects were split into two halves (A on one side of the road and B on the other side) and composite samples were collected over a 100-m transect on each side of a line running perpendicular to the road going to the target. The wheel sampling pattern was also used to collect surface samples some 12 ft away from the tank target, in composite domain A1 (W samples) [2]. Three depth samples were taken below sample W1 in the center of the wheel and were named W1 D1, D2, and D3 at depths between 5 and 10 cm, 10 and 15 cm, and 15 and 20 cm, respectively. Depth sampling was not performed until a large area had been cleared. Surface samples were taken between 0 and 5 cm. Small discrete samples were also collected at the surface using the wheel pattern and were named W2, W3, W4, W5, W6, and W7. As for the other ranges, the surface was covered with fine-grained sands; however, several chunks of HE that were tentatively identified by dissolution in acetone were picked up around the target. Some chunks were thought to be Tritonal (TNT and aluminum) and others TNT or Composition B. Burn areas on both sides of the road leaving the Shaver River Range were also sampled. Two composite samples named S-SR-OD were collected in an old burn area; one on the North side and one on the South side of that road. Again, fine sands dominated the samples.

The Alpha Range, in front of Primrose Lake, is a practice range for dropping bombs. This range was lightly covered with grasses growing in fine-grained sand. The concentric domain sampling approach was performed around the stationary target, which included composite sample duplicates, and composite vegetation samples from each ring (A, B, and C made from C4 and C13). Linear sampling was performed along transects (100 m each side of the access road) in front of the target going from the entrance of the range to the target at distances of 0, 200, 400, 600, 800, 1000, and 1200 m. Two biomass samples were taken at 800 m (LS 80 percent).

The Bravo Range in front of Primrose Lake is also a practice range for dummy bombs and rockets. Six dummy bombs and four rockets (CRV7) (2.75 in. diameter) were dropped/fired at the target just prior to sampling. Concentric domain sampling was performed around the target. (Note: All shots observed during the live firing were hitting the ground at distances smaller than 50 m from the target, two hits were at distances smaller than 10 ft from the target.) Three soil duplicates in the three circles (A, B, and C) were collected along with two biomass samples in rings A and B. Linear transects were collected 40, 60, 80, 100, 120, and 140 percent from the entrance of the range to the target, which was considered the 100 percent, for a 110-m range. Two hot spots that perhaps had propellant on the surface were sampled. One was a crater some 40 m up range, and the other was material on the surface in the A1 domain.

A specific sampling strategy was used in the CLAWR rifle range, which consisted of a series of numbered targets having conventional sand butts (berms) in front of them. Surface soils and one biomass sample were collected in front of the targets. Surface soils were collected from 0 to 10 cm deep, using stainless

steel spoons. Five composite surface soil samples were built of at least 20 subsamples and were collected in front of groups of three nearby targets (15 targets sampled). The biomass sample was collected by compositing at least 30 subsamples in the area in front of a group of four close targets (1-4) (Figure 5-3). In addition two composite samples were collected along firing point positions some 10 and 100 m uprange.

Figure 5-3. Soil sampling pattern designed for rifle range

Results and Discussion

A total of 193 soil, 16 biomass, and 4 surface water samples were collected during Phase I in August 2002. The parameters analyzed in soils were as follows: Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Hg, Mo, Ni, Se, Ag, Sr, Tl, Sn, U, V, and Zn. The parameters analyzed in biomass were as follows: Al, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V, Zn. The parameters analyzed in surface water were as follows: Al, Sb, As, B, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Se, Ag, Sr, Tl, Sn, Th, Ti, U, V, Zn and Zr. Thus, a total of 4,053 analyses were conducted for soils, 320 for biomass, and 108 for surface water samples. The results for plants correspond to the total amount of metals both bio-accumulated and deposited on the plants, since digestion of the total plants was accomplished. Analyzing leachates to discriminate between metals in and on plants was not judged necessary, since wildlife ingest the metals, in both cases by eating the entire plants. A total of 56 soil samples were collected by DCC during the preliminary phase in March 2002. Out of the 193 soil samples, 131 samples were analyzed for energetic materials. Ten parameters were screened for explosives, including the most common explosives RDX, HMX, and TNT, using the HPLC method, while nine parameters were screened using the GC/ECD method. No biomass samples were analyzed for explosives during Phase I.

The mean values for background samples were the mean of all collected backgrounds for each parameter measured. When results lower than detection limits were encountered for specific parameters, one-half the detection limit value for this parameter was chosen as the result for the calculation of the mean

value and for the comparison of all results with the background mean values. The results obtained in training areas were compared to the mean value of the background to which was added twice the standard deviation. This allowed the selection of results having values greater than the background means, while being statistically representative. Results are presented for each parameter instead of per sample to facilitate the analysis of the results, since trends can be easily seen for each parameter. Backgrounds were always tabulated first with mean, standard deviation, mean plus twice the standard deviation and Canadian Council of Ministers of Environment (CCME) threshold criteria values for each metal. Then, results for samples collected in the training areas were tabulated. Surface soil samples were compared to the most stringent agricultural CCME threshold levels for metals that were included in the latest published CCME quality guideline (see *<www.ccme.ca>*). For metals that were not included in the CCME list, results were compared to the mean values added to twice the standard deviation of all soil background samples and results exceeding this value are shown in blue font in Table 5-2. Even if not applicable to DND properties, the CCME agricultural soil criterion is the most stringent reference, and, therefore, it shows where contamination should be looked at first and monitored. When metal concentrations were above the agricultural criteria, they were also compared to the industrial soil criterion, which is the most permissive criterion. These results are shown in red font in the tables. For biomass, there are no CCME criteria. Results higher than the mean values added to twice the standard deviation are shown in blue font in Table 5-3. Metals concentrations in surface water samples exceeding the CCME water criteria, shown in red font, are presented in Table 5- 4. In these instances, the CCME aquatic life threshold criterion is the most appropriate value to use.

For Phase I, the analytical results obtained for the parameters tested in all types of samples showed no major detections related to the training activities. In soils, the accumulation of some heavy metals associated with ordnance was observed in some parts of ranges, but concentrations did not reach levels of concern. Phase I results clearly demonstrated no major problems associated with soil contamination except in a few locations.

During the preliminary phase in March 2002, 59 samples were analyzed for energetic materials according to the sampling described in the sampling strategy section. These samples were analyzed at DRDC-Valcartier using the GC/ECD method. The GPS locations for all these samples can be found in Table 5-1. No energetic materials were found in these samples with the exception of samples ssr-bombcirc-50m A and B and ssr-bombcirc-25m A in Shaver. These samples were composite samples collected in a circular pattern at 25- and 50-m radius from the Shaver River range target. TNT, amino TNT, and tetryl were found at levels between 0.3-2.0 ppb in these samples.

For Phase I, the results for energetic materials are presented in Table 5-6. In the four ranges, both linear transect patterns (between 20 and 140 percent of the range length at each 20-percent interval) and circular patterns around targets were used. Samples were analyzed for explosives. Moreover, hot spot samples (HS) were collected where munitions or munitions debris were encountered. These samples were named HS with the GPS locations where they were collected. All samples were composite samples built of at least 20 subsamples

either in linear transects, circles around targets, or circles around the hot spots. When munitions were visually observed, the samples were collected as near as possible to the UXO with subsamples around it.

Alpha Range

The Alpha Range is adjacent to Primrose Lake and is roughly 1.0 km long. This range was lightly covered with grasses growing in fine-grained sand. The concentric domain sampling approach was performed around the stationary target, which included composite sample duplicates, and composite vegetation samples from each ring (A, B, and C made from C4 and C13). Linear sampling was performed along transects (100 m each side) in front of the target going uprange at distances of 0, 200, 400, 600, 800, 1000, and 1200 m. Two biomass samples were taken at 800 m (LS 80 percent). In Alpha Range, 46 soil samples and 5 biomass samples were collected.

Soils. As shown in Table 5-2 A, B, and C, some parameters exceed the BGL value added to twice the standard deviation and are in blue font. Of the 21 parameters analyzed, only Be, Mo, Se, Ag, Tl, and Sn were not detected at values higher than the BGL in any samples collected on Alpha Range. All the other parameters were detected at values higher than the BGL. Out of the 46 soils samples, Sb (7 samples, 15 percent of all samples), As (27, 59 percent), Ba (3, 6.5 percent), Cd (2, 4.3 percent), Cr (12, 26 percent), Co (2, 4.3 percent), Cu (3, 6.5 percent), Fe (8, 17 percent), Pb (4, 8.7 percent), Hg (1, 2.2 percent), Ni (13, 2.8 percent), Sr (1, 2.2 percent), U (2, 4.3 percent), V (12, 26 percent), and Zn (1, 2.2 percent) concentrations were higher than the BGL added to twice the standard deviation. No metals were detected at concentrations higher than the CCME agricultural soil criteria. For each parameter having blue hits, a mean of these values was calculated and compared to the BGL added to twice the standard deviation and also to the CCME Agriculture Soil Quality Guideline (ASQGL) to determine if the levels of concentrations were closer to the BGL or to the CCME criteria. A complete list of these tendencies is as follows:

- Sb: mean 0.23: $1.8 \text{ X} > \text{BGL}$ and $87 \text{ x} < \text{CCME}$ ASQGL
- As: mean 1.8: 1.6 x > BGL and 6.6 x < CCME ASQGL
- Ba: mean 60.2 : 1.1 $x > BGL$ and 12.5 $x < CCME$ ASQGL
- Cd: mean 1.04 : 2.9 x > BGL and 1.3 x < CCME ASQGL
- Cr: mean 12.8: $1.3 \text{ x} > \text{BGL}$ and $5 \text{ x} < \text{CCME}$ ASQGL
- Co: mean 5.0: 1.2 x > BGL and 8 x < CCME ASQGL
- Cu: mean 11.2: $1.6 \text{ x} > \text{BGL}$ and $5.1 \text{ x} < \text{CCME}$ ASQGL
- Fe: mean 10560: $1.2 x > BGL$, no ASQGL for Fe
- Pb: mean 4.25 : 1.3 x > BGL and 16.5 x < CCME ASQGL
- Hg: mean 0.084: $2.4 \text{ x} > \text{BGL}$ and $79 \text{ x} < \text{CCME }$ ASQGL
- Ni: mean 7.7: $1.3 \text{ x} > \text{BGL}$ and $6.5 \text{ x} < \text{CCME}$ ASQGL
- Sr: mean 22.3 : $2 \text{ x} > \text{BGL}$, no ASQGL for Sr
- U: mean 0.55: $1.0 x > BGL$, no AQGL for U
- V: mean 18: $1.3 \text{ x} > \text{BGL}$ and $7 \text{ x} < \text{CCME}$ ASQGL
- Zn: mean $1.8: 1.5 x > BGL$ and $4 x <$ CCME ASQGL

As can be seen, most of the values are at 1-3 times higher than the background levels (BGL) added to twice the standard deviation, but all parameters are below the agricultural soil criteria. No anomalies were observed for the duplicate samples, i.e., the values for the duplicates were similar to values for the original sample. The impact of the activities is measurable, but at a very low extent. No action is required on this site.

Biomass. The results for the biomass samples are found in Table 5-3. Every biomass sample analysis was done twice, and some parameters are missing in the second analysis. It is probable that the analytical lab repeated some of the analyses on separate subsamples. On many occasions, the values for the same sample are quite different. Nevertheless, the analysis was done even if it was stated earlier that the number of background samples was inadequate to realize a valid statistical evaluation. If one examines Table 5-3, some parameters are seen to exceed the BGL value added to twice the standard deviation and are in blue font. Of the 20 parameters analyzed, only Al, Ba, Cd, Cr, Cu, Fe, V, and Zn were detected at values higher than the BGL. A complete list of the parameters and the number of hits is as follows:

• Al: 3 out of 5 results exceeded the BGL added to twice the standard deviation

• Ba: 7 out of 10 results exceeded the BGL added to twice the standard deviation

• Cd: 1 out of 5 results exceeded the BGL added to twice the standard deviation

• Cr: 1 out of 10 results exceeded the BGL added to twice the standard deviation

• Cu: 4 out of 10 results exceeded the BGL added to twice the standard deviation

• Fe: 1 out of 5 results exceeded the BGL added to twice the standard deviation

• V: 1 out of 10 results exceeded the BGL added to twice the standard deviation

• Zn: 1 out of 5 results exceeded the BGL added to twice the standard deviation

All of the parameters that exceeded the BGL added to twice the standard deviation in biomass samples also exceeded the BGL in soils. It is highly possible that these metals are preferentially extracted from the soils and may represent a risk for wildlife.

Energetic materials. For the purposes of this report, one can consider that energetic compounds fall into two classes, those that are related to propellants and those related to high explosives. Nitroglycerine (NG), dinitrobenzene (DNB), dinitrotoluene (DNT), and trinitrobenzene (TNB) are either major ingredients or impurities in various types of propellants such as those used in rocket motors. Usually, rockets use either double-based propellants composed of nitrocellulose and nitroglycerine or a thermoset polymeric matrix based on hydroxyl terminated polybutadiene containing ammonium perchlorate as the oxidizer. Perchlorate analyses should be performed; however, these analyses are costly. The singlebased propellants also contain DNT as a plasticizer, and impurities such as DNB and TNB come from the synthesis of energetic materials starting from toluene containing benzene as an impurity.

High explosives used by both Canada and the United States generally contain either TNT (2,4,6-trinitrotoluene) or mixtures of TNT with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine), or for some older munitions, tetryl. Most of the air weapons contain TNT with aluminum (tritonal explosives). The most powerful weapons contain Composition B (TNT with RDX) or octol (TNT with HMX). When UXOs are found on sites, they are often blown in place (BIP) using C-4, a mixture of RDX with a polymer. These BIP operations often spread explosives into the environment [11]. In Alpha Range most of the samples did not contain detectable concentrations of propellant-related compounds (Table 5-6A). 2,4-DNT was detected by CRREL in samples around the target in sectors B-3, C-12, C-16, and at LS 100 percent A at 3, 2, 4 and 3 ppb, respectively. The samples in which 2,4- DNT were found also had much higher concentrations of TNT. The 2,4-DNT detected in these samples is likely to have originated as an impurity in TNT. The concentrations of 2,4-DNT were low and did not represent a problem.

TNT was found in almost all samples collected at the Alpha Range at concentrations varying from 2 to 1100 ppb. RDX was also detected in more than half of these samples, but the concentrations were always less than 50 ppb. The highest RDX concentration samples do not correlate with the samples with the highest TNT concentrations, possibly indicating that the sources of the two residues may be different or more likely that the transport properties are different. It is known that RDX moves more rapidly than TNT in soil.

Finding explosives in nearly all of the samples from Alpha Range was surprising since the Alpha Range is supposedly used only for practice bombs. Some practice ordnance has spotting charges, though, and these residues could have resulted from these spotting charges. If residues were found at this range, the highest concentrations should have been near the target in circle A, then in B, then in C. This was not the case because in all three circles, TNT concentrations of the same magnitude were encountered at about 400 ppb. In fact, one of the highest concentrations of TNT for Alpha Range samples was found for a sample in the C circle at C 12.

For samples collected using the linear sampling strategy, the concentrations should increase as one moves toward the target. Indeed, the highest concentrations were found at the 100-percent linear transect, which is nearest the target, but for other samples no correlation between concentration and location appears to exist. The concentrations in the linear transects were quite low except at the entrance of the range, which was very surprising. It is possible that an open detonation (OD) operation on a UXO close to this point was done and spread explosives on this side of the range (LS 0 percent A). In linear transects, the mean concentrations of TNT were around 100 ppb.

RDX was found in almost all samples from the circular approach, but in very few of the linear transect samples. One explanation, which is also valid for all of the other explosives, is the fact that the linear transects were built by walking

away from the center line of the range, and in doing so, walking away from the direction of firing. Furthermore, since the samples were collected by walking a 100-m distance, the concentrations were possibly diluted compared to the circle where the samples were collected in a smaller area. RDX concentrations varied from 5 to 57.4 ppb in the circular samples, while they varied from 4 to 21 ppb in the transect samples. Amino DNTs, which result from TNT degradation, were found at concentrations of 0.98 to 29.74 ppb in circular samples and at concentrations of 7 to 21 ppb in linear samples. The highest concentrations were for the 100-percent samples, which were near the target. The highest hit for amino DNTs in the linear transect corresponded to the highest hit for TNT, which makes sense since TNT is the parent compound. Tetryl and HMX were not detected except for HMX in LS 80 percentB at 123 ppb.

In most of the analyses, good correlation between CRREL and DRDC-Valcartier analyses was found, the values being always in the same order of magnitude (Table 5-6 A and B). As explained in the analytical methods section, on some occasions, discrepancies occurred between results from the laboratories, such as in B2 and C8, which shows that the distribution of analytes in the samples was often very heterogeneous. Even with good preparation of the samples with a homogenization process using acetone, small chunks of analyte could be found in one part of the sample, while another part did not contain any explosives due to preferential crystallization during evaporation of the solvent or solvent saturation. The distribution of chunks in heterogeneous samples is the most important factor to explain results divergence. This is particularly true for duplicate samples. As an example, in the analyses for LS 100 percent A and LS 100 percent A dup, both samples were collected almost at the same locations and TNT results varied from 11 to 1100 ppb, a factor of a hundred difference. The same situation was encountered with sample A2 and A2 dup. This result is explained by the fact that, while collecting these samples, one might have collected a small explosive chunk in one of the samples, but not in the other, resulting in very different concentrations upon analysis. By looking at the maximum concentrations of explosives at that range, which for TNT was 1,100 ppb, and considering that the ecotoxicological threshold criteria developed by the Biotechnology Research Institute (BRI) for TNT is 80 ppm for soils, the Alpha Range concentrations are far below that level; therefore, no action is required for that range.

Bravo Range

The Bravo Range, also adjacent to Primrose Lake, is composed mainly of sandy soil with vegetation. Live firing at this site occurred just before sampling and all of the weapons hit the ground in front of the target at distances encompassed by the circular strategy, supporting the appropriateness of this strategy. Concentric domain sampling was performed around the target. Three soil duplicates in the three circles (A, B, and C) were collected along with two biomass samples in circles A and B. Linear transects were collected at 40, 60, 80, 100, 120, and 140 percent uprange, for a 1.1-km-long range (Figure 5-1). Two sites that perhaps had propellant on the surface were sampled. One was a crater some 40 m uprange (HS- 0560425), and the other was in the A1 domain (HS-0560345).

Soils. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font (Table 5-2 A, B and C). Of the 21 parameters analyzed, only Sb, Cd, Cu, Pb, and V were detected at values higher than the BGL or the ASQGL. Of the 39 soil samples, Sb (3 samples, 7.7 percent of all samples), Cd (33, 84.6 percent), Cu (5, 13 percent), Pb (7, 18 percent) and V (10, 26 percent) concentrations were higher than the BGL added to twice the standard deviation or the ASQGL. Cadmium was detected at concentrations higher than the CCME agricultural soil criteria (12 samples). For each parameter having hits, a mean of these values was calculated and compared to the BGL added to twice the standard deviation and also to the CCME ASQGL to determine whether the levels of concentrations were closer to the BGL or to the CCME criteria. A complete list of these tendencies is as follows:

- Sb: mean 0.4: $3.1 \text{ x} > \text{BGL}$ and $50 \text{ x} < \text{CCME}$ ASQGL
- Cd: mean 1.12: $3.1 \text{ x} > \text{BGL}$ and 12 samples $> \text{CCME ASQGL}$
- Cu: mean 8.6: 1.2 x > BGL and 7.3 x < CCME ASOGL
- Pb: mean 4.6: $1.4 x > BGL$ and $15 x < CCME$ ASQGL
- V: mean 20.9: $1.5 \text{ x} > \text{BGL}$ and $6.5 \text{ x} < \text{CCME}$ ASQGL

As can be seen, fewer parameters exceeded the BGL compared to the Alpha Range, but the situation was similar. Most of the values were 1-3 times higher than the BGLs added to twice the standard deviation, but all parameters except cadmium respected the agricultural soil criteria. No anomalies were observed for the duplicate samples; values for the duplicates were similar to values for the original sample. The concentrations are lower at this site than in the Alpha Range, but a cadmium problem exists. Nevertheless, even if cadmium concentrations were higher than the ASQGL criterion, concentrations exceeded neither the residential nor the industrial soil criterion. No action is required on this site.

Biomass. Every biomass sample was analyzed twice. Not only were values for the same samples often quite different, but, some parameters detected in one analysis were undetected in the second analysis (Table 5-3). These data illustrate the extreme heterogeneity in the distribution of contamination. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font. Of the 20 parameters analyzed, only Al, Ba, Cd, Cr, Cu, Fe, Ni, V, and Zn were detected at values higher than the BGL. A complete list of the parameters and the number of hits is as follows:

• Al: 2 out of 2 results exceeded the BGL added to twice the standard deviation

• Ba: 4 out of 4 results exceeded the BGL added to twice the standard deviation

• Cd: 2 out of 2 results exceeded the BGL added to twice the standard deviation

• Cr: 1 out of 4 results exceeded the BGL added to twice the standard deviation

• Cu: 2 out of 4 results exceeded the BGL added to twice the standard deviation

• Fe: 2 out of 2 results exceeded the BGL added to twice the standard deviation

• Ni: 2 out of 4 results exceeded the BGL added to twice the standard deviation

• V: 4 out of 4 results exceeded the BGL added to twice the standard deviation

• Zn: 2 out of 4 results exceeded the BGL added to twice the standard deviation

All of the parameters that exceeded the BGL added to twice the standard deviation in biomass samples also exceeded the BGL in soils. It is highly possible that these metals are preferentially extracted from the soils. The situation in Bravo Range is almost identical to the one in Alpha Range, except for cadmium. These two ranges are located very close to each other, and the same types of activities were very likely conducted on these two ranges.

Energetic materials. Analytical results for analysis of explosives- and propellant-related compounds are given in Table 5-7. Of the propellant-related compounds, only NG was detected by CRREL for samples near the target (samples A-1, B-2, B-4, B-6, and B-8). NG was also detected in one other location that was suspected of containing propellants. The concentrations were, respectively, 27, 18, 22, 27, 39, and 19 ppb. The highest hit was found at B-8, which is close to the target. These concentrations are low and do not represent a problem.

TNT was found in almost all samples from Bravo Range at concentrations ranging from 3 to 298 ppb. This result is similar to the Alpha Range results, but the TNT concentrations were lower and only one sample had a detectable concentration of RDX. It is interesting to note that, unlike the Alpha Range sample, no detectable levels of the amino-DNT transformation products were observed. Considering that the Bravo Range geology is similar to that encountered in Alpha, this may indicate that the residues of TNT detected at the Bravo Range were very recently deposited and had no time to transform prior to sample collection. As noted above, live fire training occurred just prior to sampling, and was probably the source of these residues.

The results for energetic compounds at the Bravo Range correspond well with the results for metals analyses, which demonstrated that this site was similar to Alpha Range, but less contaminated. The same situation was observed for explosives, indicating that this site is less used than the Alpha Range. Again, the concentrations in the circular samples were higher than in the linear transect samples, indicating that the contamination is restricted to the area around the target and has not spread everywhere on the range. In this case, the C circle seems to contain more TNT than the B or A circles. TNT concentrations in the C circle were around 100-150 ppb. One of the highest hits was found into the C-15 sample. Sampling a D circle at a future visit to see if concentrations are decreasing farther away from the target seems prudent. Looking at the linear sampling strategy, the concentrations were lower than in the circular samples with the highest TNT concentration again at 100 percent. Looking at all of the results, however, we do not see any progression while going towards the target. In linear transects the mean concentrations were around 20 ppb, which is five times lower than on Alpha Range.

RDX was detected in only one sample at the linear transect 100 percent A by DRDC at a concentration of 5 ppb. CRREL did not detect RDX in this or any other Bravo Range samples. Since DRDC-Valcartier did not have the confirmation column for the GC analyses, the RDX detected by DRDC was possibly an interference rather than RDX. Tetryl and HMX were not detected by either laboratory for Bravo Range samples. Based on these results, no action is required at this range.

Jimmy Lake Range

At the Jimmy Lake Range, a practice target was sampled using the concentric circular sampling, and the linear sampling strategy was used for the 20-mm firing range. Composite soil samples were collected behind three targets in transects that were split into A and B (west and east) sections. Transects were perpendicular to targets at distances of 20, 40, 60, 80, and 100 percent of a 120-m range. In addition, samples of vegetation were taken just beyond 120 m and at about 30 m in front of targets. The soil samples collected in this range were finegrained sand. The Jimmy Lake Range is located between Jimmy Lake and Primrose Lake. At the Jimmy Lake Range, 43 soil samples and 6 biomass samples were collected.

Soils. Some parameters exceeded the background level value added to twice the standard deviation (BGL) and are shown in blue font in Tables 5-2A, B, and C. Of the 21 parameters analyzed, only Be, Hg, Tl, and Sn were not detected at values higher than the BGL in any samples collected in Jimmy Lake Range. All of the other parameters were detected at values higher than the BGL or the ASQGL, and on some occasions were higher than the Industrial Soil Criteria. In the 43 soil samples, Sb (2 samples, 4.7 percent of all samples), As (38, 88 percent), Ba (25, 58 percent), Cd (29, 67 percent), Cr (29, 67 percent), Co (1, 2.3 percent), Cu (43, 100 percent), Fe (17, 39.5 percent), Pb (29, 67.4 percent), Hg (1, 2.2 percent), Mo (1, 2.3 percent), Ni (29, 67.4 percent), Se (1, 2.3 percent), Ag (2, 4.7 percent), Sr (1, 2.3 percent), U (23, 53 percent), V (29, 67 percent) and Zn (29, 67 percent) concentrations were higher than the BGL added to twice the standard deviation or the ASQGL or the Industrial Soil Criteria. For each parameter having hits, a mean of these values was calculated and compared to the BGL added to twice the standard deviation and also to the CCME ASQGL to determine whether the concentrations were closer to the BGL or to the CCME criteria. These tendencies were as follows:

- Sb: mean 0.20: 1.5 x > BGL and 100 x < CCME ASQGL
- As: mean 1.73: $1.5 x > BGL$ and $6.9 x < CCME$ ASQGL
- Ba: mean 62 : 1.1 $x > BGL$ and $12 x < CCME$ ASQGL

• Cd: mean 8.5: $23.6 \text{ x} > \text{BGL}$ and $6 \text{ x} > \text{CCME}$ ASQGL, (29 samples exceeded)

- Cr: mean 14.6: 1.5 x > BGL and 4.4 x < CCME ASQGL
- Co: mean 5.0: $1.2 x > BGL$ and $8 x < CCME$ ASQGL
- Cu: mean 58: 16 samples at 1.2 to 2.4 x > CCME ASQGL and 5 samples

at 1.1 to 1.7 x $>$ industrial soil criteria

• Fe: mean 9138: $1.1 x > BGL$, no ASQGL for Fe

- Pb: mean 10: $3.1 \text{ x} > \text{BGL}$ and $7 \text{ x} < \text{CCME}$ ASQGL
- Mo: mean 0.8: 1.2 x > BGL and 6.3 x < CCME ASQGL
- Ni: mean $13.3: 2.2$ x > BGL and 3.8 x < CCME ASQGL
- Se: mean 1.0: $1.8 \text{ x} > \text{BGL}$ and equal to CCME ASQGL
- Ag: mean 3.0: $2 x > BGL$ and $6.6 x < CCME$ ASQGL
- Sr: mean 16.9: $1.3 x > BGL$, no ASQGL for Sr
- U: mean 0.55: 1.1 x > BGL, no AQGL for U
- V: mean $68: 4.9$ x $>$ BGL and 1.9 x $<$ CCME ASQGL

Zn: mean 89: S-JL-T1-C15 concentration is at 1.8 x > CCME ASQGL

and 1.04 x industrial soil criteria.

Most of the values were 1-23.6 times higher than the BGLs added to twice the standard deviation. Twenty-nine samples had Cd concentrations higher than the ASQGL, 16 had Cu concentrations higher than the ASQGL, with 5 higher than the Industrial Soil Criteria. One sample had Zn concentrations higher than the Industrial Soil Criteria. The impacts of training activities on Jimmy Lake are clearly important; therefore, more sampling will be done to complete the evaluation at this range.

Biomass. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font in Table 5-3. Of the 20 parameters analyzed, only Al, Ba, Cd, Cr, Cu, Fe, Mo, Ni, Th, U, V, and Zn were detected at values higher than the BGL. A complete list of the parameters and the number of hits was as follows:

• Al: 3 out of 5 results exceeded the BGL added to twice the standard deviation

• Ba: 1 out of 11 results exceeded the BGL added to twice the standard deviation

• Cd: 3 out of 6 results exceeded the BGL added to twice the standard deviation

• Cr: 1 out of 11 results exceeded the BGL added to twice the standard deviation

• Cu: 7 out of 11 results exceeded the BGL added to twice the standard deviation

• Fe: 3 out of 6 results exceeded the BGL added to twice the standard deviation

• Mo: 2 out of 6 results exceeded the BGL added to twice the standard deviation

• Ni: 1 out of 11results exceeded the BGL added to twice the standard deviation

• Th: 1 out of 6 results exceeded the BGL added to twice the standard deviation

• U: 1 out of 6 results exceeded the BGL added to twice the standard deviation

• V: 5 out of 11 results exceeded the BGL added to twice the standard deviation

• Zn: 2 out of 6 results exceeded the BGL added to twice the standard deviation

All of the parameters that exceeded the BGL added to twice the standard deviation in biomass samples also exceeded the BGL in soils. It is highly possible that these metals are preferentially extracted from the soils. Biomass has a great tendency to accumulate the same parameters in Alpha, Bravo and Jimmy Lake Ranges, but at higher concentrations in Jimmy Lake, which is normal since the levels of metals concentrations are higher in Jimmy Lake.

Energetic materials. On Jimmy Lake Range, most of the samples contained the propellant-related compound NG (Table 5-7). Concentrations of NG in samples from the Jimmy Lake Range varied from 21 to 816 ppb. These results indicate propellant residues deposited on the site near Jimmy Lake. DNT was also detected in B2 and C12 at 3 and 2 ppb, respectively, which was quite low. TNT was detected in all of the samples from the Jimmy Lake Range with concentrations varying from 2 to 216 ppb. CRREL did not detect any other explosives in Jimmy Lake samples, but DRDC-Valcartier found RDX in one sample, C-12, at 81 ppb, and amino DNT in another sample at 8 ppb. Since these peaks were not confirmed, these small hits were possibly interferences from the soil matrix. Tetryl and HMX were not detected by either laboratory. The Jimmy Lake Range was sampled more intensively at the next visit in August 2003.

Shaver River Range

Shaver River Range is close to the Shaver River and remote from Jimmy Lake. At the Shaver River Range, air dropping of 250-, 500-, and 1000-lb HE bombs at the stationary target is a regular occurrence. Again, the circular strategy was applied. Also, three duplicates, one taken within each of the three rings, were collected. Downrange from the target, transects were made at 100, 200, 300, 400, and 500 m. Transects were split into two halves (A and B) and composite samples were collected over a 100-m transect on each side of the access road perpendicular to a line running from the entrance of the range to the target. The wheel sampling pattern was also used to collect samples 12 ft from the tank target in composite domain A1 (W sample) [2]. Three depth samples were taken below sample W1 in the center of the wheel. Deep sampling was not performed until a large area had been cleared. Surface samples were taken between 0 and 5 cm, and deep samples were taken between 5 and 10 cm, 10 and 15 cm, and 15 and 20 cm. As for the other ranges, the surface was covered with fine-grained sands; however, several chunks of HE, which were tentatively identified by dissolution in acetone, were picked up around the target. Some chunks were thought to be tritonal (TNT and aluminum) and others TNT or Composition B. In Shaver River Range, 47 soil samples and 1 biomass sample were collected. In this range, the efforts were concentrated mainly on the analyses of energetic materials, since this range was the one used mainly for live firing. The area surrounding the target position at the Shaver River Range was tilled to minimize the vegetation and reduce the chance of the live-fire activities initiating a forest fire.

Soils. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font in Table 5-2 A, B, and C. Of the 21 parameters analyzed, only Sb, Cd, Cu, Pb, Hg, and Zn were detected at values higher than the BGL or the ASQGL, and, on some occasions, higher than the

Industrial Soil Criteria. In the 47 soil samples, Sb (8 samples, 17 percent of all samples), Cd (34, 72 percent), Cu (21, 44.7 percent), Pb (32, 68 percent), Hg (1, 2.1 percent), and Zn (6, 13 percent) concentrations were higher than the BGL added to twice the standard deviation or the ASQGL or the Industrial Soil Criteria. For each parameter having hits, a mean of these values was calculated and compared to the BGL added to twice the standard deviation (BGL) and also to the CCME ASQGL to determine whether the concentrations were closer to the BGL or to the CCME criteria. A complete list of these tendencies is as follows:

• Sb: mean $0.27: 2 \text{ x} > \text{BGL}$ and $74 \text{ x} < \text{CCME}$ ASQGL, one hit in S-SR-T-C3 exceeded the industrial soil criteria at 80.80 ppm

• Cd: mean 1.8: $5 x > BGL$ and $5 x > CCME$ ASOGL, (23 samples exceeded)

- Cu: mean 12.5: $1.8 \text{ x} > \text{BGL}$ and $5 \text{ x} < \text{CCME }$ ASOGL
- Pb: mean 12.3: $3.9 \text{ x} > \text{BGL}$ and $5.7 \text{ x} < \text{CCME }$ ASOGL
- Zn: mean 30.91 : 1.1 $x > BGL$ and 5.9 $x < CCME$ ASOGL

Most of the values are 1-5 times higher than the background levels added to twice the standard deviation. Twenty-three samples had Cd concentrations higher than the ASQGL; one sample had Sb concentration higher than the Industrial Soil Criterion. This range had fewer metals at concentrations higher than the BGL added to twice the standard deviation, and for most of the hits, they were similar in impact to the ones observed in Alpha Range. Again, Cd is seen at higher concentrations and Sb had one concentration at a very high concentration; however, this can be an anomaly from the laboratory. This sample was recollected in August 2003. The impacts by metals on this range are clearly less important than on the Jimmy Lake Range.

Biomass. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font in Table 5-3. Of the 20 parameters analyzed, only Cd, Cu, Fe, Th, and Zn were detected at values higher than the BGL in the only sample collected at the Shaver River Range. Cadmium was very high, at a concentration of 10 times the BGL. All these data will be reexamined when more biomass background samples are available following the August 2003 sampling event. All of the parameters that exceeded the BGL added to twice the standard deviation in biomass samples also exceeded the BGL in soils, except for Sb and Fe. Thorium was not analyzed in soils. Collection of additional biomass samples during the August 2003 sampling effort was planned. However, vegetation was tilled under just prior to the event.

Energetic materials. All of the soil samples collected at the Shaver River Range were analyzed for energetic materials. The transect samples from the Shaver River Range were analyzed using the GC-ECD method (Table 5-7) as were those from the Alpha and Bravo Ranges. The soil samples from the target area, however, were analyzed using the RP-HPLC method (Table 5-8), because much higher concentrations were expected in these samples.

For the transect samples, fairly low TNT concentrations were found over much of the range, except near the target (80-percent and 100-percent samples), where much higher concentrations of TNT were found (Table 5-7). Where high

(ppm) concentrations of TNT were found, detectable concentrations of 2,4-DNT, 2,6-DNT, and the amino-DNTs were also found. These compounds are either manufacturing impurities or environmental transformation products of TNT.

The TNT concentrations for the soil samples collected in a circular pattern around the target were much higher than the concentrations found in transects samples (Table 5-8, note values are in ppm in this table). Concentrations above 50 ppm were found in samples from the A, B, and C rings, with the highest concentration (332 ppm) for sample location C11. Here again, much lower concentrations of TNT-related compounds, such as 2,4-DNT, 2,6-DNT, TNB, 2A-DNT, and 4-ADNT, were found in these samples. In a few samples for the target area, very low concentrations of RDX and HMX (always less than 1.6 ppm) were found, but neither RDX nor HMX were detected in the samples that contained the highest concentrations of TNT. Thus the source of the small amount of RDX found on the Shaver River Range appears to be different from the source of the TNT. The source of TNT at this range is thought to be the tritonal used as the high explosive in Air Force bombs.

Tetryl was also detected in the circular samples at B7, C4 and C7 at concentrations of 130, 320 and 70 ppb, respectively. In linear transect samples, tetryl was detected only in LS-100 percent B at 98.8 ppb. HMX was detected in many circular samples mainly in B and C circles at concentrations ranging from 130 to 310 ppb. HMX was also found in linear transect samples LS-40 percent A and LS-100 percent B at concentrations of 20.4 and 53.8 ppb, respectively. It is strange to find HMX in more samples than RDX. It is possible that anti-tank weapons were fired at the tank target at the Range at some point in the past, which would explain HMX being found more frequently than RDX. It should be reemphasized, though, that the concentrations of RDX and HMX are quite low at the Shaver River Range, even in the relatively few samples where they were detected.

TNT and the amino-DNTs were detected in every surface wheel sample collected in front of the target and in the depth samples collected in the center of the wheel pattern as well. Surprisingly, the highest TNT concentration in the wheel samples was found in sample D4 at a depth of 15-20 cm. This phenomenon had been observed in other sites and has been explained by suggesting that explosives crystals can move downward by a sieving action due to vibrations from repeated detonations. At Shaver River Range, though, the higher concentration at depth may be due to the soils having been tilled, perhaps depositing crystals of TNT deeper in the profile. Concentrations of TNT in the seven surface samples collected in the wheel pattern vary from 6.6 to 56.4 ppm, a factor of about 9, indicating substantial short-range variability in surface soils concentration because all seven samples were collected within a 4-ft circle.

The concentrations of explosives (mainly TNT) at the Shaver River Range are much higher than in the other ranges sampled at Cold Lake. Most of the explosives-related compounds were found in almost all the samples except for RDX and HMX that were found at very low concentrations. TNT was the most important contaminant. Looking at the maximum concentrations of explosives at the Shaver River Range, especially for example TNT at 500 ppm, the concentration is above the ecotoxicological criteria of 80 ppm. Fortunately, TNT

has a great tendency to transform into metabolites that react with the organic matter of the soils and the contamination stays stabilized on the site. A hydrogeological study should be done at this site to see if RDX has not already moved towards the groundwater. The absence of RDX in most of the bombs used by the Air Force makes it unlikely.

Open Detonation (OD) Area

The OD area is 1 km from the entrance of the Shaver River Range. Materials are burned or detonated at two locations. Burn areas on both sides of the road leaving the Shaver River Range were sampled. Two composite samples were collected in an old burn area on the north side and one on the south side of that road. Again, fine sands dominated the soils.

Soils. No parameters exceeded the background level value added to twice the standard deviation (BGL) (Table 5-2 A, B,and C). This is not surprising since this area was quite clean of metal debris.

Biomass. No biomass samples were taken in this area.

Energetic materials. 2,4 DNT was detected in OD-3 at 540 ppb, and NG was detected in OD-1 and OD-2 at 17.8 and 14.9 ppb, respectively (Table 5-7). The presence of these compounds can be the result of the burning of propellants. Open burning of propellants has been demonstrated to be a dirty process [13]. Discussions with the Department of National Defence (DND) headquarters are ongoing to address the problem of open burning of propellants. Solutions were proposed and are under evaluation to solve this problem.

TNT was also found in all three of the OD samples at concentrations of 14 to 400 ppb, which are not very high. Concentrations of amino-dinitrotoluenes were detected in OD-2. These explosives are transformation byproducts of TNT that are likely forming after TNT deposition. Clearly, this area is not impacted by explosives.

Rifle range

The rifle range in CLAWR consists of a series of numbered targets having conventional sand butts (berms) in front of them. A specific sampling strategy was used for the rifle ranges. Surface soils and one biomass sample were collected in front of the targets. Surface soils were collected from 0 to 10 cm deep, using stainless steel spoons. Five composite surface soil samples were built of at least 20 subsamples and were collected in front of groups of three nearby targets (15 targets sampled). The biomass sample was collected by compositing at least 30 subsamples in the area in front of a group of four close targets (1-4). In addition, two composite samples were collected along firing point positions 10 and 100 m uprange.

Soils. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font in Table 5-2 A, B, and C. Of the 21

parameters analyzed, only As, Be, Cd, Mo, Se, Ag, Sr, Tl, Sn, and Zn were not detected at values higher than the BGL in any samples collected in the rifle range. All of the other parameters were detected at values higher than the BGL. In the 8 soil samples, Sb (3 samples, 37.5 percent of all samples), Ba (1, 12.5 percent), Cr (1, 12.5 percent), Co (1, 12.5 percent), Cu (2, 25 percent), Fe (1, 12.5 percent), Pb (6, 75 percent), Hg (1, 12.5 percent), Ni (1, 12.5 percent), U (1, 12.5 percent), and V (1, 12.5 percent) concentrations were higher than the BGL added to twice the standard deviation. No metals were detected at concentrations higher than the CCME Agricultural Soil Criteria. For each parameter having blue hits, a mean of these values was calculated and compared to the BGL added to twice the standard deviation (BGL) and also to the CCME ASQGL to determine whether the levels of concentrations were closer to the BGL or to the CCME criteria. These tendencies were as follows:

- Sb: mean $0.67: 5 \text{ x} > \text{BGL}$ and $30 \text{ x} < \text{CCME}$ ASQGL
- Ba: mean 62.1 : 1.1 $x > BGL$ and 12 $x < CCME$ ASQGL
- Cr: mean 13: $1.4 \text{ x} > \text{BGL}$ and $4.9 \text{ x} < \text{CCME }$ ASQGL
- Co: mean 5.0: $1.2 x > BGL$ and $8 x < CCME$ ASQGL
- Cu: mean 12.5: $1.8 \text{ x} > \text{BGL}$ and $5 \text{ x} < \text{CCME}$ ASQGL
- Pb: mean 12.3: $3.9 \text{ x} > \text{BGL}$ and $5.7 \text{ x} < \text{CCME }$ ASQGL
- Hg: mean 0.058: 1.7 x > BGL and 114 x < CCME ASQGL
- U: mean 0.61 : 1.2 x > BGL, no ASQGL for U
- V: mean 18.7: $1.4 \text{ x} > \text{BGL}$ and $7 \text{ x} < \text{CCME }$ ASOGL

Most of the values are 1-5 times higher than the background levels added to twice the standard deviation, but all parameters respect the Agricultural Soil Criteria. No anomalies were observed for the duplicate samples; the values for the duplicates are similar to the original sample. The impact of the activities is measurable, but at a low extent compared to other sites [28]. As usual in rifle ranges, lead concentrations are higher than concentrations of other metals. No Cd problem was detected at this range. No action is required on this site.

Biomass. Some parameters exceeded the BGL value added to twice the standard deviation and are shown in blue font in Table 5-3. Of the 20 parameters analyzed, only Al, Ba, Fe, and Pb were detected at values higher than the BGL. All of the parameters that exceeded the BGL added to twice the standard deviation in biomass samples also exceeded the BGL in soils. Nevertheless, the accumulation of these metals was not extensive, being generally 1.4 times the BGL added to twice the standard deviation.

Energetic materials. No energetic materials analyses were done in this range, since no energetic materials are typically used in this type of range.

Surface water

Four surface water samples were collected at Primrose Lake, Jimmy Lake, Shaver River, and a last one in a pond containing ammunition and water at Shaver River Range. Some parameters exceeded the CCME water quality guidelines (WQGL) and are shown in red font in Table 5-4. Of the 27 parameters

analyzed, only Sb, Cd, Fe, Mn, Se, and Ag were detected at values higher than the WQGL. In the four surface water samples, Sb (1 sample, 25 percent of all samples), Cd (4, 100 percent), Fe (3, 75 percent), Mn (1, 25 percent), Se (4, 100 percent), and Ag (1, 25 percent) concentrations were higher than the WGQL. When available, the aquatic life criteria were used, but on some occasions, drinking water or irrigation criteria were the only available WQGL criteria (see Table 5-4 footnote). In Jimmy Lake, Sb was detected at 9 ppb, which exceeds a CCME interim concentration value for drinking water. Cd and Se are shown in red in Table 5-4 because the WQGL criteria are lower than half the detection limit. A value half the detection limit was used when the metals were not detected, which resulted in red values, but these metals were simply not detected. Fe was detected in all samples, except in Jimmy Lake, at concentrations higher than the aquatic life criteria. However, this can be a regional characteristic. Since background surface water was not available for comparison, nothing can be concluded for these detections. Mn was detected at 1350 ppb in the pond in Shaver River Range. This detection represents a local impact not representative of the area, since munitions at the bottom of the pond could be the source of this metal. Finally, Ag was found in Jimmy Lake at twice the aquatic life criteria. This value was verified in August 2003 when more sampling was done in Jimmy Lake.

Global Results in All Ranges

Generally, the levels of metals in soils on the four ranges were quite low. Most of the metal exceedances were no more than two times the value of the BGL added to twice the standard deviation. Furthermore, concentrations were typically far below the ASQGL. Some metals systematically present at high concentrations, such as Cd, Cu, and Zn, can be related to firing activities. Nevertheless, most of the values were quite low. The soil background values at Cold Lake were very low compared to those observed in Québec Province. A comparison of soil background values at Cold Lake with the ones observed in the province of Alberta should prove interesting. The fact that metals concentrations are low in the ranges is the direct result of good management of the sites performed at Cold Lake. During a visit, the sites were clean of debris and large pieces of metal. This removal of metals, which is performed on a regular basis, is an excellent practice and makes a significant contribution to environmental stewardship.

When the ranges are compared for metal concentrations, the Jimmy Lake Range has the highest concentrations, Bravo has lower concentrations than Alpha, and Shaver has fewer metals detected but their concentrations are similar to Alpha concentrations. The rifle range in CLAWR is not as contaminated as the Army rifle ranges evaluated, which is likely the result of a less intensive use [26, 28].

A direct relationship between soil and biomass concentrations was identified in almost all of the ranges. Not all the metals are taken up and this can be the result of selective absorption. Additional biomass sampling will be analyzed to evaluate the risk for wildlife. Cd-contaminated biomass is of specific concern.

Additional surface water was also sampled during August 2003. Surface water background was collected and compared to the surface water values on the ranges. In general, the surface water in lakes is not contaminated.

The EM analyses revealed some impacts in all ranges. In Alpha Range, TNT and RDX were the most important contaminants, with RDX at very low concentrations. However, TNT concentrations were well below the ecotoxicological criteria for TNT of 80 ppm. No progression in the concentrations was observed in the linear transect samples. In fact the concentrations were more important in the circular samples, meaning that the impacts are quite localized around the target. In Bravo, the situation was similar to the one encountered in Alpha, but at lower levels of concentration. TNT and RDX were the main contaminants at very low concentrations, indicating that this range was used less than the Alpha Range. In Jimmy Lake, surprisingly, a problem with propellant residues was observed, especially with NG. The concentrations in explosives were also low and do not represent a major problem. Generally, no action has to be taken on these sites, except to collect more samples to get a better assessment of the contamination.

In Shaver River Range the situation was different. This range was the most impacted area of CLAWR. A progression of the explosive concentrations was observed in the linear sampling. The highest concentrations were observed around the target, especially in the B and C circles. TNT was again the most important contaminant at a concentration maximum of 400 ppm. Curiously, RDX was not found in that site. HMX was present in some samples at low concentrations. In the OD area, some explosives were detected, but at low concentrations. Some propellant residues were also detected that probably came from open burning.

Summary and Conclusions

During March 2002, a preliminary phase was conducted by DCC in CLAWR. Soils were collected to be analyzed for metals and energetic materials. The energetic materials analyses were performed at DRDC-Valcartier using the GC-ECD method. No energetic materials were detected in any of the samples except for three in Shaver River Range. Metal analyses are not included in this report.

In August 2002 DRDC-Valcartier and CRREL conducted Phase I of the study to characterize the soils, biomass, and surface water samples for metals and energetic materials. A total of 193 soil, 16 biomass, and 4 surface water samples were collected during Phase I in Alpha, Bravo, Jimmy Lake, Shaver River, OD, and rifle ranges. The surface water samples were collected in Primrose Lake, Jimmy Lake, Shaver River, and a pond containing ammunition on Shaver River Range. For statistical analysis and quality evaluation, 8 background and 18 field duplicate (9 percent) samples were collected for soils analyses. All samples were analyzed for metals (193), while a limited number were analyzed for energetic materials (131 soils - 12 field duplicates (9 percent)). For biomass analyses, an insufficient number of background samples were collected. This situation was

corrected in August 2003. Nevertheless, the evaluation was done and results compared to background values. The energetic materials analyses were performed by DRDC-Valcartier and CRREL to evaluate the heterogeneity of the samples and to validate the results between laboratories. The GC/ECD method was used to analyze soils from Alpha, Bravo, and Jimmy Lake, while the HPLC method was used for the Shaver River Range, which was suspected to be more contaminated by explosives. The HPLC method is more suitable to analysis of samples at higher concentrations of explosives.

Two strategies were used to collect the samples across the ranges. The first consisted of using a linear sampling pattern. This approach was used to evaluate whether the level of contamination by metal or energetic materials was following a pattern with distance from the target in the ranges. Composite samples were collected at distances 20, 40, 60, 100, 120, and 140 percent of the distance from the entrance of the range to the targets. The second sampling strategy was a new approach and consisted of sampling around targets by compositing samples taken in a circular pattern. This strategy was based on the circular sampling used at CFB Shilo and was used for specific target evaluation. The strategy was modified to adapt to the specific context of air-to-ground targets and was designed to allow a comparison of the relative concentrations in front of and behind a target. A semi-circular pattern was used to collect composite samples at specific distances from the targets. Twenty-six soil samples were collected around targets, one within each of the cells around the target. These cells are defined by three circles located at 10-, 30-, and 50-m radii of the target. Two composite samples (A1 and A2) were collected in hemispheres of the first 10-m-diameter ring (front and back of target). Eight equal-sized rectangles were sampled between 10 and 30 m (B1- B8), and 16 between 30 and 50 m (C1-C16). Twenty or more increments were collected to build 800-g to 1.5-kg composite samples.

Generally, the impacts by metals in soils in the four ranges were quite low. Most of the time, the metals detected at concentrations higher than the BGL added to twice the standard deviation were at concentrations approximately 1 to 2 times the BGL value. Most of the time, concentrations were far below the ASQGL except for some metals that were present at higher concentrations, such as Cd, Cu, and Zn. These metals are related to firing activities. Nevertheless, most of the values were quite low. The soil background values at Cold Lake compared to the Québec Province background values were also very low. It should be interesting to compare the soil background values at Cold Lake with the ones observed in Alberta. The fact that metals concentrations are low in the ranges is the direct result of the good management of the sites performed at Cold Lake. The practice of regularly removing the pieces of metals must be pursued.

More specifically, for soils on Alpha Range, most of the values were 1.1 to 2.9 times higher than the background values, but no concentrations were higher than the CCME ASQGL. While an impact on the range is recognized, the impact is very small. For Bravo Range soils, most of the values were 1.2 to 3.1 times higher than the background values, but no concentrations were higher than the CCME ASQGL, except for Cd concentrations, which were, however, below the Industrial Soil Criteria. For Jimmy Lake, most of the values were 1.1 to 2.4 times higher than the background values, but 67 percent of the samples had Cd concentrations higher than the CCME ASQGL, 12 percent of the Cu

concentrations were higher than the industrial soil criteria, and 2 percent of the Zn concentrations were also higher than the ISQGL. These data were reexamined and confirmed at the next sampling event in August 2003. At Shaver River Range, fewer metals were detected at values higher than the background values and most of the hits were 1.1-5.9 times higher than the background values. Most of the samples did not have concentrations higher than the ASQGL, except for Cd, which had 49 percent of the samples exceeding the ASQGL, and Zn, which had 2 percent of the samples exceeding the ISQGL. In the OD area, no metals had concentrations higher than the background values. At the rifle ranges, the number of background samples was insufficient for a thorough evaluation. Nevertheless, most of the samples had values 1.1-5 times higher than the background values, indicating a small impact compared to rifle ranges located on Army properties. No sample concentrations were higher than the ASQGL. As usual in rifle ranges, Pb was one of the most important parameters that exceeded the other metals. In general, even if Cd concentrations were, on many occasions, higher than the ASQGL in some ranges, this does not represent a problem, since the ranges are not dedicated to agricultural purposes. When industrial criteria are excluded, the situation must be looked at more seriously. More samples will be needed to understand these impacts.

For biomass samples, some metals were preferentially adsorbed into the plants. Metals in plants were usually at higher concentrations than in soils. This is particularly true for Cd found in plants. Since this metal is very toxic, more biomass samples were collected in August 2003 to evaluate if this represents a risky situation for wildlife that can ingest these contaminated plants. More biomass background samples were also collected in August 2003 to validate the statistical evaluation for the metals. For surface water samples, metals did not demonstrate a strong impact, with a few exceptions. More surface water was also sampled during the August 2003 sampling to have a better idea of the situation. Surface water background will be collected and compared to water sample values on the ranges. In general, the surface water in lakes is not contaminated.

When all of the sampled ranges are compared for metal contamination, the Jimmy Lake Range is the most impacted site, Bravo is less impacted than Alpha, and Shaver is also less impacted than Alpha. In Shaver, fewer metals were detected and the concentrations were similar to Alpha Range concentrations. The rifle range was not as contaminated as the rifle ranges evaluated on Army bases. This is the result of less intensive use. No immediate actions are required in all sites.

The energetic materials analyses revealed some impacts in all ranges. In Alpha Range, TNT was the most important contaminant with RDX at low concentrations, but the concentrations were well below the ecotoxicological criteria for TNT at 80 ppm. No progression in the concentrations was observed in the linear transect samples. In fact the concentrations were more important in the circular samples, meaning that the impacts are quite localized around the target. At the Bravo Range, the situation was similar to the one encountered at Alpha Range, but to a lower extent. TNT and RDX were the main contaminants at very low concentrations, indicating that this range was used less than the Alpha Range. At Jimmy Lake, surprisingly, a problem with propellant residues was observed, especially with NG. The concentrations of explosives were also low
and do not represent a major problem. Generally, no action has to be taken on these sites, except collecting more samples to get a better assessment of the contamination.

At Shaver River Range the situation was different. This range is the most impacted area of CLAWR. A progression of the explosive concentrations was observed in the linear transect sampling. The highest concentrations were observed around the target, especially in the B and C circles. TNT was again the most important contaminant at a concentration maximum of 400 ppm. Curiously, RDX was not found at this site; HMX was present in some samples at low concentrations. At the OD area, some explosives were detected, but at low concentrations. Propellant residues that would come from open burning were also detected.

In conclusion, this study demonstrated that the ranges have some accumulation of metals due to the firing activities, but the extent of contamination is very low except in Jimmy Lake where Cd, Cu, and Zn concentrations were higher than the CCME criteria. The contamination by explosives is also minimal except in Shaver River Range where TNT was found at concentrations up to 400 ppm. More analyses will have to be done to completely understand these ranges, and a hydrogeological study will have to be performed. More efforts will have to be made to evaluate the accumulation of Cd in biomass, since this represents a potential problem for wildlife ingestion of a contaminated food source.

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Table 5-2A (Concluded)

(a) agricultural soil threshold criteria

(b) half values of the detection limits are used when metals are not detected

Note: Values in blue font exceed background. Values in red font exceed agricultural and industrial soil criteria.

(Sheet 5 of 5)

Table 5-2B Metals Concentrations in Soils (Cu to Se)

Note: Values in blue font exceed background. Values in red font exceed agricultural and industrial soil criteria.

(Sheet 5 of 5)

Table 5-2C (Continued) ppm (mg/kg) Sample **Ag Sr Tl Sn U V Zn** S-SR-LS-60 percent A \vert 0.15 | 1.80 | 0.03 | 0.50 | 0.21 | 5.00 | 18.10 S-SR-LS-60 percent A (DUP) 0.15 1.50 0.02 0.50 0.17 4.80 14.90 S-SR-LS-60 percent B 0.15 1.20 0.01 0.50 0.12 4.30 10.50 S-SR-LS-80 percent A 0.15 1.60 0.02 0.50 0.17 5.40 12.70 S-SR-LS-80 percent B \vert 0.15 \vert 2.10 \vert 0.03 \vert 0.50 \vert 0.20 \vert 5.90 \vert 15.30 S-SR-LS-100 percentA 0.15 1.30 0.01 0.50 0.22 3.70 12.90 S-SR-LS-100 percentB 0.15 2.60 0.02 0.50 0.18 5.10 18.50 S-SR-LS-100 percentB (DUP) 0.15 2.30 0.03 0.50 0.18 5.80 16.20 S-SR-LS-120 percent A 0.15 2.10 0.02 0.50 0.13 4.10 16.10 S-SR-LS-120 percent B \vert 0.15 \vert 2.30 \vert 0.03 \vert 0.50 \vert 0.20 \vert 5.80 \vert 27.00 S-SR-LS-140 percent A 0.15 | 1.30 | 0.01 | 0.50 | 0.14 | 4.60 | 11.40 S-SR-LS-140 percent B 0.15 2.10 0.03 0.50 0.27 5.20 12.20 S-SR-T-A1 0.15 3.80 0.03 0.50 0.18 5.60 34.70 S-SR-T-A1 (DUP) 0.15 3.50 0.05 2.00 0.21 5.10 35.70 S-SR-T-A2 0.15 3.40 0.03 2.00 0.23 6.10 33.40 S-SR-T-B1 0.15 2.90 0.03 1.00 0.20 5.40 28.10 S-SR-T-B2 0.15 2.80 0.03 2.00 0.24 5.10 24.60 S-SR-T-B3 0.15 2.30 0.03 2.00 0.21 5.60 25.20 S-SR-T-B4 0.15 3.40 0.02 2.00 0.24 5.60 33.00 S-SR-T-B5 0.15 2.00 0.02 3.00 0.18 4.80 21.30 S-SR-T-B5 (DUP) 0.15 2.20 0.02 0.50 0.20 4.60 21.10 S-SR-T-B6 0.15 2.30 0.05 0.50 0.23 5.00 21.30 S-SR-T-B7 0.15 8.10 0.04 0.50 0.27 6.00 34.10 S-SR-T-B8 0.15 2.90 0.04 1.00 0.24 5.40 26.40 S-SR-T-C1 0.15 2.50 0.03 0.50 0.24 5.60 20.20 S-SR-T-C2 0.15 2.10 0.03 0.50 0.16 5.10 33.50 S-SR-T-C3 0.15 2.60 0.02 0.50 0.24 6.10 25.60 S-SR-T-C4 0.15 2.20 0.03 0.50 0.23 5.30 20.30 S-SR-T-C5 0.15 2.00 0.03 2.00 0.20 5.30 21.80 S-SR-T-C6 0.15 2.00 0.03 1.00 0.28 6.00 24.00 S-SR-T-C7 0.15 1.70 0.01 0.50 0.17 5.30 20.50 S-SR-T-C8 0.15 2.10 0.02 0.50 0.20 5.40 28.40 S-SR-T-C9 0.15 2.80 0.03 0.50 0.23 6.30 30.20 S-SR-T-C10 0.15 3.10 0.02 0.50 0.18 6.00 26.00 S-SR-T-C10 (DUP) 0.15 2.80 0.02 0.50 0.22 5.80 26.20 S-SR-T-C11 0.15 2.30 0.02 0.50 0.26 5.30 18.40 S-SR-T-C12 0.15 2.00 0.03 0.50 0.26 5.50 15.40 S-SR-T-C13 0.15 2.00 0.02 0.50 0.28 5.50 14.70 S-SR-T-C14 0.15 2.10 0.02 0.50 0.17 5.40 16.00 S-SR-T-C15 0.15 2.50 0.02 0.50 0.23 6.00 15.60 S-SR-T-C16 19.30 **Shaver open detonation area** S-SR-OD-1 0.15 2.80 0.02 0.50 0.18 6.90 11.90 S-SR-OD-2 0.15 1.70 0.01 0.50 0.20 4.30 8.90 S-SR-OD-3 0.15 2.50 0.01 0.50 0.23 5.00 9.80 **Rifle range** S-RIF-T-1-3 0.15 2.40 0.02 0.50 0.21 5.70 11.60 S-RIF-T-4-6 0.15 2.80 0.02 0.50 0.26 6.00 13.10 S-RIF-T-4-6 (DUP) 0.15 0.20 0.04 0.50 0.18 0.90 0.40 S-RIF-T-7-9 0.15 0.20 0.04 0.50 0.20 0.90 1.20 S-RIF-T-10-12 0.15 3.00 0.02 0.50 0.20 4.50 6.40

(Sheet 4 of 5)

Table 5-2C (Concluded)

(a) agricultural soil threshold criteria

(b) half values of the detection limits are used when metals are not detected

Note: Values in blue font exceed background. Values in red font exceed agricultural and industrial soil criteria.

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(a): criteria for aquatic life in freshwater

(b): Interim Maximum Acceptable Concentrations in Drinking Water

(c): Maximum Acceptable Concentrations in Drinking Water

(d): criteria for irrigation and/or livestock

(e): half values of the detection limit are used when metals are not detected

Note: Values in blue font exceed background. Values in red font exceed agricultural and industrial soil criteria.

Appendix A

Figure 5-A1. Map of CLAWR

Appendix B — DCC Report for the Preliminary Phase

Introduction

In 2002 Defence Construction Canada (DCC) was retained by Defence Research and Development Canada (DRDC - formerly Defence Research Establishment Valcartier) to assist with the characterization of the Cold Lake Air Weapons Range (CLAWR). The characterization involved identifying potential contamination of the CLAWR by energetic materials (EM), metals, and related compounds at 4 Wing Cold Lake. The Base Environmental Officer and the Commanding Officer at 4 Wing Cold Lake supported the project on the basis of sustainable development and training for the CLAWR.

The proposed program to fully characterize the range utilizes a systematic approach, phasing the project into a five-year program. This report was developed to summarize the proceedings of the preliminary phase of the fourphase program.

Description of preliminary phase

As described in the proposal submitted by DRDC, the preliminary phase included the assessment of metals and EM in a limited number of soil samples at areas of main concern within the CLAWR. The assessment was required to provide DRDC with preliminary soil quality data for the CLAWR. This preliminary data helped with the derivation of the subsequent phases of the program.

Prior to collecting soil samples, personnel from DRDC, DND and DCC conducted an initial inspection of the range. DRDC provided their professional opinion on the key locations (i.e., suspect areas of concern) that should be evaluated as part of the preliminary phase assessment. The main focus areas within the CLAWR were identified as Alpha, Bravo sites within the Primrose Lake Evaluation Range, and Jimmy and Shaver River sites within the Jimmy Lake Range. Once prioritized locations were determined, DCC initiated the proceedings of the preliminary phase.

Field sampling

Due to the time of year, remoteness of the CLAWR, and limited funding for the year, it was deemed most cost-effective for DCC to conduct the field sampling for the preliminary phase. Field work began on 5 March 2002 with the assistance of 4 Wing's Range Control personnel, who provided proofing requirements prior to soil sampling. Fifty-six samples were collected and analyzed for CCME metals, 11 for physical soil characterization, and 29 samples for energetic compounds. The CCME metals and physical characteristics of soil samples were submitted to an independent laboratory (Enviro-Test in Edmonton,

Alberta) and the energetic samples were sent to DRDC for analysis. It should also be noted that approximately 12 percent of the samples were duplicated as part of the QA/QC program.

Prior to sampling, all equipment was cleaned and sterilized. Physical sampling was done using stainless steel trowels, and samples were placed into clean bags as provided by Enviro-Test Laboratories. New, powderless nitrile gloves were worn during each sampling event as well.

The locations of sampling points were referenced using a handheld Gerber global positioning system (GPS) unit provided by Range Control. The following is a representative rendition of the sampling locations with respect to each specified bombing range.

Sampling schematics

Prior to sampling, the target located at the center of the circle was pinpointed and referenced using GPS coordination. Once the center of the target was determined, a measurement rope was used to locate sampling distances around the target in a 360° circumference. This was the basis of sampling at all the target locations. The only variation was the distances that were sampled from the center/target. At these points, grab samples were taken at a minimum of 10 locations surrounding the tank (on the line) to provide a representative sample. Refer to Figure 5-B1 below for an example diagram of sampling distances from the target.

Figure 5-B1. Example of VIP sampling schematics

The remainder of the samples were taken at pinpoint locations with referencing GPS locations. The following table highlights the locations of samples throughout the range.

* CCME- Samples were analyzed in accordance with the Canadian Council For Ministry of the Environment metal scan via ICP/MS Gas Chromatography SW846-3051/6020 methodologies

*Physical- Select samples were submitted for Cation Exchange Capacity, Total Carbon, and Particle Size

* Energetics- Select samples were submitted to Defence Research and Development Canada (Formerly DREV) for analysis of Energetic Materials

Conclusion

Sampling was completed by DCC on 7 March 2002. A total of 56 samples were collected and analyzed by Environ-Test Laboratories from Edmonton, Alberta. All the samples were analyzed for total metals using CCME methodologies and eleven samples were analyzed for physical parameters. Twenty-nine select samples were also sent to DRDC in Valcartier, Quebec for EM analyses. All sample results from Enviro-Test were compiled by DCC and delivered to DRDC Valcartier for their interpretation.

6 Estimates for Explosives Residue from the Detonation of Army Munitions

Abstract

Snow was used as a collection medium to examine explosives residues following the high-order detonation of various military munitions. After detonation, sets of large $(1-m^2)$ samples of residue-covered snow were collected, processed, and analyzed for explosives without cross-contamination from previous detonations and other potential matrix interferences. Trials were performed to quantify explosives residues following the detonation of 60-, 81-, and 120-mm mortar rounds, 105- and 155-mm howitzer rounds, M67 hand grenades, 40-mm rifle grenades, blocks of C4, several different types of land mines, bangalore torpedoes, and a shaped demolition charge. Munitions were detonated following both common military live-fire and blow-in-place techniques. When possible, the same munition was detonated several times using the same conditions to provide a more reliable estimation of the percentage of high explosives that was deposited on the snow surface. In addition to using the snow surface as a collection medium, aluminum trays and steel plates were used in some of the detonation trials.

The blowing-in-place of TNT-filled munitions often resulted in the deposition of near-percent levels of TNT from the main charge that was estimated to lead to mg/kg concentrations in surface soils. When high concentrations of TNT were observed in residue samples, often 2,4-DNT, 2,6-DNT, TNB, 2-ADNT, and 4-ADNT were also present at much lower concentrations. In contrast, the percentage of high explosives deposited from live-fire detonations of Composition-B-filled howitzer rounds, mortar rounds, and hand grenades was always less than 0.002 percent, leading to low µg/kg or ng/kg surface soil concentrations. Overall residue deposition from live-fire, high-order detonations was much lower than for munitions destroyed using blow-in-place techniques. Detonation residues for other munitions that were evaluated fell between these two ranges. Residues from blown-in-place detonations collected on pre-positioned aluminum trays and steel plates showed concentrations similar to the adjacent snow surfaces, and for one detonation allowed for an energetic particle size distribution analysis.

Introduction

Background

Recently, awareness has been increasing that routine military training and testing exercises involving munitions can potentially cause a buildup of explosives residues in soil that can result in contamination of underlying groundwater (U.S. EPA 2000; Jenkins et al. 2001). For example, munitions training and testing were curtailed at Massachusetts Military Reservation (MMR) following the discovery of low concentrations of RDX in the groundwater aquifer below the impact range (U.S. EPA 2000). At MMR and other military testing and training ranges, candidate sources for this contamination include releases from breached casings of unexploded (UXO) or partially exploded ordnance, poor disposal practices, open burn and open detonation (OB/OD) operations, and the accumulation of high-order detonation residues in impact areas. The explosives residue contributions from these various activities on training ranges are often confounded by their co-location. Determining the relative importance of these candidate sources of explosives residues on ranges is important if management practices are to be developed to minimize the possibility of their off-site migration.

To help develop sound management practices for military testing and training ranges, the Strategic Environmental Research and Development Program (SERDP) initiated studies focusing on the distribution and fate of explosives residues. The goal of this effort is to identify source strengths and pathways so that corrective measures can be implemented to reduce or eliminate the presence of explosives residues. One of the knowledge gaps identified by this program was the quantification of explosives residues resulting from the high-order detonation of different munitions commonly used during military training exercises. More specifically, the amount and specific explosives compounds composing the explosives residues that are dispersed into the environment as a result of a munition detonation is a major knowledge gap.

The major products of the detonation of energetic materials are typically $CO₂, CO, H₂O, N₂,$ and carbon (i.e., "soot" [U.S. Army Materiel Command 1972]), while forensic analysis of post-blast residues has established the presence of trace quantities of explosives (Yinon and Zitrin 1993). Recent impact range characterization studies have confirmed the presence of explosives residues both at elevated levels (Jenkins et al. 1997, 1999, 2001; Thiboutot et al. 1998; Pennington et al. 2001, 2002, 2003) and trace levels (Ogden Environmental and Energy Services 2000; USACHPPM 2000; U.S. EPA 2000; Jenkins et al. 2001; Walsh et al. 2001). To quantify explosives residues following the high-order detonation of a munition, Jenkins et al. (2000a,b, 2002) developed a systematic approach that utilizes a fresh snow surface as a collection medium. This approach was influenced by an earlier observation that a darkened soot plume existed on the surface around impact craters when munitions were fired into a snowpack (Collins and Calkins 1995). Advantages of using a snow surface as a collection medium are that the areas of deposition are clearly delineated, residues exist in a matrix that is free of interferences, residues from previous range activities are avoided (if little or no surface soil is disturbed), and a large surface area can be
sampled to help address the spatial heterogeneity that is common to the deposition of particulates.

Objective

The objective of this study was to use the systematic approach developed by Jenkins et al. (2000a,b, 2002) to quantify the explosives residues produced by the high-order detonation of a variety of munitions using accepted military protocols. When possible, five or more replicate detonations were performed to provide statistically based estimates. Munitions were detonated using two different operational procedures, i.e., live-fire and blow-in-place. A live-fire (i.e., used as intended) trial encompasses artillery- and mortar-fired projectiles, thrown hand grenades, fired rifle grenades, and other detonations where the munition was initiated with pre-set fusing (e.g., impact, timed, or proximity). Munitions were also blown in place using C4 or blasting caps. More attention will be given to those munitions that are fired into the impact ranges (e.g., artillery rounds and grenades) than those munitions used by battlefield engineers (i.e., demolition munitions and land mines). Because very low concentrations of explosives residues were anticipated, large surface samples were collected and, when necessary, a new gas chromatographic electron capture detection (GC-ECD) method that was developed recently by Walsh and Ranney (1999; USEPA 1999) was used, which has lower levels of detection than reversed-phase highperformance liquid chromatography (RP-HPLC).

Experimental Methods

General sampling scheme

All detonation trials were performed over snow-covered ranges. Flat locations were chosen for blow-in-place operations, and, when possible, as target locations for live-fire trials. When snowpack depths exceeded 30 cm or when sampling inside an impact range, snowshoes were used to assist with mobility and to reduce the possibility of disturbing UXO. Following the high-order detonation of a munition, the area where energetic residues were deposited on the snow surface was identified by the presence of a black soot plume. The formation of soot is characteristic of the detonation of materials with an oxygen-to-carbon ratio of less than one (U.S. Army Material Command 1972). Trinitrotoluene (TNT, $C_7H_5N_3O_6$), motor oil, waxes, and some of the plasticizers (e.g., phthalates) and stabilizers are examples of materials in the main charge of various munitions that would contribute to the formation of soot particles during detonation. Tape measurements and recordings taken by a global positioning system (GPS) were used to map the soot plumes, craters, and sampling locations. A set of large (approximately 1 m^2) snow samples was randomly collected within each plume.

An unpainted aluminum snow shovel, covered with a sheet of Teflon film, was used to remove the top 0.5 to 2 cm of the surface, depending on the conditions. Typically, the wetter the snow (tending to clump), the greater was the sampling depth. Upon completion of the collection process, no or very little visible

soot remained within the sampling plot. In a couple of instances, when soot penetrated deeper into the snow column, the shovel or a small scoop was used to collect these deeper portions. Within the crater it was impractical to use a large shovel since the walls were conical, very irregular, and in some cases partially covered with soil and ice as a result of the intense release of energy and heat associated with the detonation point. For crater sampling, the surface snow and ice samples were collected with a small stainless steel scoop, and we estimated the percentage of the total crater surface that was sampled. The snow shovel and scoop were cleaned between trials by washing with soap and water, rinsing with water, and rinsing several times with acetone. In the field, these sampling tools were cleaned between sampling locations by inserting them into a clean snowpack and wiping with a clean towel. All surface snow samples were transferred to particulate-free polyethylene bags closed with a cable tie. The sampling date, munition type, sample number, surface area sampled, and distance to the crater were recorded for each sample. In cases where live-fire detonation plumes overlapped, the distance to the crater was omitted. The size of the soot plumes varied both with the type of munition and with the ambient conditions (e.g., wind speed) at the time of detonation. Whenever possible, detonations were performed under low wind conditions. When several munitions of one type were detonated, one of the replicates was intensively sampled. Background snow samples also were collected prior to a detonation trial.

During several of the blow-in-place trials, steel plates $(46 \times 46 \times 0.64$ cm) were used to minimize the disruption of soil below the detonation point. Munitions were placed directly on top of the steel plates in some cases and in others the munition was placed on top of snow and the steel plate was buried at the base of the snowpack. In both orientations, the steel plate helped to minimize the amount of topsoil that was distributed by the detonation. When the munition was placed directly on the steel plate, the surface of the plate was sampled. In addition, for a few trials, aluminum cooking trays $(46 \times 66 \text{ cm}, 0.3 \text{ m}^2)$ were prepositioned to collect detonation residues for both chemical residue analysis and particle characterization. Following a detonation, the trays were placed in large plastic bags. Lastly, for two of the blow-in-place trials, pre-positioned video cameras photographed the detonation event.

Detonation trials

Camp Ethan Allen, VT: 19 January 2001. At two locations in an open area, EOD personnel from the Vermont Air National Guard blew in place a fuzed 81-mm mortar round (0.95 kg of Composition B, "Comp B," 60 percent RDX, 39 percent TNT, 1 percent wax) and a demolition block of C4 (0.57 kg, 91 percent RDX). The 81-mm mortar round was laid sideways on top of the 45 cm-deep snowpack and a fused (M6 blasting cap) demolition block of C4 was laid across the top of the round. At a second location, a 0.57-kg block of C4 was laid on top of the 45-cm-deep snowpack and detonated with an M6 blasting cap. Both detonations were initiated with a radio-transmitted signal. Several surface snow samples and a single crater sample were obtained from each of the detonation plumes. The amount of soot-covered snow that was sampled in each case was less than 2 percent of the total plume. Figures 6-1 and 6-2 show the sampling locations and plume boundaries for these two detonations.

Figure 6-1. Residue plume from blowing in place an 81-mm mortar round with a block of C4, with sampling and crater locations marked

Figure 6-2. Residue plume from blowing in place a block of C4, with sampling and crater locations marked

Fort Drum, NY: 7 February 2001. U.S. Army personnel detonated a bangalore torpedo, two unfuzed anti-tank mines, and a Claymore mine at four locations within a training range. The bangalore torpedo (4.86 kg, Comp B4: 59.75 percent RDX, 39.75 percent TNT, 0.5 percent wax) was used in a training exercise to breach a barbed-wire barrier and was detonated with a timed fuse.

Two anti-tank mines, an M19 (9.53 kg of Comp B) and an M15 (10.3 kg of Comp B), were blown in place after being turned upside down with half of a demolition block (0.28 kg) of C4 placed on exposed surface (bottom) of the mine. A blasting cap with a 5-minute time fuse was used to initiate the block of C4. At a fourth location, a Claymore mine (0.68 kg of C4) was detonated using a 5-minute time fuse. Following the detonation of the bangalore torpedo, ten snow samples were collected within the soot plume and three snow samples were collected from the walls of the crater. Ten, nine, and six snow samples were collected, respectively, from within the soot plumes created by the detonation of the M19, M15, and Claymore mines, respectively. Also, at least one crater sample was collected for each of these mines. For these four munitions, less than 2 percent of the snow surface covered with soot was sampled, similar to what is shown in Figures 6-1 and 6-2.

Camp Ethan Allen, VT: 16 February 2001. Six 60-mm mortars (0.36 kg, Comp B) with the fuse set to detonate 1 to 2 m above the surface (proximity setting) and seven 40-mm (32 g, Comp B) rifle grenades set to detonate upon impact were fired into an impact range by a unit from the Vermont National Guard. Five of the 60-mm mortars' detonation plumes were sampled by collecting large (10 to 80 percent) portions of the soot-covered snow. Because these projectiles detonated in the air, there was no distinct crater. The sixth mortar had an airburst some 3 to 4 m above the surface (apparently set off by a treetop), leaving little visible residue on the surface; therefore, it was not sampled. Three of the 40-mm grenades fired did not detonate because they failed to hit a target. Because of the safety concerns with one of these UXOs in the snowpack, we were able to sample only three of the detonation plumes. The three 40-mm grenades impact sites that we sampled were located behind a rectangular steel structure, behind a target vehicle, and around the left front corner of the same target. As with the 60-mm mortars, these rounds detonated above the surface and did not have distinct craters. For the 40-mm rifle grenades, 50 percent or greater of the soot-covered snow surface was collected.

Fort Drum, NY: 8 March 2001. At the Fort Drum hand-grenade training range, seven hand grenades (186 g, Comp B) were thrown by U.S. Army personnel. Each grenade was intentionally thrown to a separate location in the range so that the detonation plumes would not overlap. This impact range was covered with between 30 and 60 cm of snow that, in places, had a hard crust less than a centimeter below the snow surface. Surface snow samples and at least one crater wall sample were collected for all seven detonation areas. In each case more than 20 percent of the soot-covered snow was collected. Figures 6-3 through 6-9 depict the sample sizes relative to the plume dimensions and give the respective surface concentrations $(ng/m²)$ of RDX for each sample.

Figure 6-3. Residue plume #1 from live-fire detonation of M67 hand grenade with surface area sampled and concentrations of RDX determined

Figure 6-4. Residue plume #2 from the live-fire detonation of M67 hand grenade with the surface area sampled and concentrations of RDX determined

Figure 6-5. Residue plume #3 from the live-fire detonation of M67 hand grenade with the surface area sampled and concentrations of RDX determined

Figure 6-6. Residue plume #4 from live-fire detonation of M67 hand grenade with surface area sampled and concentrations of RDX determined

Figure 6-7. Residue plume #5 from live-fire detonation of M67 hand grenade with surface area sampled and concentrations of RDX determined. Sample S3 is the combination of both circular areas

Figure 6-8. Residue plume #6 from live-fire detonation of M67 hand grenade with surface area sampled and concentrations of RDX determined

Figure 6-9. Residue plume #7 from live-fire detonation of M67 hand grenade with surface area sampled (intensively sampled) and concentrations of RDX determined (plume area 99 m²)

Camp Ethan Allen, VT: 19 March 2001. Seven 120-mm mortar rounds (2.99 kg, Comp B), set for detonation upon impact, were fired into an impact range by a unit from the Vermont National Guard. The depth of the snowpack in the impact area ranged between 40 and 60 cm. The detonations created a 2-m or wider diameter crater and removed about 15 cm of topsoil at the point of impact. As a result, the plume around each impact crater was a combination of soot and soil; because it was a warm sunny day, this dark layer warmed quickly, producing a brownish melt solution that sank into the snowpack. The surface snow collected for these detonations represents only 2 percent or less of the soot plume and included some discolored snow from within the snowpack that contained the brownish surface melt solution (e.g., see Figures 6-1 and 6-2). In addition to snow samples, two of the 120-mm mortar tail fins were recovered.

Camp Ethan Allen, VT: 16 January 2002. Two pairs of 0.57-kg demolition blocks of C4 (91 percent RDX) were blown in place by EOD personnel from the Vermont Air National Guard in a field covered with a 20-cm-deep snowpack. The blocks of C4 were detonated with a radio-initiated blasting cap in a training area that had recently been cleared of vegetation and graded specifically for these trials. To limit the disruption of the soil beneath the snow, each block of C4 was placed on top of a 46- \times 46- \times 0.64-cm steel plate that had been pushed down into the snowpack. For each pair of detonations, 12 aluminum cooking trays (46×66) cm) were positioned near one of the blocks of the C4, three at each of the four

compass points. Two trays were placed next to each other to collect detonation residues for chemical analysis (A and B, left to right, from the block of C4), and a third tray, used to collect particles, was positioned 1 m to the right of the B tray. Each tray was pushed down into the snow leaving the top edge flush with the snow surface. For the first pair of detonations, the trays were positioned at a distance of 7.5 m from the block of C4, and for the second pair, the trays were set at 3.5 m from the C4. Two video cameras were positioned to record the detonation of the blocks of C4 surrounded by the aluminum trays. The cameras were positioned to the north and east, about 90 degrees from each other and some 50 m or more from the detonation point.

Following each pair of detonations, the trays that were within the soot plume were covered with aluminum foil and placed inside a large plastic bag. Adjacent to each tray, a surface snow sample was collected. Trays within the soot plume had a small amount of snow thrown onto them, and some of the trays that were placed at the 3.5-m distance were moved slightly by the detonation. Two of the steel plates on which blocks of C4 had been placed were split open and two were folded over at a 90-degree angle. The surface snow samples collected represented approximately 5 percent of the area covered by soot for each plume (e.g., Figure 6-10).

Figure 6-10. Residue plume from blowing in place a demolition block of C4. Also shown are the locations for collection of snow surface samples, crater, and aluminum trays to collect residue for chemical and physical analysis

Camp Ethan Allen, VT: 2 February 2002. Seven Claymore mines (directional fragmentation mines, 0.68 kg of C4 and 700 steel balls) were detonated with an electrically initiated fuze by a unit from the Vermont National Guard in the training area created for these trials. The snow depth was 28 cm, with a 0.3-cm ice crust on the surface. The temperature was -11^oC, the wind speed and direction were variable. Four Claymore mines were detonated at 1300 hours, and three were detonated at 1500 hours. In front of the first four mines,

silhouette targets were positioned at a distance ranging from 20 to 30 m for training. Aluminum trays were set out to collect detonation residues for chemical analysis and to collect particulates, in front of and behind two of the Claymore mines that were detonated in the first set. Trays were positioned at 5, 7.5, 10, and 15 m in front of and at 3.5 m behind the Claymore mines. The subsequent soot plumes from these detonations extended some 15 m behind each mine but only about 7 m in front, and were only 3 to 4 m wide. Wind gusts caused the plumes to drift to the east in several cases. Following the detonation of each set of Claymore mines, trays (when used) and snow samples were collected. In all cases, more surface snow samples were collected behind the detonation point than in front of it (the direction the steel balls were fired was the forward direction). The surface snow collected for these detonations was about 5 percent of the soot-plume-covered area (e.g., Figure 6-11).

Figure 6-11. Residue plume from live-fire detonation of a Claymore mine. Also shown are locations for collection of snow surface samples, crater, and the aluminum trays to collect residue for chemical and physical analysis

Camp Ethan Allen, VT: 15 February 2002. Three 0.57-kg demolition blocks of C4 were individually blown in place by explosive ordnance disposal (EOD) personnel from the Vermont Air National Guard in the training area created for these trials. Each block was detonated over a $46 - \times 46 - \times 0.64$ -cm steel plate that had been buried under 20 to 30 cm of snow. The C4 blocks were set off using radio-initiated blasting caps. After detonation, the metal plates were covered with an aqueous (melted snow) black residue solution, and were only slightly deformed. Snow and crater wall samples were collected for each plume. The surface snow samples collected represented approximately 5 percent of the area covered by soot for each plume (e.g., see Figure 6-10).

Camp Ethan Allen, VT: 28 February 2002. Eight unfuzed 155-mm howitzer rounds (6.8 kg, TNT) were each blown in place in a large open area by EOD personnel from the Vermont Air National Guard. Each 155-mm howitzer round was hung about 1.3 m above the snow surface from a metal chain that attached to a four-legged wood A-frame (tall sawhorse). The metal chain hooked into a heavy metal nose ring that was screwed into the fuze hole. A 0.57-kg

demolition block of C4 and radio-initiated blasting cap were taped to the side of each round. Four of the howitzer rounds were detonated at 1000 hours and the remaining four at 1330 hours. For each set of detonations, two rounds were positioned in an area that was clear of vegetation above the snow cover, and two were in locations where there was brush and small trees. All four of the howitzer rounds were more than 100 m from one another. For the second set of detonations, the howitzer rounds were offset approximately 20 to 50 m from the first four positions.

The detonation of one of the 155-mm howitzer rounds was filmed from a distance of about 200 m by two cameras positioned 90 degrees from one another. One round was filmed for each of the two times. The round that was filmed also had aluminum trays positioned on the surface for the collection of particles. For the first detonation set, trays were positioned at the four compass points at a distance of 15 m from the howitzer round. Because of prevailing winds, during the second set of detonations, the trays were positioned only on the east, south, and west sides, at a distance of about 8 m from the round. Figures 6-12 and 6-13 show the sampling and tray locations for these two plumes. Throughout the day the sky was partly cloudy and conditions were very windy, with gusts up to 4 m/s, averaging from 1.6 to 3.0 m/s. Snow and crater samples were collected from seven of the plumes. The surface snow samples represented 1 to 2 percent of the plume area.

Figure 6-12. Residue plume from blowing in place a 155-mm howitzer round #1 with a demolition block of C4. Also shown are the locations for the collection of snow surface samples, crater, and the aluminum trays to collect residue for physical analysis

Figure 6-13. Residue plume from blowing in place a 155-mm howitzer round #5 with a demolition block of C4. Also shown are the locations for the collection of snow surface samples, crater, and the aluminum trays to collect residue for physical analysis

Camp Ethan Allen, VT: 7 March 2002. Eight unfuzed anti-personnel mines, two each of four different types, were blown in place by EOD personnel from the Vermont Air National Guard in the training area created for these trials. The four types of anti-personnel mines were PMA-1A, PPM-2, PMA-2, and VS-50. Each mine was detonated over a $46 - \times 46 - \times 0.64$ -cm steel plate that had been buried under 20 to 30 cm of snow. The PMA-1A and PMA-2 mines were detonated with blasting caps that had been placed inside a fuse well, and the PPM-2 and VS-50 mines were detonated with a half (0.28 kg) demolition block of C4 initiated with a blasting cap. Trays were positioned around one of each of the four different types of mines. These trays for the collection of particles were positioned 5 m from the mine at each of the four compass points (Figure 6-14). The surface snow samples collected represented about 5 percent of the plume area.

Figure 6-14. Residue plumes from blowing in place four different types of antipersonnel mines. Also shown are the locations for collection of snow surface samples, crater, and aluminum trays to collect residue for physical analysis

Fort Richardson, AK: 13 March 2002. Fifteen 81-mm mortar rounds (Comp B, 0.93 kg) with an impact fuse setting were rapidly fired by Army personnel into the Eagle River Flats impact range. This impact range was covered with snow that was on top of a thick sheet of ice. In the impact area only two plumes were sampled because of time limitations. One plume was created from a single round and the other consisted of overlapping plumes from 13 rounds (Figure 6-15). Within the multi-round plume, a $34 \text{-} m^2$ area was covered with an ice surface that allowed the soot to be swept into piles with a broom and shoveled into the plastic bags (four different bags), with only a small amount of snow being collected. In total, 63 snow and ice surface samples and 14 crater samples were collected. The impact detonation of these rounds did not penetrate the ice sheet; therefore, no soil was present in any of the samples. For each of these two plumes, about 5 percent of the soot-covered surface was sampled.

Figure 6-15. Single plume and a cluster of overlapping residue plumes from livefire detonations of 81-mm mortars. Also shown are locations for the collection of snow surface samples and the crater

Fort Richardson, AK: 14 March 2002. Fifteen 105-mm howitzer rounds (2.09 kg, Comp B) with an impact fuse setting were fired by Army personnel into the Eagle River Flats impact range, where nine plumes were sampled. Seven of the plumes were formed by a single round each, one from the overlapping plumes from two rounds and the remaining one consisting of four overlapping plumes (e.g., Figure 6-15). In total, 113 snow surface and 13 crater samples were collected. The impact detonation of these rounds again did not penetrate the ice sheet. The soot-covered snow samples collected represented from 1 to 8 percent of the plumes.

Fort Richardson, AK: 20 March 2002. Several 18-kg shaped demolition charges (M3A1, 13.4 kg, Comp B) and bangalore torpedos (4.86 kg, Comp B4) were set off in the impact range by Army personnel. Surface snow samples and crater samples were obtained for one of each of these two types of demolition munitions. In all, 12 surface snow and crater samples were obtained within the shaped charge soot plume and 8 within the bangalore torpedo plume. The detonation of the bangalore torpedo did not penetrate the ice sheet. The detonation of the shaped demolition charge penetrated the ice sheet; however, no soil was dispersed onto the surface. For both of these plumes, about 1 percent of the soot-covered snow was sampled (e.g., Figure 6-1).

Snow-sample processing and analysis

A complete description of snow sample processing and analysis methods was reported by Jenkins et al. (2000a,b). Briefly, the soot-covered snow samples were melted in the plastic sample bags at either room temperature or 4°C. When only a small amount of ice remained, the bag was vigorously shaken, suspending the soot in solution, then the entire sample in 1-L aliquots was quickly poured into a funnel and filtered by passing through a large glass-fiber filter (Whatman glass microfiber, 90-mm, grade GF/A). Depending on the amount of soot (and in some cases the amount of debris, e.g., soil, vegetation), one to more than ten individual filters were used. Both the filtrate (in some cases only a portion of the total snowmelt volume) and filters were immediately transferred to clean glass bottles and stored at 4°C.

A 500-mL portion of the filtrate was poured into a volumetric flask and then, pulled by vacuum, passed through a solid-phase extraction (SPE) cartridge (Jenkins et al. 1995). This technique retains the explosives on a pre-packed cartridge of Porapak RDX (Sep-Pak, 6-cm³, 500-mg, Waters Corporation). These cartridges were subsequently eluted with 5.00 mL of acetonitrile (100-fold preconcentration). Based on the concentrations of RDX and TNT in the snowmelt fraction of the sample, the soot-covered filters were extracted with acetonitrile either on a shaker table or in a Soxhlet (SOX) apparatus. When the aqueous solution concentrations of RDX or TNT were above 1.0 mg/L, the filtered portion was extracted on a shaker table for 18 hr. All other filtered portions were shipped to the Environmental Measurements Laboratory in Vicksburg, MS, for SOX extraction. Use of a shaker table for the extraction of explosives from detonation residues is unique to this study. This extraction method was used as a safety precaution because a detailed microscopic analysis of the soot fraction of a residue sample established the presence of hundreds of individual particles of energetic materials (Taylor et al., in preparation). This soot sample corresponded to a snow sample with a high $(> 1 \text{ mg/L})$ snowmelt concentration. There was concern that the SOX extraction of a sample containing milligram quantities of explosives could result in a small explosion, if accidentally allowed to go to dryness. A 20-mL portion of the final SOX extract volume (initial volume was 200 mL) was returned to the Cold Regions Research and Engineering Laboratory (CRREL) for analysis.

Some of the steel plates on which munitions were detonated for blow-inplace operations and all of the aluminum trays that were covered with detonation residues were sampled. For the chemical analysis of residue concentrations, the plates and trays were allowed to dry (snow was blown onto them by the detonation), then they were wiped with acetone-moistened cotton balls held with metal tweezers. The entire surface of the aluminum trays was wiped and one to four 10- \times 10-cm or larger soot-covered areas were wiped on the steel plates. One to five acetone-moistened cotton balls were used to wipe an area, depending on the amount of soot. The cotton balls were then dried before extracting with acetonitrile in a water-cooled sonic bath for 18 hr. Similarly, acetone-moistened cotton balls were used to wipe mortar fins collected in the field following the live-fire detonation of 120-mm mortars.

For physical characterization, the residues on the tray were swept to a corner with a small paintbrush. The residues were then transferred onto weighing paper, weighed, and transferred to a 40-mL amber vial. Each tray was then wiped down with acetone-moistened cotton balls. The cotton balls, up to three for each tray, were placed in a separate amber vial. When the presence of explosives was detected from analysis of these cotton balls, the solid residue collected from the

trays was analyzed. To help characterize the tray residues, they were dry-sieved into <53, 53- to 106-, 106- to 125-, 125- to 180-, 180- to 250-, 250- to 500-, and >500-µm-size fractions. Subsamples of each size fraction were examined under a light microscope and, when found, the explosive grains were removed from the 250- to 500- and >500-µm-size fractions. For the five smallest-size fractions, \leq 53, 53–106, 106–125, 125–180, and 180–250 μ m, the residue was dissolved in acetonitrile for mass determination.

Samples (SPE, shaker table, sonic bath, and SOX) were analyzed by either GC-ECD or RH-HPLC, or both. The GC was an HP6890 equipped with a micro cell $Ni⁶³ ECD$, and the analysis protocol followed the EPA \overline{SW} -846 Method 8095 guidelines (Walsh and Ranney 1998; U.S. EPA 1999). Primary and secondary GC-ECD analyses were performed using a $7-m \times 0.53$ -mm-ID fused silica column, with a 0.5-µm coating of 5 percent-(phenyl)-methylsiloxane (RTx-5MS from Restek, Bellefonte, PA) and a $6-m \times 0.53$ -mm-ID fused silica column with a 1.0-µm coating of a proprietary phase (Rtx-TNT-2 also from Restek), respectively. RP-HPLC analyses were performed on a modular system (Thermo Separation Products, Inc., San Jose, CA) consisting of a P1000 isocratic pump, UV2000 dual wavelength absorbance detector set at 210 and 254 nm, and AS3000 auto sampler. Analyte separations were performed using the 15-cm \times 3.9-mm (4-mm) NovaPac C-8 column (Waters Chromatography Division, Milford, Massachusetts) eluted with 15:85 isopropanol/water (v/v) , at 1.4 mL/min. Both standards and solvent extracts were diluted 1:3, acetonitrile to water. Samples with explosives analyte concentrations greater than 200 μ g/L were typically analyzed by RP-HPLC. Subsets of samples from each detonation trial were either analyzed by both RP-HPLC and GC-ECD, or by primary and secondary column GC-ECD analysis to confirm the presence of explosive analytes. Table 6-1 lists estimates of the practical reporting limits for these samples by both methods. These reporting limit estimates were based on method detection limits and certified reporting limits for soil and water (Jenkins et al. 1992; Walsh and Ranney 1998, 1999). In general, the filtered portion (soot) of the sample contained the most interferences as a result of the inclusion of vegetation and small pieces of plastic for those munitions with plastic casings.

Appendix A contains data tables for all of the individual detonation trials. These tables contain the explosives residue concentrations $(\mu g/m^2)$ that were established for each snow and crater sample. Each value is composed of the snowmelt (filtrate) and soot (filtered) explosives residue concentrations (i.e., the total mass of each of the various nitroaromatics and nitramines per surface area sampled obtained by adding the values established for both of these fractions). With the exception of the anti-personnel mines, these tables show the values for all of the explosives analytes that were frequently detected. For the anti-personnel mines, only the explosives analytes present in the main charge are reported in Appendix A. In cases where the residue plumes from multiple detonations overlapped, all of the values were placed in a single table and an average value per round was determined. To estimate the total quantity (mass) of a high explosive deposited, the mean surface concentration was multiplied by the area of the residue plume, without inclusion of the crater. The mass of the analytes deposited in the crater was similarly determined and then added to the mass determined for snow samples. The explosives residue concentration established for the crater samples were not averaged with the other samples because they had been collected using a different sampling protocol. More importantly, in cases where the crater was found to contain elevated concentrations of explosives residues, they could have a disproportional influence (craters were often less than 1 percent of the total plume area) on the estimation of the total mass for the plume.

Results and Discussion

Deposition of RDX and TNT

Table 6-2 lists composition of the explosives in the main charge of the different munitions that were detonated. Table 6-3 lists the detonation trials in chronological order and gives the total amount of the RDX and TNT that was detonated. The total amount of RDX for a munition that was blown in place with a demolition block of C4 includes the amount of RDX that is in the demolition charge. Also, for two of the munitions, the amount of RDX present in the booster was added to the main charge value. In most cases, the energetic materials in the boosters and fuses were not included in Table 6-3, because the Department of Defense Identification Codes (DODICs) and National Serial Numbers (NSNs) were not available. Appendix B lists this calculation and all others used in the presentation of information.

After establishing the total deposited mass of RDX and TNT in the detonation residue samples (Appendix A), the amount of these two high explosives that was present prior to detonation was used to determine the percentage of these two explosives that was deposited on the surface within the visible detonation plume. In the case of overlapping residue plumes, the percent deposited was calculated on a per-round basis. Four recognized sources of uncertainty in these percent deposited determinations are (1) the entire surface area where residues were visibly deposited was not sampled; (2) the area delineated by the soot plume may not be totally inclusive of all of the deposited residues; (3) the dispersion of residues (particles of unconsumed high-explosive material) is heterogeneous; therefore, sample concentrations are not necessarily characterized by a normal distribution (i.e., not Gaussian); and (4) military-grade RDX may contain anywhere from ≤ 1 to 15 percent HMX, as an impurity from the manufacturing process. Even with these potential sources of error, the mean concentration for the area visibly impacted by detonation residues can be used to establish orderof-magnitude estimates until better data become available (Jenkins et al. 2000b).

For each detonation, Tables 6-4 and 6-5 list the mass of RDX and TNT deposited, the percent of the RDX and TNT in the munition that was deposited, the mean snow surface concentrations of residues of these two high explosives, and an estimated soil concentration if these residues were deposited within the first 0.5 cm of the topsoil (density 1.7 g/cm^3). The snow and soil concentrations do not include the crater residue concentrations. These tables also include the plume area and an overall mean when five or more replicate detonations were performed. Lastly, these two tables separate those values established for live-fire exercises (Table 6-4) from those established for blow-in-place operations (Table 6-5).

Table 6-4 Estimates of RDX and TNT Deposited from the Live-Fire Detonation of Various Munitions

Thirteen overlapping plumes, values based on a per-round basis.
 F_{max} and proposing plumes, values based on a per round basis.

^e Two overlapping plumes, values based on a per-round basis.
f

Four overlapping plumes, values based on a per-round basis.
^g coverall mean for five or more replicate detonations.

Table 6-5 Estimates of RDX and TNT Deposited from the Blow-In-Place Detonation of Various Munitions

a Relative to total mass of analyte in the munition.

b Deposited in area of visual soot plume. c

 σ^2 Soil density of 1.7 g/cm³ and a 0.5-cm depth to compute the estimate.
d.Overall mean for five ar mare replied to determines

Overall mean for five or more replicate detonations.

A "live-fire detonation" involves a chain of reactions where the main charge is initiated by a shock wave generated from a fuse or fuse-booster combination that was specially designed for that munition. Moreover, this initial shock wave ignites the main charge within a sealed casing. Fuses are initiated by a variety of techniques, i.e., electrical, timed (mechanical/electrical/ignited), proximity, or impact. The types of munitions that were detonated using a live-fire sequence were 105-mm artillery rounds, 60-, 81-, and 120-mm mortars, hand and 40-mm rifle grenades, bangalore torpedos, Claymore mines, and a shaped demolition charge. The term "blow-in-place" is used to describe a detonation where the main charge is initiated by a separate charge that is not specially designed for use with that munition: for instance, the detonation of a demolition block of C4 placed against the outer casing of the munition, or the detonation of a generic blasting cap that is inserted into the fuse well of an anti-personnel mine. Both the live-fire and blow-in-place operations performed in this study resulted in high-order detonations (high-order detonation defined as an explosion that leaves no large intact casing fragments or chunks of high explosives that are readily visible to the naked eye).

Live-fire detonations

Typically, thousands of artillery and mortar rounds are fired annually into impact ranges at active training facilities. Moreover, these impact ranges cover areas that often exceed 100 km^2 . One type of artillery round and three types of mortar rounds were detonated using live-fire conditions in this study. All of these rounds contained Comp B as the main charge. The five 60-mm mortars that were detonated, having a proximity fuse setting between 1 and 2 m above the surface, showed a mean percent deposition of 3×10^{-5} percent for RDX and a percent deposition ranging from undetectable to 3×10^{-5} percent for TNT. Jenkins et al. (2002) assessed the residues remaining following the live-fire detonation of two 60-mm mortars (0.36 kg, Comp B) with an impact fuse setting. Their work showed deposition ranging from 4×10^{-5} to 9×10^{-5} percent for RDX and undetectable levels of TNT. Our mean deposition estimate for RDX appears to be a little lower than this earlier study, perhaps because of the different fuse setting. The presence or absence of TNT in the residue may be a function of the variability in the manufacturing process of Comp B. Jenkins et al. (2002) established the presence of HMX and NG, in addition to RDX. We also detected HMX and NG, as well as 2,4-DNT and 2,6-DNT.

In comparison to the 60-mm mortars, the residues from the live-fire detonation of 81- and 120-mm mortars generally showed higher percent deposition of RDX and TNT, and frequently showed the presence of 2-ADNT and 4-ADNT. We also observed that, among the analytes detected in the residues from the detonation of mortar rounds in this study and elsewhere (Jenkins et al. 2002), only the 81-mm mortar rounds fired at Fort Richardson, AK, showed no detectable HMX. The reason for this discrepancy is not known; however, a possible explanation is that the RDX in the Comp-B-filled 81-mm rounds fired at Fort Richardson was purer than the usual grade. HMX, 2,4-DNT, 2,6-DNT, 2-ADNT, and 4-ADNT are present in the residue samples either because of impurities in the manufacturing process of the primary explosives (e.g., TNT, RDX) or they are constituents of other components (e.g., booster or fuze) of the round, or both. NG most likely comes from the propellant ignition cartridge (Jenkins et al. 2000b). This theory was supported by the presence of NG on the surface of the two 120-mm mortar fins recovered during this study and elsewhere (Hewitt 2002). The residue plumes for the thirteen 105-mm howitzer rounds showed only trace quantities (at or below the GC-ECD detection capabilities listed in Table 6-1) of RDX and TNT. The resulting mean percent deposition estimates were 7.0×10^{-6} percent for RDX and 2.0×10^{-5} percent for TNT. With

the exception of the 105-mm howitzer rounds, there tended to be greater percent deposition of RDX relative to TNT.

The highest overall mean ($n \geq 5$) percent deposition for the live-fire detonations of howitzer and mortar rounds (metal-encased munitions) was 0.002 percent for RDX and 3×10^{-4} percent for TNT. These mean deposition values were estimated for 81-mm mortar rounds and indicate that up to 99.998 percent of the high explosives were consumed during the detonation. If the deposited residues were homogeneously distributed over the ground surface under the detonation plume, and were contained within the first 0.5 cm of top soil (density 1.7 g/cm³), the average surface soil concentrations would be 8.1 µg/kg for RDX and 1.0 µg/kg for TNT per round (Table 6-4). Contributions (average surface soil concentrations) of RDX and TNT to surface soils would be 1 to 3 orders of magnitude less for the howitzer and other mortar rounds detonated using live-fire conditions. Very low levels of explosives residue concentrations in surface soils are consistent with results from efforts to characterize the energetics on active artillery impact ranges, the results of which have shown that explosives residues are often below detection when using a random or systematic sampling plan (USACHPPM 2000; U.S. EPA 2000; Ogden Environmental and Energy Services 2000; Jenkins et al. 2001; Walsh et al. 2001) and are only in the low microgramper-kilogram range when judgmentally sampled around heavily impacted targets that are absent of partially detonated (low-ordered) munitions (Pennington et al. 2001, 2002; Jenkins et al. 2001; Walsh et al. 2001).

Two types of grenades were detonated in live-fire trials. Facilities for training with hand grenades are typically smaller than 1000 m^2 , and those for rifle grenades are around 1 km^2 in size. These ranges typically are heavily used, similar to an artillery range (thousands of detonations annually). Both of these munitions contain Composition B. Both RDX and TNT were found in the residues from the detonation of the rifle grenades, but only RDX was detected in the hand grenade residues. In addition to these two analytes, HMX, 2,6-DNT, 2,4-DNT, 4Am-DNT, and 2Am-DNT were present in the detonation residues of the 40-mm rifle grenade, and 2,6-DNT was detected for the M67 hand grenade. For both types of grenades, RDX was present in the highest concentrations of all the explosives analytes detected.

The three rifle grenades had depositions that ranged from 0.007 to 0.02 percent relative to the amount of RDX in the grenade and from 9.0×10^{-6} to 6.0×10^{-5} percent for TNT. The estimated range of surface soil concentrations below these residue plumes were 0.94 to 56 µg/kg for RDX and 0.041 to 0.22 µg/kg for TNT (Table 4). Walsh et al. (2001) sampled a target berm (approximately 100 m^2) that had been used for a training exercise for the firing of 1800 rifle grenades (40-mm) at Fort Greely, Alaska. The rifle grenades used at Fort Greely were filled with Composition A5 (55 g, 98.5 percent RDX) and the sampling was done 20 months after the firing exercise. Five composite samples were collected horizontally along the face of the berm at 1-m intervals. Their investigation showed that the RDX concentrations ranged from 4 to 1700 μ g/kg and that there was a distinct trend showing increasing concentrations going from the top to the bottom of the berm. The estimated level of RDX in the soil based on the detonation residue concentrations and measured levels for this target are in reasonable agreement given the time between the firing exercise and sampling event.

The live-fire detonations of M67 hand grenades had an overall mean percent deposition of 2.0×10^{-5} percent for RDX (indicating a 99.99998 percent consumption of the main charge) and an estimated soil concentration of 0.085 µg/kg (Table 6-4). Based on these findings, the presence of RDX, TNT, and HMX should be difficult to detect in surface soils in hand grenade ranges. However, surface and shallow profile surface soil samples from active hand grenade training ranges have often shown moderately high concentrations for all three of these analytes. For example, Jenkins et al. (2001) reported median concentrations of 1560, 543, and 728 µg/kg for RDX, TNT, and HMX, respectively, in surface soils from a hand grenade range. They also reported, however, that there was evidence of partial detonations, based on the discovery of large fragments of M67 hand-grenade casings with Composition B remaining on the casing surface (Jenkins et al. 2001). Therefore, to account for the apparently anomalously high soil concentrations of RDX, TNT, and HMX on this hand grenade range and on other ranges, the presence of hand grenades that partially detonated has been suggested (Walsh et al. 2002).¹

Live-fire detonation residues from three other munitions were evaluated in this study, e.g., Claymore mines, bangalore torpedoes, and a shaped demolition charge. These munitions are typically used by battlefield engineers for specific tasks and see limited use during military training and testing exercises. Of these three munitions, the detonation of a shaped demolition charge produced the highest deposition of energetics from the main charge (Table 6-4). However, since only a single munition of this type has been evaluated, use of this value is tentative. The overall mean percent deposition of RDX for Claymore mines was 0.002 percent, and the estimated soil concentration was $10 \mu g/kg$ (Table 6-4). Of this group of munitions, only the detonation of a Claymore mine (0.62 kg C4) has been evaluated on a training range (Pennington et al. 2002). Composite surface soil samples collected in front of the detonation point of a single Claymore mine failed to show the presence of RDX, which is not surprising based on the mean estimated surface soil concentration of 10 µg/kg.

Blow-in-place detonations

The results in Table 6-5 show that, for the munitions that were blown in place, the greatest percent deposited for individual detonations was 2 and 6 percent for TNT from a 155-mm howitzer round and a PPM-2 anti-personnel mine, respectively. The blowing in place of two PPM-2, a PMA-2, and two PMA-1A anti-personnel mines, along with three 155-mm howitzer rounds, showed a high (greater than 0.1 percent) percentage of deposited TNT. The main charge in all four of these munitions is TNT (RDX in the booster was added to the main charge of the PMA-2). These findings indicate that the blowing in place of TNT-filled munitions typically is not as efficient at consuming the main charge as the live-fire detonation of Composition-B filled munitions.

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¹ Personal communication, Thomas F. Jenkins, Research Chemist, CRREL, 2001.

Lewis et al. (in Pennington et al. 2003) reported that frequently there are high recoveries (greater than 0.1 percent) of RDX and TNT from the blowing in place of munitions with a demolition block of C4. The munitions blown in place in their study were 60- and 81-mm mortar rounds, M67 hand grenades, a 105-mm howitzer round, and blocks of TNT formed in the shape of a PMA-2 antipersonnel mine. Overall these findings were very complementary to our findings with respect to residue concentrations resulting from blow-in-place operations. They also blew in place four M67 hand grenades with blasting caps that were placed into the fuse well. Their experiments also used a fresh snow surface as a collection medium; however, their studies were different from ours in some other respects owing to safety concerns and study objectives. All of the munitions blown in place had their fuses removed; therefore, the casing was breached. Furthermore, when used, the amount of demolition C4 varied between 5 and 150 g (40 to 150 g for the artillery and mortar rounds). These two factors may have contributed to the high levels of deposited explosives residues.

The blowing in place of 155-mm howitzer rounds filled with TNT had percent deposition values that ranged over five orders of magnitude (7×10^{-6} to 2 percent), the widest distribution of values seen for all the munitions studied. The detonation residues also showed the presence of several other analytes (e.g., TNB, 2,4-DNT, 2AmDNT, and 4AmDNT) at lower concentrations. The estimated soil concentrations below the detonation plumes showing the lowest and highest percent deposition of TNT were 0.18 and $26,000 \mu$ g/kg (Table 6-5). Following the melting of the snowpack, approximately 2 months after the 155-mm howitzer rounds had been blown in place, composite surface soil samples (top 1–2 cm) were collected in concentric rings around both of these detonation points. A single composite sample was collected 3 m from the detonation point for the round that showed the lowest TNT deposition. Three separate composite samples were collected at distances of 3, 5, and 10 m (nine total) around the detonation point of the round with the highest TNT deposition (Hewitt and Walsh 2003). TNT was not detected in the composite soil sample collected for the round showing the lowest deposition of this analyte. In contrast, TNT was present in all of the composite surface soil samples collected around the round that had the highest deposition, and the overall average was 49,000 µg/kg. This overall average presumably would have been even higher if the sampling depth had been limited to the top 0.5 cm. Even so, the TNT concentrations obtained for the surface soil samples collected around both of these detonation points are within a factor of two of the levels anticipated.

Jenkins et al. (in Pennington et al. 2002, Chapter 2) presented information about the blowing in place of three UXOs and a 500-lb bomb containing TNT that had low-ordered, i.e., about half of the main charge remained unconsumed in the bomb's breached casing. All of these munitions were found on an active training range. The UXO items consisted of two separate 155-mm howitzer rounds and the combination of 155-mm howitzer round and an 81-mm mortar round found side by side. Composite soil samples were collected around each of these blow-in-place operations before and after detonation, using the same sampling design. The 155-mm howitzer rounds and the combination of the 155-mm howitzer round and 81-mm mortar round were each blown in place with two demolition blocks (0.57 kg) of C4. Three demolition blocks of C4 were used

for the bomb. Explosives residue concentrations in the surface soil samples increased following each of these operations. On average, the high explosive that showed the largest increase in concentration ranged from greater than 6000-fold $($ <10 to 65,600 µg/kg RDX) to less than 50-fold (129 to 6100 µg/kg TNT). Increases of TNT in the composite samples that were collected at 3, 5, and 10 m from the low-order bomb after detonation ranged from 3.1 to 39 times. The main charge in the 155-mm howitzer rounds could not be established prior to detonation because no visible markings remained on their exposed surface. However, based on the concentrations of high explosives found in the soil samples following the detonation of the 155-mm howitzer round that showed greatest deposition of energetics, this round most likely contained Composition B. The U.S. Army Engineering and Support Center (USAESC) has also reported on the blowing in place of different Composition-B-filled artillery rounds (60-, 81-, 120-mm mortar rounds and 105- and 155-mm howitzer rounds) with C4 (USAESC 2002). A sand pit and metal trays were used as collection surfaces to obtain four composite samples to assess residue concentrations. Overall, the highest post-detonation residue concentrations were obtained for RDX and the values for this high explosive often exceeded 1000 µg/kg. These findings indicate that efficiency of consuming the high explosives for blowing in place of Composition-B-filled rounds is similar to what was obtained above for TNTfilled rounds and that the dispersion of unconsumed RDX can lead to milligramper-kilogram levels in surface soils.

Detonation residues from the blowing in place of demolition blocks of C4 and six different types of land mines were also evaluated. Of these munitions, the blowing in place of anti-personnel mines resulted in the highest deposition of energetics (TNT) from the main charge and also showed the highest estimated soil concentrations (Table 6-5). High residue concentrations from land mines are expected, since their design is not optimal for the buildup of detonation pressure as compared to artillery and mortar rounds.¹ Overall, the deposition of explosives from the main charge of these anti-personnel mines ranged from 6 to 0.002 percent. Residues from the blowing in place of the anti-personnel mines filled with TNT also showed the presence of manufacturing impurities (2,4DNT and 2,6DNT) and TNT transformation products (TNB, 2AmDNT, and 4AmDNT). Values for these other analytes were not reported in Appendix A, because they often were much lower than TNT in concentration and had not been confirmed by a second analysis.

The mean percent deposition of RDX for blowing in place of demolition blocks of C4 was 0.003 percent, and the mean estimated surface soil concentration was 10 μ g/kg (Table 6-5). These values are consistent with the live-fire detonations of Claymore mines, a munition that contains a slightly greater (17 percent) quantity of C4 as the main charge (Table 6-3). Based on this finding, explosives residues from the detonation of a single block of C4 would be difficult to detect in surface soils. C4 was used to blow in place two antipersonnel mines (PPM-2 and VS-50), two anti-tank mines (M15 and M19), an 81-mm mortar round, and seven 155-mm howitzer rounds. The PPM-2 and 155-mm mortar rounds were filled with TNT, the VS-50 with RDX, and the

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¹ Personal communication, P. Brousseau, Canadian National Defense Scientist, Defence Research Establishment-Valcartier (DREV), Val-Belair, Quebec, March 2003.

anti-tank mines and 81-mm mortar round contained Composition B. Half a block of C4 (0.28 kg) each was used to blow in place the anti-personnel and anti-tank mines, and a full block (0.57 kg) was used for each of the other munitions. For the TNT-filled munitions, the percent deposition of RDX ranged from below detection to 0.02 percent for, respectively, the 155-mm howitzer rounds and two PPM-2 anti-personnel mines. For the RDX-filled munition, the percent deposition of RDX ranged from 0.03 to 0.06 percent, and for the Composition Bfilled munitions, the percent deposition of RDX ranged from 4×10^{-5} to 0.001 percent. Clearly, RDX in the block of C4 contributed to the detonation residues from the blowing in place of the PPM-2 anti-personnel mine; however, C4 was most likely efficiently consumed in the blowing in place of the 155-mm howitzer rounds. A 155-mm howitzer round contains a much larger quantity of energetics than an anti-personnel mine. For the other munitions (81-mm mortar round, VS50 anti-personnel mine, and anti-tank mines) blown in place with C4, the contribution of RDX from this demolition munition could not be distinguished from the main charge contribution of this high explosive.

Collection of residues on trays and plates

Along with the collection of snow samples, aluminum trays were set out to collect residues for chemical analysis during the blowing in place of two demolition blocks of C4 and two Claymore mines. For the first block of C4, the aluminum trays were placed 7.5 m from the detonation point. No residues (soot) were deposited on any of the trays for this trial. For the second block of C4, the trays were positioned 3.5 m from the detonation point. In this detonation trial, six (three sets) of the trays were within the detonation soot plume. A snow sample was collected adjacent to each set of the trays that was within the soot plume. For two of the Claymore mines, one set of aluminum trays (one for chemical and one for particle analysis) was positioned behind and four sets were positioned directly in front at 5, 7.5, 10, and 15 m. The detonation plume from one of the Claymore mines encompassed three sets of trays, while the other only covered one set of trays.

A chemical analysis also was performed on four steel plates that had demolition blocks of C4 detonated on top of them. The surface residue concentrations of RDX established for the trays and plates and for the adjacent snow surface were similar (Table 6-6). Therefore, multiple trays and plates could have been used instead of the snow cover to collect detonation residues from blow-in-place operations. However, precautions would have to be taken to prevent contaminated soil from previous detonations from interfering with subsequent detonations. Other obvious disadvantages would be the inability to predict where the detonation plume will deposit residues and the inability to place plates or trays close to the detonation point without disruption. One way some of these concerns have been addressed was to use a pit filled with clean sand for the detonation point

(USAESC 2002). Another way some of these concerns have been addressed is to use a raised thick steel plate as a detonation platform.¹

Some of the aluminum trays were set out with the express purpose of finding explosive particles, so as to describe their appearance and size distribution. The analysis of the cotton balls used to wipe the trays after the removal of particles established that only the blowing in place of the TNT-filled anti-personnel mines and two 155-mm howitzer rounds warranted further investigation (Note: Most of the trays had no detonation residues on them). To establish that certain classes of particles contained TNT, tetra-butyl-ammonium hydroxide was used, a reagent that reacts with TNT to form a red product. Explosive grains were found on only one of the trays that was deployed during the blowing in place of a 155-mm howitzer round. Despite high concentrations of TNT in the residues recovered from some of the trays with the cotton balls for the other howitzer round and for two of the antipersonnel mines, no explosive grains were found in these samples. This finding suggests that the particles were very small and enmeshed in the ubiquitous soot generated by the detonation (Taylor et al., in prep.).

For the 155-mm howitzer tray sample with grains of TNT, actual sizes of all TNT particles greater than 250 µm were measured in the following manner: all TNT grains were photographed using a digital camera attached to the microscope. National Institute of Health (NIH) image, a freeware imageprocessing program, was used to process each image and obtain the number of TNT particles, as well as the perimeter length, and the length of the major and minor axes for each particle. To estimate the number of TNT particles in the five smallest size fractions, the sample was extracted and analyzed as described above and the concentration of TNT in the sample was used to estimate the number of particles (assuming a given diameter) in each size fraction needed to give the

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¹ Personal communication, Sonia Thiboutot, Canadian National Defence Scientist, Defence Research and Development Canada –Valcartier (DRDC), Val–Belair, Quebec, September 2001.

measured concentration (Taylor et al., 2004). The diameters chosen were 40, 75, 110, 150, and 200 µm, respectively, for the <53-, 53- to 106-, 106- to 125-, 125 to 180-, 180- to 250-µm-size fractions. Figure 6-16 shows the size distribution of particles collected on a tray. Clearly, there are several orders of magnitude more particles that are less than 0.1 mm in diameter than particles that are greater than 1 mm. However, the majority of the unconsumed TNT mass is in the particles larger than 0.1 mm in diameter. Likewise a soot (filtered) portion of a snow sample from this 155-mm howitzer detonation plume was also analyzed for TNT particles. Overall, the same general trend was established for the particle size distribution (Taylor et al., 2004).

Figure 6-16. Size distribution of residue TNT particle measured for the blowing in place of a 155-mm howitzer round

Video records of some of the detonations were made to provide the data needed to model the detonation and compare the predicted particle distribution with that measured. This work is being done in collaboration with Aerodyne and is not yet completed.¹

Summary

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Findings show that the high-explosives filler in the main charge of howitzer rounds, mortar rounds, and hand grenades is efficiently consumed during live-fire operations that result in high-order detonations. Analysis of detonation residues collected on snow following the live-fire detonations of three different mortar rounds, one type of howitzer round, and one type of hand grenade, all filled with Composition B, shows that on average 99.997 percent or more of the RDX and

¹ Personal communication, Susan Taylor, Research Physical Scientist, CRREL, February 2003.

TNT was consumed. The high explosives that are not consumed during these detonations are presumably very fine particles $(<50 \mu m$) that are spread over an area that would, on average, contribute 10 µg/kg/round or less of these energetics to the ground surface. This amount of explosives residue is consistent with the very low concentrations of energetic residues that have been established for a majority of the landscape on 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-ordered; breached casing and presence of unconsumed main charge). Therefore, high-order detonation from live-fire training does not appear to distribute large amounts of explosives residues on Army training ranges.

Using C4 to blow in place UXOs contributes RDX to the detonation residues when this operation is performed with small munitions. More importantly, the practice of blowing in place a munition with a block of C4 frequently results in the random dispersion of percent, or near-percent, levels of the unconsumed high-explosives filler from the main charge. The majority of mass of unconsumed explosives appears to exist in the particle size range from >0.1 mm to a couple of millimeters. When only 90 percent to 99.9 percent of the main charge is consumed, the dispersion of energetic materials contributes milligramper-kilogram quantities to the ground surface. In comparison to partial detonations, the release of energetics from a single blow-in-place operation is typically smaller. With the exception of the small training ranges (e.g., hand grenade, rifle grenade, ground-to-ground rocket, or missile ranges) both blowing in place and partial detonations are often spatially isolated. Large munitions that have partially detonated, small areas where partial detonations frequently occur, and locations (demolition ranges) where blow-in-place-type operations are repeatedly performed, are all likely candidate source zones of high explosives that may be of environmental concern.

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Appendix A: Data

Table 6-A2 Surface Concentrations of Explosives Residues from the Detonation of a 1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 1/19/01 Area: Soot plume 150 m² ; Crater 2.5 m²

Table 6-A4 Surface Concentrations of Explosives Residues from the Detonation of an M19 anti-tank mine with a 0.62-lb (0.28-kg) Block of C4 at Ft. Drum, NY, 2/7/01 Area: Soot plume 870 m² ; Crater 5 m²

Sample collected just outside of visual soot plume, not include in estimate of residue concentration.

Surface Concentration of Explosives Residues from the Live Fire Detonation of a 60-mm Mortar with a Proximity Fuse Setting of Approximately 2 m at Camp Ethan Allen, VT, 2/16/01

Table 6-A8

Surface Concentration of Explosives Residues from the Live Fire Detonation of 40-mm Rifle Grenades with Impact Fuse Setting at Camp Ethan Allen, VT, 2/16/01

Surface Concentrations of Explosives Residues from a 120-mm Mortar Round with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 570 m² ; Crater sample lost (2 of 7)

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Table 6-A18 Surface Concentrations of Explosives Residues from a 120-mm Mortar Round with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 780 m² ; Crater 10 m² (3 of 7)

Table 6-A19

Surface Concentrations of Explosives Residues from a 120-mm Mortar Round with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 180 m² ; Crater 10 m² (4 of 7)

Table 6-A20 Surface Concentrations of Explosives Residues from a 120-mm Mortar Round with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 320 m² ; Crater 10 m² (5 of 7)

Table 6-A21

Surface Concentrations of Explosives Residues from a 120-mm Mortar Round with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 1280 m² ; Crater 10 m² (6 of 7)

Table 6-A22 Surface Concentrations of Explosives Residues for a 120-mm Mortar with Impact Fuse Setting at Camp Ethan Allen, VT, 3/19/01 Area: Soot plume 870 m² ; Crater 10 m² (7 of 7) (µ**g/m2) Sample Distance to Crater (m) Sample area** $(m²)$ **) RDX TNT HMX 2,6-DNT 2,4-DNT 4AmDNT 2AmDNT NG** S7-1 7.4 1.05 5.0 0.071 ND ND 0.10 ND ND 0.058 S7-2 | 5.5 | 1.44 | 29 | 0.73 | 0.35 | ND | 0.54 | ND | ND | ND | ND S7-3 11.5 1.98 4.5 ND 0.098 0.091 0.25 ND ND 0.041

S7-4 11.4 2.06 1.9 ND ND 0.057 ND ND ND 0.49 S7-5 | 11.7 | 1.40 | 0.71 | ND | 0.041 | ND | ND | ND | 0.38 S7-6 |9.3 |1.38 |1.5 |ND |ND |0.033 |0.13 |0.10 |ND |ND |ND S7-7 14.1 1.05 0.83 0.041 ND 0.086 0.039 0.11 ND 0.071 Crater -- 0.5* 20 ND 2.7 ND 9.7 ND ND 3.6 **Total mass (**µ**g) deposited**

) 5300 | 150 | 60 | 150 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 | 130 |

5500 150 87 | | | | | | | 170

Without Crater (860 m²)

* Estimated that 5 percent of the crater was sampled.

With Crater (870 m^2)

Area: Soot plume 90 m² ; Crater 1.5 m² (2 of 7)

Surface Concentrations of Explosives Residues from the Detonation of 1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/15/2002

Area: Soot plume 179 m² ; Crater 1.8 m² (5 of 7)

Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 496 m² , Crater 1.0 m² (1 of 7)

Table 6-A38 Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 311 m² ; Crater 1.8 m² (2 of 7)

Table 6-A39

Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a 1.25-lb Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 345 m² , Crater 1.7 m2 (3 of 7)

Table 6-A40 Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 344 m² ; Crater 0.56 m² (4 of 7)

Table 6-A41 Surface Concentrations of Explosives Residues from the Detonation of a 155-mm

Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 344 m² ; Crater 0.56 m² (4 of 7)

Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 301 m² ; Crater 1.3 m² (6 of 7)

Table 6-A43

Surface Concentrations of Explosives Residues from the Detonation of a 155-mm Howitzer Round with a1.25-lb (0.57-kg) Block of C4 at Camp Ethan Allen, VT, 2/28/2002 Area: Soot plume 473 m² ; Crater 2.2 m² (7 of 7)

Table 6-A52 Surface Concentrations of Explosives Residues from the Live-Fire Detonation of an 81-mm Mortar Round at Ft. Richardson, AK, 3/13/2002 Area: Soot plume 230 m² ; Crater 5.8 m² (1 of 2)

Surface Concentrations of Explosives Residues from the Live Fire Detonation of Thirteen 81-mm Mortar Rounds at Ft. Richardson, AK, 3/13/2002. Plumes for rounds designated 2 through 14 overlapped.

Surface Concentrations of Explosives Residues from the Live Fire Detonation of Two 105-mm Howitzer Rounds at Ft. Richardson, AK, 3/14/2002. Plumes for rounds designated 2 and 3 overlapped Area: two overlapping Soot plume 780 m² ; Crater 9.8 & 8.8 m² (2 and 3 of 13)

Area: Soot plume 780 m² , Crater 9.4 m² (4 of 13)

Table 6-A57

Surface Concentrations of Explosives Residues from the Live-Fire Detonation of Four 105-mm Howitzer Rounds at Ft. Richardson, AK, 3/14/2002. Plumes for rounds designated 5 through 8 overlapped.

Area: Four overlapping Soot plumes 1880 m²; Craters 9.1, 7.2, 11.8 **& 8.4 m² (5, 6, 7 and 8 of 13)**

Sample	Distance to Crater (m)	Sample area $(m2)$	$(\mu g/m^2)$	
			RDX	TNT
$S7-1$	1.9	1	0.34	0.92
$S7-2$	4	1	0.28	0.85
$S7-3$	4.1	1	0.08 j	0.18j
$S7-4$	5.5	1	0.20j	0.22j
$S7-5$	9.4	1	0.49	0.29
S7-6	11	1	ND	0.42
S7-7	13	1	ND	ND
$S7-8$	14	1	ND	0.38
S7-9	12	1	ND	ND
S7-10	12	1	ND	0.31
S7-11	16	1	0.08j	0.21
S7-12	19	1	0.10j	0.32
$S7-13$	7.7	1	0.31	ND
S7-14	12	1	0.19	0.31
$S7-15$	12	1	0.24j	3.3
(Continued)				

Table 6-A58 Surface Concentrations of Explosives Residues from the Live-Fire

j Concentration at or below estimated detection level.

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Appendix B: Calculations

Step 1. Calculate area covered by soot

The area of the soot plume was usually established with the geographical information system (GIS), by walking the perimeter and recording locations under an area function. In the few cases where this system was not available, or for all of the craters, the diameter was measured and the area of a circle was calculated. When plumes overlapped, the area was reported on a per-round basis.

Area = πr^2

Step 2. Calculate amount of explosives residues in a surface snow sample

Soot. The soot and debris trapped on the glass fiber filter after passing the entire melted sample through a vacuum filtration system was extracted with acetonitrile. The volume of extractant was multiplied by the concentration to determine the mass of explosives in the soot. If more than one vessel (soxhlet extraction thimble) was needed for a given sample, then the masses were added together.

Example 0.025 mg RDX/L \times 0.145 L = 3.6 µg RDX

Melt. The total snow melt volume was recorded, and then a 500-mL portion was passed through a solid phase extraction cartridge. The explosives sorbed to the solid support were extracted with 5.00 mL of acetonitrile, for a 100-fold preconcentration factor. To calculate the mass of explosives in the snow melt, the concentration measured was divided by 100, then multiplied by the total melt volume.

Example 0.055 mg RDX/L \div 100 \times 4.22L = 2.3 µg RDX

Step 3. Calculate the mass of explosives per meter squared of a sample (i.e., surface concentration)

The mass of an analyte determined for the soot and melt fraction for a given sample was added together and divided by the surface area sampled.

Example 3.6 µg RDX (soot) + 2.3 µg RDX (snow melt) ÷ 0.78 m² = 7.6 µg RDX/m²

Step 4. Mean surface concentration

The mean surface concentration for a given analyte was established for the samples obtained within a soot plume. In the case of overlapping plumes the mean per round was determined. The mass of explosives in the crater was not used to determine the mean surface concentration.

Step 5. Mass deposited

The mass deposited was determined by multiplying the mean surface concentration per round by the total plume (or in the case of overlapping plumes, the plume area per round) area not including the crater, then adding the mass of analyte determined for the crater (or for the mean of the craters, when plumes overlapped). The example is for a hand grenade:

0.58 µg RDX/m² (mean surface conc.) \times 99 m² (area without crater) + 1.7 µg RDX/m² × 1.0 m² (area of crater) = 59 µg RDX

Step 6. Percent deposited

The mass deposited was divided by the total mass of analyte in the munition detonated, including the explosives in the demolition munition used for blow-inplace operations (see Table 3).

Step 7. Estimated mean soil concentration

Once the snow melted the mean explosives residue concentrations in the soil (1.7 g/cm^3) density) beneath the plumes was estimated by dividing the mean surface concentration by an area 1 m square by 0.5 cm deep.

Example 0.73 μ g RDX/m² ÷ (100 cm x 100 cm x 0.5 cm) × 1.7g/cm3 = 0.000086 μ g/g or 0.086 µg/kg

7 Estimation of the Quantity of Explosive Residues Resulting from the Detonation of Unconfined Explosives Charges

Abstract

In the last ten years, awareness has grown concerning the environmental impact of the detonation of munitions during live training or range clearance operations. Characterization of military live-fire training ranges has shown that the contamination coming from residues of explosives varies depending on the type of range sampled, but is usually very low. Despite this, detectable quantities of explosives residues in the groundwater at the Massachusetts Military Reserve led to its eventual shutdown. The source of contamination has not been clearly identified; the disposal of unexploded ordnance, broken munitions leaking into the surroundings, or the accumulation of residues from intensive training over the last two decades are all possibilities. A portion of the explosive content of a munition is known to be dispersed into the environment after detonation. To sustain environmentally friendly training, a better definition of that portion of the explosive content, both in terms of types and quantities of residues, is needed. To achieve this, highly systematic studies are required.

This work was undertaken to develop a better understanding of detonation phenomena and of the parameters having a strong influence on detonation. Charges of unconfined explosives (20 to 100 g) were detonated in controlled conditions. Explosives included C4, trinitrotoluene, Composition B, Octol, a plastic-bonded explosive, and an experimental insensitive melt-cast explosive. Residues were collected on witness plates, which were thoroughly swabbed after each detonation. Parameters that were recorded included the barometric pressure and the weather conditions; high-speed images were also taken at each detonation. Mean percentages of residues dispersed after detonation events ranged from 0.0001 percent to 19.4 percent.

This trial was co-sponsored by the Director General Environment (DGE) from Canada and the Strategic Environmental Research and Development Program (SERDP) from the United States of America.

Executive Summary

Live-fire testing and training ranges are essential to maintain combat readiness of the military forces. However, more and more attention is being given to the environmental and human health impacts of military training activities because of the potential contamination of air, soil, and water. To ensure that such activities can be conducted on a sustainable basis with minimum adverse environmental impact, range-management practices need to be evaluated and, if necessary, improved. While this environmental concern may seem trivial compared to the immediate physical danger presented by explosives, consider that approximately three million explosive rounds have been fired at Canadian Force Base Shilo since 1919. This represents potentially hundreds of thousands of kilograms of explosives or their by-products released into the environment. Considering that explosives and their by-products are potentially carcinogenic and mutagenic, the situation could become dramatic if these products were to reach the groundwater.

The main sources of immediate contamination are unexploded ordnance (UXO) and low-order detonations; long-term contamination can, however, also result from the accumulation of residues from properly functioning munitions. Although the dispersion of explosives and their metabolites into the environment as a result of incomplete detonation is known to occur, the phenomenon has seldom been quantified. This study is aimed at better understanding the impacts of blow-in-place operations and was conducted on unconfined charges to study the relative impacts of detonation set-ups.

Detonation is a complex phenomena driven by a wide variety of factors, such as the type, the weight, the diameter and the shape of the explosive, the position and orientation of the detonator, the quantity of C4 used, and the weather conditions. Experiments need to be done in controlled environments to better understand the influence of each parameter on the detonation. The primary objectives of this work are to evaluate the types and quantities of residues that result from the detonation of 20-g to 100-g charges of unconfined explosives and to establish the relationship between the amount of residues dispersed into the surrounding environment and the amount of explosives being detonated. Explosives tested include C4, trinitrotoluene, Composition B, Octol, a plastic-bonded explosive (PBX), and an experimental insensitive melt-cast explosive (XRT, for Experimental Rubbery TNT). Residues were collected on witness plates that were thoroughly swabbed after each detonation.

Results show that the amounts of residues recovered were generally very low, making it hard to draw clear conclusions on the effect of the weight of the charge on the amount of dispersed residues. It was observed, however, that large charges tended to yield generally smaller or comparable amounts of residue. More residues were also recovered for the detonation of TNT cylinders; the

insensitive formulations (PBX and XRT) also yielded much higher dispersion of explosives. Finally, the detonations of C4 blocks also led to higher levels of RDX dispersion than spheres or cylinders.

Introduction

Background

Conventional munitions are filled mainly with secondary explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Detonation of munitions is now known to lead to the dispersion of a part of the explosive into the surrounding environment, causing a potential problem, because TNT, RDX, and HMX may be toxic at relatively low concentrations to a number of ecological receptors (Robidoux et al. 2003). Although their solubility in water is relatively low (< 130 mg/L), explosives can be leached by rainfall and become mobile in the groundwater. Moreover, explosives are all subject to photolysis, chemical reduction, biodegradation, and sorption. The mobility of explosives and their byproducts is influenced by their solubility, their dissolution rate, and their adsorptive properties. For instance, TNT can degrade to more than 20 by-products with various solubilities and toxicities, such as 2- and 4-aminodinitrotoluene (ADNT), 2,4- and 2,6-diaminonitrotoluene (DANT), and, under strictly anaerobic conditions, 2,4,6-triaminotoluene. The ADNT and DANT are much more soluble than TNT, but they also tend to bind strongly to organic matter in the soil. Thus, RDX migrates faster than TNT or HMX because of the attenuation of TNT on soil particles and of the poor water solubility of HMX. The migration of these explosives and by-products could become a serious problem if they reach the groundwater and contaminate drinking water supplies.

Such a situation was encountered at the Massachusetts Military Reservation (MMR) in the United States. The MMR was closed because RDX was found in the groundwater. One source of RDX was identified to be an open burning/open detonation (OB/OD) and explosive ordnance disposal (EOD) training area where various types of munitions containing RDX were detonated. A second source of RDX appears to originate within an artillery and mortar impact area. It is suspected that low-order detonations release explosives residues to the environment, which then are dissolved and transported to the water table. Other sources such as secondary detonation of unexploded ordnance (UXO) and high-order detonation have not been ruled out. A third source for RDX groundwater contamination is associated with a contractor test range. Activities identified as being responsible for RDX include those discussed above as well as melt-pour facility and disposal activities. RDX has not been found in groundwater associated with an anti-tank rocket range at MMR.¹

All military training ranges cannot be shut down to prevent potential contamination problems, however. Testing and training ranges are essential to maintain troop combat readiness. Therefore, ways need to be found to sustain

¹ J. Clausen, private communication, 2004.

environmentally friendly military training. To address this situation, it is necessary to assess the extent of contamination in military ranges. Also, fundamental work is needed to estimate the portion of the explosive that is dispersed into the surrounding environment after a blow-in-place detonation, to be able to identify critical situations.

The characterization of military ranges will not be addressed in this report. Many ranges have been characterized to date (Ampleman et al. 1998, 2000, 2001; Dubé et al. 1999; Jenkins et al. 1997, 2000, 2001; Thiboutot et al. 1998, 2000, 2001a, 2001b; Walsh et al. 2001). However, a lot of work remains to be done to assess the extent of contamination. Some ranges are hard to characterize because they have very large surface areas that make systematic sampling very difficult and expensive. Moreover, UXO is often encountered, posing significant security and safety hazards. The extent of contamination is also hard to assess due to the large heterogeneity of residues. Results obtained so far indicate that explosives contamination in most ranges is usually very low. Higher levels of contamination have, however, been detected in anti-tank and grenade ranges (Jenkins et al. 1997, 1998, 2001; Thiboutot et al. 1998). Higher levels of explosives were also detected near blow-in-place events, which were conducted by EOD teams to get rid of surface UXO. This type of operation is conducted on a regular basis in training areas to get rid of the safety problem presented by UXOs.

The second approach to sustaining environmentally friendly military training is the identification of the residues dispersed into the surroundings along with estimation of quantities for several types of detonation under various conditions. This objective can be reached only by conducting very systematic studies. Since concern in this area has arisen only recently, data are still relatively scarce.

The first systematic studies were a U.S. Army Armament, Munitions and Chemical Command Test Series (1992a and 1992b) and a U.S. Air Force study (1994). The authors carried out an extensive study to develop emission factors for the main OB/OD contaminants, to obtain information on the characteristics of the plumes, and to find means to control the contamination released by OB/OD. For OD, preliminary tests were done with small-scale detonations in a closed vessel (bang box) of 1000 $m³$ in which small quantities of TNT (220 g) were detonated. Reaction products sampled included carbon and nitrogen dioxides and monoxides, and volatile and semi-volatile organic compounds (VOC/SVOC). Larger scale (900 g) OD field tests were also conducted with TNT, Composition B (Comp B), ammonium picrate, and RDX, either directly on the surface of the soil or suspended above ground level.

Results showed that carbon from TNT was mostly (>92 percent of the total TNT carbon content) converted to carbon dioxide $(CO₂)$ and that the remaining carbon was transformed in carbon monoxide (CO) (0.6 - 5.6 percent), methane (< 1.4 percent), other VOC (< 1.3 percent), particulate organic carbon $(0.01 -$ 1.4 percent), and elemental carbon (soot) $(0.7 - 1.7$ percent). Nitric oxide (NO) and nitrogen dioxide $(NO₂)$ emission factors were 0.1 and 0.4 percent, respectively. $CO₂$ emission factors were lower for surface detonations than for suspended or bang box detonations. The presence of soil particles in the fireball was suspected to reduce the temperature, the duration of elevated temperatures within

the fireball, and the degree of penetration of air into the fireball, thus producing more CO than $CO₂$.

Results also indicated that the SVOC emission factors were not as dependent on the type of OD as were gaseous species. The most frequently encountered SVOCs were 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 2 nitronaphtalene, naphtalene, benz[a]anthracene, pyrene, dibenzofuran, and diphenylamine. The overall quantity of SVOCs decreased sharply with distance; approximately 98 percent of the SVOCs were found in the immediate vicinity of the crater.

Global results for Comp B (RDX:TNT 60:40) and RDX are very similar to those of TNT. However, the degree of Comp B and RDX carbon conversions to $CO₂$ are 95 and 97 percent, respectively, which are slightly higher than for TNT. The authors relate these small differences in detonation efficiencies to the oxygen balance of each explosive, which increases from RDX (22 percent) to Comp B (53 percent) to TNT (74 percent). The degree of penetration of air into the fireball was, however, identified as the major factor influencing detonation efficiency. Contaminants detected are the same as those for TNT, except that 2,6-dinitrotoluene (DNT) and 2-nitrodiphenylamine were also found for both explosives, in addition to 1-nitropyrene, RDX, and benzo[a]pyrene for RDX.

Another study by Jenkins et al. (2000) assessed the dispersion of explosives and their metabolites into the environment by the destruction of three 81-mm mortars with C4 and the firing of two 60-mm mortars. Experiments were conducted on snow-covered ranges to be able to estimate the area contaminated using the soot produced by the detonation. The pattern of dispersion was quite heterogeneous and sampling of a very large area was necessary to get representative results. The recovered amounts of explosives remained low, but varied from round to round. Some general trends could, however, be drawn. For example, the RDX contamination was always much higher than that of TNT, even though both mortars were filled with Comp. B. Also, the concentration of RDX was higher for the 81-mm mortars than for the 60-mm, suggesting that some contamination could come from C4. And finally, nitroglycerin was unexpectedly found in all of the samples.

Lewis et al. (2002) also conducted a study with on-snow detonations of 60 and 81-mm mortars, hand grenades, and mimics of PMA-1A mines. Static detonations and blow-in-place UXO destruction were conducted. Up to 1.5 percent of the total explosive of the munition was dispersed into the environment after the detonation, which is almost three orders of magnitude higher than the values reported by Jenkins et al. (2000). They also reported that using C4 to destroy the munition as a UXO, as the military do in the field, increased the amount of RDX dispersed in the environment.

These earlier studies generated interesting results, but also raised many questions. The work reported in this document was undertaken to try to answer some very basic questions about the extent of contamination coming from controlled detonations of specific explosives or munitions and to gain a better understanding of the parameters leading to the spread of explosives into the environment. To do this, a basic knowledge of detonation dynamics and the parameters affecting

them is necessary. An overview of the theory of detonation follows. A thorough review is beyond the scope of this work; the interested reader is instead referred to specialized publications (Zukas and Walters 1998; Cooper 1996).

Theory of detonation

Detonation is a special kind of combustion. It takes place when a material reacts so quickly that the reaction products are not able to escape from the reaction front, causing a rapid increase in pressure. Eventually, during the reaction of certain mixtures, the pressure experiences a sudden nonlinear increase, which is a *shock wave* that travels at supersonic speed through the reactive mixture. The *detonation wave*, which is caused by the shock wave, is the name for the narrow zone (reaction zone) where chemical transformations take place.

A given detonation is characterized by a specific pressure and velocity that do not vary with time. These parameters are dependent on the type of explosive, the length of the reaction zone, the initial density, geometry, temperature, and weight of the explosive, and the degree of confinement. The detonation pressure and velocity increase with the increasing initial density and decreasing initial temperature of the explosive. This increase can be easily explained by the interrelationship of density and temperature, i.e., a rise in material temperature generally decreases its density.

Each explosive is also characterized by a critical weight, a critical diameter, and a critical ratio length/diameter (L/D) below which detonation does not occur. Above these critical parameters, the detonation velocity and pressure increase steadily until the maximum and constant value is reached. These critical parameters are in turn dependent on the degree of confinement, i.e., smaller quantities than the critical weight could detonate if the explosive is under confinement. Table 7-1 lists the critical diameter for the explosives used in this study.

Parameters such as the orientation of the detonator also affect the blast wave and, hence, the spreading of residues into the environment. For example, a detonator installed vertically on a charge will produce a blast wave in the direction of the soil that should lead to a symmetric dispersion of the residues around the explosive. If instead the detonator is leaning on the soil and is in contact with the

side of the explosive, the blast wave will be parallel to the surface of the soil and the residues should be spread in front of the blast wave.

The above-mentioned parameters are very fundamental. Detonics is a complex science, and many other parameters may play an important role in the detonation of real munitions. To better understand the dynamics of detonation, however, and allow identification of some of the critical parameters strongly influencing the detonation, detonation of explosives and munitions in controlled environments is required.

Objectives

The main objective of this work was to assess the extent of contamination resulting from blow-in-place experiments on unconfined charges. Thus, the type of residues and the amounts dispersed into the surrounding environment were evaluated and analyzed together with some critical detonation parameters. Another objective was to verify if there was a relationship between the weight of the charge and the quantities of residues dispersed in the environment. This hypothesis was based on the detonation of small charges producing lower fireball temperatures than larger charges, and hence possibly leaving more residues after the detonation.

Thus, the specific objectives of this study were:

- To evaluate the type and quantities of contaminants resulting from the detonation of small charges of unconfined explosives.
- To establish the relationship between the initial weight of explosive being detonated and the amount of residues dispersed into the surroundings.
- To verify the hypothesis that the amount of residues dispersed in the surrounding environment decreases with the increasing amount of the charge being detonated.
- To determine the effectiveness of witness plates in representing the total amount of dispersed residues.

Thus, small charges of various unconfined explosives were detonated in controlled conditions while parameters such as the type and amount of explosive, the shape of the charge, and the orientation of the detonator were varied. Explosives included C4, TNT, Comp B, Octol, a plastic-bonded explosive (PBX), and an experimental insensitive melt-cast explosive (XRT, for experimental rubbery TNT).

Experiment Description

Explosives

Experiments were conducted on sandy soil at a demolition range at Canadian Forces Base (CFB) Valcartier. Each detonation was recorded with a high-speed video camera. Explosives were detonated on a steel plate and residues were collected on several witness plates. The swabs used for sampling were extracted and the extracts analyzed by high-pressure liquid chromatography (HPLC) using EPA SW846 Method 8330 (USEPA 1998). The air-blast pressure and meteorological data were also recorded for each detonation.

The explosives used in this study included C4, TNT, Comp B, Octol, PBX, and XRT. Table 7-2 lists the proportion of TNT, RDX, and HMX found in each explosive; the complete chemical composition can be found in Appendix A. Octol and Comp B were of type II (MIL-O-45445B) and I (Flakes, Grade A, MIL-C-401E), respectively. PBX was made of CX-84 that contains 84 percent RDX and 16 percent polymeric binder. XRT is an experimental explosive containing Octol (90 percent) and an energetic thermoplastic elastomer based on a glycidyl azide polymer (GAP) of molecular weight 2000 (10 percent).

4 GAP-2000 (XRT)

Military grade TNT generally contains up to 1 percent impurities made of a mixture of isomers of TNT and dinitrotoluene (DNT), especially 2,4-DNT, 1,3 dinitrobenzene and 1,3,5-trinitrobenzene (Leggett et al. 1977; George et al. 1999). Military-grade RDX is generally contaminated with 8 to 12 percent HMX. Military-grade HMX also contains up to 10 percent RDX as an impurity. The main contaminants (RDX, HMX) have been accounted for in the compositions given in Table 7-2.

C4 was shaped into spheres, cylinders, and rectangular blocks having weights varying between 20 and 100 g. The other explosives were cast as cylinders 2.5 cm in diameter with variable lengths. 75-g cylinders (5.6-cm diameter) were also used. PBX and some charges of TNT were primed with 20 to 30 g of

C4, but Comp B and Octol were used without any primer by attaching a number12 detonator directly to the main charge. The small cylinders of XRT could be detonated without primer, but C4 had to be used for the larger ones. The 55 trials accomplished for this study are described in Table 7-3.

Number 12 detonators were usually inserted into the explosive or the primer so that they lay parallel to the surface of the soil; this configuration is designated as horizontal in Table 7-3 (see Figure 7-1). For some cylinders and all C4 blocks, however, the detonator was perpendicular to the surface of the soil (listed as "vertical" in Table 7-3). Explosives were detonated electrically by an ammunition specialist.

Figure 7-1. Charge configuration schematic

Site setup

Experiments were conducted on sandy soil at the CFB Valcartier demolition range. Each explosive was placed in the middle of a heavy steel plate (1.34 x 1.77 x 0.1m). Four commercially available polyethylene tarps measuring 3.7 by 5.5 m were spread on the soil to avoid contamination from previous demolition activities. Aluminum witness plates (1 m x 1 m x 3 mm) were placed on the tarps around the steel plate to collect the residues. Between 8 and 12 aluminum plates were used, depending on the size of the charge being tested. To help with sampling, these witness plates were gently bent diagonally, from corner to corner, which created a slightly concave surface. Short aluminum feet (approximately 25 mm) were welded at each corner to keep the sampling surface off the ground, prevent the projection of contaminated soil particles by the blast wave onto the plates, and keep the witness plate flush with the surface of the detonation plate. Figure 7-2 shows the installation, and Figures 7-3 and 7-4 illustrate the witness plates and the site setup together with the geographic orientation of the plates. The tarps had to be changed regularly because they did not resist the heat produced by the fireball.

Figure 7-2. Aluminum witness plates set up around the detonation plate

Figure 7-3. Aluminum witness plate schematic

Figure 7-4. Geographic layout of test area

Two pressure gauges (PCB 113B51) (PCB Piezotronics Inc, Depew, NY) were used to evaluate the variation of pressure produced by the detonation. The gauges were calibrated using a PCB calibrator model 907A02 (PCB Piezotronics Inc.) before and after the trial. The gauges were placed 5 and 10 m from the middle of the steel plate and at a height of 1.22 m. They were connected to inputs 1 and 2 of a PCB power supply, model 481 (PCB Piezotronics Inc.), while the

outputs were connected to a Nicolet oscilloscope, model 440 (Nicolet Instrument Technologies Inc, Rexdale, Ontario). The oscilloscope was calibrated in October 2000. The chosen acquisition frequency was 500 KHz for all the detonations.

The time zero signal came from a small-caliber wire wrapped around the explosive and connected to a signal conditioner from ECI (ECI Telecom Ltd, Ottawa, Ontario). The detonation broke the wire inducing the emission of an impulse from the signal conditioner. This impulse acted as the time zero signal for the pressure gauges.

The meteorological station used was a Weather Monitor II from Davis Instruments Corp. (Hayward, CA). Atmospheric pressure, temperature, wind direction, and minimum and maximum wind speed were all registered every 5 minutes. A Kodak CR2000 and a Sony Betacam, operating at 1000 and 30 frames per second, respectively, were used to record each trial. The Kodak camera was located about 18 m from the detonation plate and secured in a photo shack, while the Sony Betacam was installed on the roof of the bunker.

Sampling

To avoid the degradation of the explosives residues, the plates were sampled after each detonation. The sampling began approximately 15 min after the detonation to allow inspection of the site by the EOD specialist to ensure that the site was secure after the detonation. The solid residues, if any, that were projected onto the aluminum plates were first transferred with a clean swab to a 250-mL amber bottle. Each plate was then thoroughly wiped with acetone-soaked swabs that were then put into a 250-mL amber bottle together with the particles already collected. The samples were immediately put into an ice-box containing crushed ice and kept from direct sunlight. At the end of the day, the samples were transferred in a conditioning chamber and kept at -20 °C until extraction.

The plates were then thoroughly sprayed with methanol, distilled water, and acetone to remove any residual explosives. The clean plates were put back into place for another detonation. The tarps were replaced only when necessary, because some detonations did not produce much residue. Sampling was conducted with 4-ply rayon-polyester swabs of 10.2 cm x 10.2 cm from Johnson $\&$ Johnson (Montreal, Quebec).

Extraction and analysis

Swabs used to wipe one witness plate were inserted into a plastic 60-mL syringe fitted with a one-way plastic stopcock. The remaining solid residues in the amber bottles were transferred to a vial. Each syringe and vial was then filled with acetonitrile; approximately 50 mL for the syringes and 10 mL for the vials. All of the syringes and the vials were put into an ultrasonic bath for 18 hr.

Because only traces of explosives were expected, and also to minimize the number of analyses, the extracts from each witness plate were combined. Therefore, the extracts coming from the eight witness plates (A to H, see Figure 7-4) around

the detonation plate were combined to a single extract, and the remaining extracts (I to L, see Figure 7-4) were combined to another extract. Therefore, after the ultrasonic extraction, syringes A to H were filtered with a 0.45-µ filter (nylon 25-mm diameter acrodisc from Gelman (Pall Ltd, Mississauga, Ontario)) into the same evaporating round-bottom flask. Each syringe was carefully rinsed twice with acetone to ensure that explosives were completely extracted from the swabs. After each filtration, the solvent was thoroughly expressed from the swabs using a compression press slightly modified for this operation by adding a syringe support (see Figure 7-5). Extracts were recovered in a beaker and transferred to the corresponding evaporating flask. Acetone was used to carefully rinse the beaker. The vials A to H containing the mixture of solid residues and acetonitrile were transferred into a syringe fitted with a 0.45-µ filter that was also filtered into the same evaporating flask used for syringes A to H.

Figure 7-5. Syringe press and support showing stopcock

The solvent was then evaporated under vacuum using a rotary evaporator until a final volume of 50 to 100 mL was reached. The solution was then transferred to a 200-mL Zymark tube (Zymark Corp, Hopkinton, MA) and evaporated to precisely 50 mL using a TurboVap II (Zymark Corp.) concentration workstation, operated at 25 ºC.

A precise quantity of the final solution (700 µL) was then transferred with an Eppendorf pipet (Brinkmann Inc, Mississauga, Ontario) in a 3-mL Luer-Lok (BD, Oakville, Ontario) syringe fitted with a 0.45-µ filter. The same amount of water was added to the syringe, and the resulting solution was filtered into a 2 mL HPLC amber bottle. The analyses were made following EPA method 8330 using an Agilent 1100 HPLC (Agilent Technologies Canada Inc, Mississauga, Ontario) with a Supelcosil ™ LC-8 column (Supelco, Bellefonte, PA).

The accuracy of the extraction method was tested with 2-ppm spikes of the 14 metabolites of EPA Method 8330 on swabs slightly contaminated with 2-µ carbon particles. Results are given in Table 7-A1 in the appendix.

Results and Discussion

Air-blast pressures

The air-blast pressures and weather conditions for each detonation are reported in Table 7-A2 in the appendix and the variations of air-blast pressures with the weight of unconfined explosive are plotted in Figure 7-6. In the cases where a priming charge was used to detonate the explosive, the weight used to draw the curves is the total weight of the explosive being detonated (priming charge + unconfined explosive). Values taken from the 5-m gauge have been chosen for plotting because their proximity to the detonation makes them more accurate than those from the 10-m gauge. A linear relationship is expected between the pressure and the cube root of the charge (Cooper 1996).

As expected, the air-blast pressure generally increases with the weight of explosive being detonated. For C4, no distinct variations of the air-blast pressure are detected between cylinders, spheres, and blocks. However, the air-blast pressures for TNT do not vary as much with the weight of the charge as for the other explosives. Also, the pressure yields for all TNT cylinders and 20- to 40-g XRT cylinders are lower than for the other explosives. The small XRT cylinders show a low-pressure yield because they were detonated without C4, as opposed to the larger charges of 50 g, 75 g, and 100 g that were detonated with 20-g C4. However, the low air-blast pressures of TNT are due more to its small explosive power and its critical diameter. The explosive power of TNT is smaller than for other explosives. For example, Comp B has a TNT equivalent of 1.11, which means that 1 kg of Comp B performs as 1.11 kg of TNT. Secondly, small charges of TNT often under-perform when their size is close to the critical diameter of TNT (25 mm). Thus, the low air-blast pressures observed for TNT are not unusual.

Figure 7-6. Variation of the pressure of detonation with the weight of unconfined explosive at 5 m

Explosives residues

Quantities and types of contaminants. Table 7-A3 in the appendix shows the amounts of explosives residues found after each detonation. TNT and RDX are often detected, and HMX and TNB are also occasionally present. The results are divided into the following two parts: the first column of values corresponds to the quantity of explosives found in the first 8 m^2 around the detonation plate (plates A to H, see Figure 7-4), and the second column of values is the total amount of explosives collected on all of the plates (plates A to L, see Figure 7-4). Plates A to H cover approximately 80 percent of the first 1-m outer perimeter around the detonation plate. The quantities of residues found in plates A to H reported in Table 7-A3 have not been corrected to account for the missing $2 m²$ and, therefore, can be considered underestimated by approximately 20 percent. The percentages of residues reported in Table 7-A3 correspond to the ratio of the total amount of explosives collected on the witness plates to its initial amount in the charge. In all cases, the presence of C4 (to initiate the detonation) and of impurities in the explosives (such as 12 percent w/w HMX in military grade RDX) has been accounted for.

RDX residues. The total amount of explosives found after each detonation is generally quite small. For C4, quantities of RDX varying between 0.04 and 29 mg, regardless of the shape of the charge, have been detected. These amounts range from 1.1 to 25 mg for TNT cylinders and 2.7 to 115 mg for Comp B cylinders. For PBX, between 5.3 and 94 mg were detected; for XRT, between 3.1 and 350 mg. RDX was also detected twice for the detonation of Octol cylinders, but given the quantities involved $(< 0.08$ mg), it is difficult to determine if these values come from the 10 percent RDX impurity in HMX or from the error in the measurement.

Further testing will be required to determine the precision of the percentages of residues recovered after a detonation. However, the recovery of 4.2 and 0.63 mg RDX after the detonation of 75-g and 100-g TNT cylinders without C4 gives an idea of the precision of the measurements, because no RDX should have been

detected during these two detonations. Therefore, each amount of RDX recovered should be considered subject to an absolute minimal error of \pm 4 mg; this corresponds to 0.02 to 0.004 percent of the initial weight of the charge. Also, a mean relative uncertainty of 0.02 percent was calculated with the values obtained for three duplicates of C4 performed on different charges (Table 7-A3).

TNT residues. TNT residues recovered after each detonation also represent very small quantities of explosives for the Comp B (0.03 to 1.9 mg) and Octol cylinders (0.39 to 9.7 mg) (Table 7-A3). Extremely small quantities of TNT were found in one of the seven PBX samples (0.06 mg) and in one charge of C4 (0.04 mg), which gives an indication of the minimal absolute error associated with these tests. As shown in Table 7-2, no TNT is used in PBX or in the C4 primer charge, so none was expected in the detonation products. For XRT, up to 119 mg of TNT were recovered.

HMX residues. HMX was also found in the residues of detonations. In the C4 and TNT samples, HMX was rarely detected (in only 2 samples out of 22 for the C4, and then only in extremely small quantities). This contamination could come from the 12 percent HMX present as an impurity in military-grade RDX. However, given the small amounts encountered $(< 0.23$ mg for C4, see Table 7-A3), the HMX could also be due to an error in the measurements. HMX has indeed been detected at quantities as high as 1 mg in residue after detonation of TNT cylinders for which no RDX was used (Table 7-A3). Small amounts (<8.9 mg) of HMX could, however, be found following the detonation of Comp B, Octol, and PBX cylinders. Much higher values were observed for XRT (0.61 to 642 mg).

Relationship between weight of explosive and quantities of residues

Figures 7-7, 7-8, and 7-9 show the relationship between the percentages of residues recovered after each detonation and the initial weight of the explosives for RDX, TNT, and HMX, respectively. For clarity, only the results from horizontal detonations were used to draw the plots, except for the C4 blocks, for which only the results from vertical detonations were plotted.

Unfortunately, due to the small quantities of explosives recovered, determining the effect of the amount of explosive being detonated on the dispersion of residues into the surrounding environment proves to be difficult. Nonetheless, relatively clear trends could be observed in some cases, as described below.

RDX residues. Figure 7-7 shows that the percentages of RDX recovered were either stable or inversely proportional to the initial size of charge. The R^2 values for the curves are generally low, but the trends are quite consistent. However, given the small quantities of RDX recovered and the large estimated uncertainty on each value, these results must be interpreted with caution.

Figure 7-7. Percentages of RDX found in the residues after the detonation of TNT, Comp B, PBX, XRT, and C4

Figure 7-8. Percentages of TNT found in the residues after the detonation of Octol, TNT, XRT, and Composition B cylinders

Figure 7-9. Percentages of HMX found in the residues after the detonation of Octol, PBX, Comp B, and XRT cylinders

TNT residues. The corresponding variations of the percentages of TNT residues recovered after horizontal detonations as a function of the initial weight of explosive detonated are shown in Figure 7-8. The trends are not as clear as for the RDX samples, although the uncertainty is expected to be comparable. For two of the four types of explosives, the amounts of residues recovered are very small and do not seem to vary with the initial weight of the charge. The other two explosives show opposite trends: an increasing trend for TNT and a decreasing trend for XRT. As for RDX, the small amounts of residues recovered after a detonation obscure a clear conclusion on the effect of the amount of explosive on the quantities recovered after the detonation.

The detonation of TNT cylinders in particular leads to a very interesting pattern: quantities of TNT residues varying between 2.3 and 2539 mg are recovered (Table 7-A3). The percentage of residues clearly increases from 20- to 75-g charges, after which it decreases markedly for the 100-g charge. The presence of C4 is not the cause of this variation because it was used only for the charges of 20 to 50 g (Table 7-3).

The strong trend for dispersion of TNT for the 20- to 75-g charges is probably due to critical diameter effects. As shown in Table 7-2, the critical diameter for TNT is between 22 and 25 mm. The actual diameter of the cylinders was 25 mm. As the actual diameter is almost equal to the critical diameter, the detonation cannot be expected to propagate well and would die before reaching the end of the cylinder. Consequently, more and more TNT would be thrown into the surroundings as the cylinder length increased. This was observed with cylinders of 20 to 80 g. Therefore, the greatest residue would be expected in the longest and largest 100-g sample. This was not the case; perhaps due to the fact that the propagation of the detonation wave died before the end of the cylinder was reached, projecting chunks of TNT outside the sampling area. Also, the large 75 g TNT cylinder (5.6 cm) detonated vertically as if it were a candle, and showed much lower contamination (1 percent) than the smaller diameter, 75-g cylinder (3.4 percent), which detonated horizontally. The other explosives under study are not subject to this effect because their actual diameters $(> 2.5 \text{ cm})$ are much larger than their critical diameters (Table 7-2).

HMX residues. The trendlines for HMX (Figure 7-9) are more ambiguous than those of TNT or RDX. The R^2 values are quite weak and, particularly in the case of the XRT, trends are difficult to assign. The PBX showed the best R^2 value at 0.76, and the trend is clearly less residue with the increasing size of the explosive. On the other hand, in the case of the Comp B, the only detectible quantities of HMX were found in the four largest explosive samples.

Mean percentage of residues

Because the results are subject to considerable error, the data were also treated statistically to establish a mean percentage of residues found after the detonation of each type of explosive. The results are reported in Table 7-4.

The mean percentage reported for RDX in C4 spheres (0.004 percent) is similar to the one reported by Hewitt et al. (2003), 0.003 percent for the blowing in place of 570-g blocks of C4 on snow. The slightly higher value of 0.007 percent for C4 cylinders detonated by their end may indicate difficulties of propagation of the shock wave in the explosive due to the presence of "corners" at the end of the cylinder connected to the detonator. The higher value of 0.04 percent found for C4 blocks, which corresponds to rectangular pucks 2 cm in height by 7 to 9 cm in diameter (mimic of "mine shape") detonated by the upper end, certainly reflects difficulties in propagating the shock wave, which lead to the dispersion of more residues into the area surrounding the detonation.

The highest dispersion of TNT into the environment came from the detonation of TNT cylinders. A mean percentage of 0.8 percent of TNT is dispersed after detonation (Table 7-4), regardless of the use of C4. The TNT dispersion was higher (1 percent vs. 0.5 percent) when C4 was used to detonate TNT. This can be explained, as stated earlier, by the critical diameter effect.

Interestingly, the mean percentage of RDX dispersed (0.05 percent) in the TNT cylinder tests was one order of magnitude higher than for corresponding C4 cylinders and was closer to the 0.04 percent reported for C4 rectangular blocks. The reasons for this are unclear. The only RDX in the TNT samples was in the booster charge, and the three largest TNT samples did not use a booster. Despite this, RDX was detected. The only reasonable explanation is cross-contamination. The dust thrown up by each explosion could carry explosive residues onto the witness plates. This theory fails to explain the lower RDX values observed in the Octol cylinders. This form of cross-contamination would be expected to yield relatively uniform levels of contamination across the different types of explosive. Contaminated witness plates can be ruled out, as the cleaning process was standard, and no relationship between the quantities of residues found from one trial to the next was observed. No residues were detected on cleaned witness plates.

The PBX showed a level of RDX similar to that shown by TNT; however, the XRT showed the highest mean of RDX dispersion. This is attributable to the two smallest XRT samples showing extremely high levels of RDX residues. The reasons for this are unclear. Post-detonation, these samples did not appear any different from any other samples in terms of visible residue. The 40-g XRT sample was clearly a low-order detonation, yet the percent RDX recovery is lower

than for the 30- and 20-g XRT samples, neither of which were observed as being low-order. However, the TNT and HMX recoveries from the 40-g sample are higher than for the 20- and 30-g samples. What is clear is that the four largest XRT samples have significantly reduced residues. Whether this resulted from the use of a C4 booster (which was not used in the three small samples), or is an effect of the larger size is unclear.

Much smaller percentages for TNT dispersion were obtained from the detonation of Comp B cylinders (0.004 percent). However, this explosive showed high RDX and HMX dispersion (0.1 and 0.02 percent, respectively; see Table 7-4). RDX was detected for all detonations, but HMX was only seen for charges of 75 and 100 g. The detonation of Octol cylinders leads on an average to the dispersion of 0.03 percent TNT and 0.006 percent HMX (Table 7-4).

Effectiveness of witness plates for residue collection

The collection of explosives residues is always a challenging task because of the heterogeneous dispersion of the residues. This heterogeneity may be due to the detonation itself; the position and configuration of the charge and the detonator may not be exactly the same at each detonation. Variations in weather conditions, such as the wind speed and direction, are also a source of variability. The charges themselves, which may have microscopic cracks or not be completely heterogeneous in chemical composition, are another source of variability. In any event, all of these factors lead to heterogeneous dispersion of the residues that challenges collection.

Using witness plates to collect the detonation residues provides many advantages, such as easy sampling of the collection area, fast installation setup, fast collection time if enough manpower is available, and easy cleaning of the witness plates. Collection swabs do not require much space in a freezer, and extraction of the swabs is relatively easy, although a little time-consuming. Another advantage, not exploited in this work but possibly useful for bigger charges, is the knowledge of the directional dispersion of the residues relative to the position of the munition on the detonation plate, to the configuration of the detonator on the charge, and to the weather conditions.

Drawbacks are also associated with using witness plates. The distribution locations of the witness plates around the detonation plate must be well chosen to collect the highest possible amount of explosive. Another drawback is the possibility of losing data if the plates are flipped over or if the residues miss the plates. The area over which the residues are dispersed, and thus the percentage of the contaminated area that has been sampled is difficult to evaluate. Witness plates cannot be used in rain, because the water may wash the residues out of the plates. Also, the aluminum plates become very hot in summer; thus needing to be swabbed as soon as possible after detonations to avoid thermal degradation or volatilization of the residues.

Recovery of all residue is always hard to accomplish. The total area covered by the residues is easier to estimate for on-snow detonations, because the plume is clearly visible. Even so, residues could still be projected outside the visible

plume area. Witness plates must be well placed to avoid the loss of a significant portion of detonation residues. In this case, the distribution of residues with distance for most of the charges was unknown. However, the amounts of residues collected on the plates outside the first 8 m^2 after the detonation of the biggest charges (75 g and 100 g) represent only a fraction of the values obtained in the first 1-m perimeter (Tables 7-3 and 7-A3). Also, detonation trials with 60- and 81-mm mortars and hand grenades showed that, except for very highly dispersed residues, the quantities of explosives recovered decreased very quickly with distance from the charge. So, *most* of the residues dispersed after the detonation of the unconfined explosives were very likely recovered, although the collection of *all* of the residues was not possible. The very small amounts of explosives recovered, coupled with their heterogeneous dispersion in the surrounding environment, contribute significantly to the uncertainty in defining the relationship between the amount of the explosive detonated and the quantities of dispersed residues. To overcome this uncertainty, the same experiment should be repeated several times.

Another difficulty, not specific to the use of witness plates, comes from the adsorption of explosives to soot that makes their extraction difficult. In-house experiments have shown that the recovery of explosives from real detonation soot spiked with the 14 metabolites of EPA Method 8330 were very low, with only RDX coming out at 30-50 percent w/w. Although no experiments used swabs soiled with real detonation soot to verify the percentages of explosive recovery, similar results may be expected. In the detonation of unconfined explosives, however, the soot is often concentrated on only one or two plates, leaving most of the swabs relatively clean. The effect of residue adsorption onto soot is thus minimized because each set of swabs used to wipe one plate is extracted separately from the swabs of another plate, and the extracts are combined in the final step only.

Measuring the impact of wind direction and speed was not possible because the extracts of residues were combined before analysis by HPLC. Given the small amounts of explosives recovered on the first eight plates, analysis of each plate separately would have resulted in a failure to detect residues at all. Also, no relation could be found between air-blast pressure, temperature at the time of detonation, or atmospheric pressure, and the amounts of dispersed residues.

Summary

The first objective of this detonation trial, the estimation of the quantities and types of residues resulting from the detonation of unconfined explosives, was met. The detonation of unconfined explosives of 20 to 100 g of various shapes leads to the dispersion of very small amounts of explosives in the surrounding environment. The maximum percentages dispersed were 3.4 percent for TNT (TNT cylinders), 19.42 percent for RDX (XRT cylinders), and 2.81 percent for HMX (XRT cylinders). The high dispersion of TNT residues was attributed to the critical diameter effect. If those cylinders are excluded from the analysis, the overall maximum dispersion of TNT falls to 0.2 percent for Octol and XRT cylinders. The mean percentages of residues for a given explosive are, however, one

to two orders of magnitude lower. Again, excluding TNT cylinders, the highest mean percentages of residues for TNT, RDX, and HMX are all found in the XRT samples (0.2 percent TNT, 4.5 percent RDX, and 0.6 percent HMX). Although these values may seem high (the detonation of a single 81-mm munition containing 857-g Comp B would lead to an average dispersion of 1-g TNT, 47-g RDX, and 1-g HMX into the surroundings), the values reported in this report are only typical of unconfined explosives. The confinement of explosives in munitions permits the buildup of much higher detonation pressures and temperatures that lead to better consumption of the explosives. Furthermore, the percentage of residues reported in this work are conservative due to the heterogeneity of the dispersion of the residues, the sampling of only a portion of the detonation plume and to the adsorption of the explosive onto the detonation soot. It should be kept in mind, however, that the detonation plume of the charges used for this study is relatively small.

The second and third objectives of this detonation trial were the establishment of a relationship between the amount of explosive being detonated and the amount of residues dispersed into the surrounding environment, and the verification of the hypothesis that the quantities released in the environment decrease as the weight of the charge increases. These objectives turned out to be hard to meet, because the amounts of residues recovered were generally very low, close to the experimental error, and only a few replications were conducted. Future tests should be replicated no less than three times. Mean percentages of residues dispersed into the surrounding environment after the detonation of unconfined explosives were, however, estimated. The following general trends were observed:

- Larger charges yield generally smaller or comparable amounts of residue.
- Detonations of TNT cylinders lead to the dispersion of larger quantities of TNT grains.
- Detonations of C4 blocks lead to higher levels of RDX dispersion than spheres or cylinders.
- Detonations of PBX and XRT (both insensitive formulations) yield much higher dispersion of explosives.

This last point should be kept in mind as insensitive munitions are designed. Insensitive munitions are designed to be safer for allied troops by not reacting to secondary stimuli such as bullet impact or fire. However, these new munitions might produce more residues in training or blow-in-place operations.

Conclusions

Detonations of unconfined explosives (C4, TNT, Composition B, Octol, PBX, and XRT) of various shapes resulted in extremely small quantities of residues. Establishment of a relationship between quantity detonated and residue produced was confounded by the extremely small amounts of residues observed and the high variability inherent in the tests. Nevertheless, larger charges

generally tended to yield smaller or comparable amounts of residues; C4 blocks yielded greater RDX residues than spheres or cylinders; and the insensitive munition formulations, PBX and XRT, produced more residues than the other explosives. Unconfined detonations represent a "worst case" scenario, since munitions produce far greater pressures and temperatures and explode more efficiently when confined by a casing. Therefore, the observation of such small quantities of residues in these unconfined tests suggests that high-order detonations are relatively environmentally clean unless the case is ineffectually breached. Thus, the contamination resulting from blow-in-place operations or open detonation of large stockpiles of munitions should be rather low if the setup is planned to provide high-order detonations.

The development of a *modus operandi* to establish environmentally sound policies is critical to minimize the environmental impacts of defense activities. The basic work accomplished in this study proved to be very useful to determine the general trends of the origin of explosive contamination without having to deal with the complexity of real munitions. Additional work in this area is needed, however, to get a clearer picture of the situation. Also, work with real munitions is still ongoing to better understand the environmental impact of the destruction of UXO or obsolete munitions.

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Appendix A

Table 7-A2 Blast Pressure Recorded at 5 and 10 m from the Explosive and Weather Conditions for Each Trial

Table 7-A3 Quantity of Explosives Residues Collected on First 8 m² Around Detonation Plate and on All Plates

8 Environmental Impacts of Blow-in-Place Activities for Various Explosives, Munitions, and Charges

Abstract

The percentage of nonfunctioning munitions may be between 3 and 10 percent of fired ammunition, while for some types of munitions, such as antitank weapons, this proportion can be as high as 50 percent. This unexploded ordnance (UXO) may be buried or lie at the surface in training areas. Once a year, military experts of the Explosive Ordnance Disposal (EOD) Unit perform a clearance level 1 (surface clearance) at all Canadian training areas to dispose of the surface UXOs. Because they are considered unsafe to move, UXOs are blown in place with a charge of C4. Blow-in-place (BIP) activities are considered dangerous, but necessary to address the safety problem that these UXOs represent. The environmental impact of BIP has not been highly documented; consequently, a systematic study was needed. DRDC-Valcartier designed specific experiments in which various munitions and charges were detonated using either C4 in various quantities, or shaped charges, both commercial and military, with either fused or unfused ordnance, to verify the relative environmental impacts of each event. An experimental setup involving the use of witness plates and the collection of detonation residues for analysis of their energetic material contents was designed. Despite the presence of contamination in some trials, some generalizations can be made. The greatest concentrations, in the percent levels for TNT, RDX, and HMX, came from low-order detonations. When high-order detonations were obtained, the highest TNT concentration was 324 mg/m^2 , coming from a PMA-1A anti-personnel mine imitation. This value represents 1 percent of the weight of TNT in the ordnance item. The greatest RDX deposited was 47 mg/m² (0.6 percent) coming from an M67 grenade. Finally, the greatest value obtained for HMX was 4.8 mg/m^2 (0.5 percent) coming also from an M67 grenade. These indicate that TNT and Comp B-filled munitions are not always efficient at consuming all the main charge in BIP conditions. The amount of residues collected after an event was influenced by the blow-in-place conditions. For example, the greatest residue recoveries were obtained when a linear shaped charge and a commercial 6.5-g RDX shaped charge were used. Moreover, the BIP of various
primer charges detonated alone showed that their potential contribution in explosive residues was low.

Executive Summary

This study is part of a larger effort undertaken in the context of sustaining operational military activities. Canadian Forces need to be informed about the potential environmental and human health impacts of activities such as live firing, detonation of unexploded ordnance (UXO), and detonation of surplus ammunition. To ensure that such activities can be conducted on a sustainable basis with minimum adverse environmental and health impacts, the way that the ranges are managed needs to be evaluated and, if necessary, improved. The complete destruction of energetic materials during a blow-in-place (BIP) detonation depends on a variety of factors, such as the type of munitions, the confinement, the priming position, the position and orientation of the detonator, the quality and the quantity of the booster charge used, and the weather conditions. To better understand the influence of these factors, BIP detonation experiments need to be done in controlled conditions. The main objective of this work was to evaluate the types and amounts of residues that can result from detonation and provide recommendations to Explosive Ordnance Disposal (EOD) personnel to minimize impact. In this work, BIP detonations of 60- and 81-mm mortar rounds, M67 hand grenades, C4, and PMA-1A land mines were performed using C4 and different shaped charges to establish a relationship between the amounts of residues dispersed in the surroundings and the effects of various factors (mentioned above). Residues were collected on witness plates that were thoroughly swabbed after each detonation. The samples were analyzed for explosives and their breakdown products.

The results showed that the greatest concentration of explosives residues was generated by low-order detonation events that produced residues in the percent level. High-order detonations produced fewer TNT, RDX, and HMX residues but the amount of residue varied in accordance with the blow-in-place conditions. The use of linear shaped charges and commercial 6.5-g RDX shaped charges showed a high incidence of low-order detonation. Moreover, the type of detonation of PMA-1A mines, but not for the M67 grenade, depended on the position of the detonator. For the mortar rounds, the order of detonation was more dependent on the quantity and type of primer (C4 or shaped charges) than on its position on the round; however, priming with C4 in the nose of the munition seems to lead to a larger dispersion of the residues than priming from the lateral position. Finally, the presence of a fuse did not appear to influence the explosives residue generation. The contribution of the primer charge, detonated alone, was also evaluated: the recovery of explosives residue was low for both C4 and commercial shaped charges. Finally, nitroglycerin (NG) was unexpectedly found in some post-detonation mortar residues. The use of witness plates as a collection medium introduced experimental errors such as contamination between trials. In addition, the area covered by the plume of the detonation could not be estimated, which caused explosives residue to be underestimated. Even with those problems, however, interesting and pertinent information was obtained that will help to draft future recommendations. Study results offer important information about the

environmental impact of explosives detonation during range clearance operations and the critical detonation parameters that should be considered.

Introduction

The environmental impacts of particular activities such as routine military training and exercises involving munitions have recently brought increased awareness of the potential buildup of explosives residues in soil that may result in the contamination of groundwater [1]. Such a situation has been encountered at the Massachusetts Military Reservation (MMR) in the United States, where ranges were closed because low RDX concentrations were found in the groundwater [2]. RDX and other high explosives (HE) have been identified as potential carcinogens by several environmental authorities [3]. In the case of MMR, the RDX could come from leaking or buried UXO, residues from past ammunition disposal, or from accumulated residues over the years.

In the context that military training ranges cannot be shut down because testing and training ranges are essential to maintain troop combat readiness, ways to sustain environmentally friendly military activities need to be found. One approach to address the problem is the identification and estimation of the explosive content that is dispersed to the surroundings after a detonation. This approach needed to be addressed because forensic analysis of post-blast residues has established the presence of explosives [4]. In this approach, two common techniques of detonation were evaluated: live-fire detonation and BIP operations.

Previous studies have revealed potential contamination after a detonation. Jenkins et al. [5] determined the quantity of explosives residues produced by common military live-fire and BIP techniques of mortar rounds containing HE. Experiments were conducted on snow-covered ranges to be able to estimate the area potentially contaminated using the soot produced by the detonation. The pattern of dispersion was heterogeneous, requiring sampling of large areas to obtain representative results. The recovered amounts of explosives remained low, but varied from round to round. Some general trends could, however, be drawn. For instance, a higher percentage of TNT was consumed when the main charge was Composition B (Comp B). Moreover, the RDX concentration was higher when C4 was used. Finally, nitroglycerin (NG) was unexpectedly found in postdetonation mortar residues.

A study related to on-snow detonation was also performed at DRDC-Valcartier [6]. Detonations of 60- and 81-mm mortars, hand grenades, and imitation PMA-2 mines were evaluated. Only the BIP detonation conditions were evaluated. The results showed that approximately 0.24 percent of the total explosive present prior to the detonation remained as residue following a BIP detonation. No information was available about the level of detonation. Some trends were underlined in the study. The presence of C4 in the setup of the detonation influences the RDX concentration in the residues. Also, the configuration is important for effective detonation of a charge.

A recent study related to detonation residues was performed by Hewitt et al. [7], where live-fire, high-order, and BIP detonations were evaluated. Results showed that live-fire, high-order detonations of different types of munitions consumed an average of 99.997 percent or more of RDX and TNT. In BIP detonations, C4 contributed to the detonation residues and randomly dispersed the residues. This effect was even more pronounced when BIP operations led to loworder detonation: a non-negligible amount of explosive residues was spread to the surroundings.

Finally, Brochu et al. [8] estimated the quantity of explosive residues resulting from the BIP detonation of unconfined explosive charges. Similar techniques such as on-soil witness plate sampling were used. The difference between the present study and Brochu et al. [8] is that unconfined explosives were evaluated instead of various common munitions and charges. The results showed that the detonation of unconfined explosives dispersed a small amount of explosives in the surroundings. Also, unconfined TNT charges with small diameters led to higher dispersion of unconsumed explosive.

In the present work, the detonation trials were performed either over a soilcovered range or a concrete slab. Large polyethylene tarps were spread on the soil to eliminate possible contamination from previous activities and to minimize the contamination of the range. Aluminum witness plates were spread on the tarps to collect post-detonation residues. The witness plates were thoroughly swabbed after each detonation. Because this setup offers a higher potential of contamination compared to on-snow detonation, efforts were made to minimize this possibility. The advantages of using witness plates as a collection medium were numerous; more trials could be performed at the same site, less machinery was needed, the trials were not dependent on the amount of snow, and installation was fast and easy. The amount and the identification of explosive residue contamination resulting from BIP detonations were assessed. This study focused on the detonation of common Canadian Forces munitions: 60- and 81-mm mortar rounds and M67 hand grenades. PMA-1A anti-personnel mine imitations were also tested because PMA-1A is heavily used in many areas around the globe. Finally, all munitions were detonated in controlled conditions while varying the parameters such as the primer charge, the priming position, and the orientation of the detonator. Moreover, because past studies have shown that C4 appeared to increase the amount of RDX residues [6], different C4 primer charges were detonated alone to determine their contribution to explosive residues.

Finally, the total mass of explosive residues was calculated from the information obtained from the laboratory analyses. The area of soot was not calculated during the trials because no visual identification of soot was available after the blasts. Hence, the results do not reflect any area calculation. The total mass of the explosives residues found on the witness plates was determined. Then, a percentage of unconsumed explosives was calculated. At the end, a concentration $(mg/m²)$ was determined taking into account the use of different numbers of witness plates during the trials. The experimental work was conducted in the spring of 2001 and in the fall of 2002 on the DRDC-Valcartier testing range located in the Valcartier Garrison. The work was conducted under the Weapons and Firepower thrust as part of the work breakdown element 12ny01 on the study of sustainable training.

Experiments

Munitions and explosives tested

The munitions and explosives and the ways they were tested are described in Tables 8-1 and 8-2. Various kinds of munitions and charges were detonated under BIP conditions. The following is a brief description of the munitions and charges tested.

Table 8-1 Description of the Explosive Samples and the Detonation Conditions Used for Each Trial of Spring 2001

Table 8-2 Description of the Explosive Samples and the Detonation Conditions Used for Each Trial of Autumn 2002

The 60-mm mortar round is 37.7 cm long and has a main charge of 300 g TNT [9]. This 60-mm mortar differs from the U.S. version, which uses Comp B as its main charge. In all trials, the propellant ignition cartridge and bags were removed because the propellant is used up during launch; it would thus not be present in either UXOs or normally detonating rounds. Since NG was detected in some trials involving 60-mm mortars, it is important to mention here that NG is only present in the ignition cartridge (1.68 g). For their part, the fuses may contain RDX, HMX, lead azide and various other primers, but the masses were not considered in the current results because they are negligible.

The 81-mm mortar round is very similar to the 60-mm mortar; however, the round is 52.9 cm long and the main charge is 857 g of Comp B [10] (59.5 percent RDX, 39.5 percent TNT, and 1 percent wax). For the same reasons as for the 60 mm mortar tests, the propellant was removed prior to testing. Since NG was also detected in some trials involving 81-mm mortars, it is important to know that NG is present in the propellant of the ignition cartridge only (4.15 g). Standard Canadian Forces M67 grenades were also detonated. The grenade is quite small, measuring 6.8 cm diameter, and is roughly spherical in shape [11]. The main charge is 185 g of Comp B. The fuse was removed for safety reasons.

PMA-1A anti-personnel mine mock-ups were tested. The explosive charge included in the mine is 200 g of TNT. The mine is mass-produced by several countries including the Czech Republic and the Republic of China. The mine is

very simple in design and is made to detonate when pressure (3 kg) is applied to its top surface. The mine is 31 mm high, 140 mm long, and 68 mm wide. The case is made of plastic [12]. BIP detonations need a booster charge. The charge used for the majority of munitions detonated in this study was C4, a plastic explosive composed of 91 percent RDX [13]. The quantity used varied between 4 and 150 g. As another booster charge, FIXOR™ explosive was also tested [14]. FIXOR™ is a Canadian-developed explosive based on two components, a flammable liquid and an inert powder, which become a high explosive when mixed together. It has been tested to possibly replace C4 and TNT blocks for traditional disposal of UXO explosive charges [14]. FIXOR™ has significant advantages over conventional explosives for use in BIP EOD operations. These include nonsuitability for terrorist use in mass-detonation devices, because the mixture becomes harmless after a couple of hours of settling. Its transportation is also easier than that of traditional explosives, because it is classified as a flammable liquid. FIXOR[™] is less expensive and more readily available than $C4$. FIXOR[™] performance equivalency is around 85 percent of TNT, by weight (as determined by air-blast tests), and it has a detonation velocity of 4300 m/s compared to 6900 m/s for TNT $[14]$.

Along with the booster charge, shaped charges were used in some cases. Shaped charges intend, by design, to focus all of their energy on a single line or point, making shaped charges very accurate and controllable. They are used to cut or perforate metal and armour. Various designs of shaped charges are used in UXO destruction. During the trials, the standard military C4 linear M7 shaped charge (LSC) and the commercial shaped charges (SC) coming from Prime Perforating Systems Limited [15] were evaluated. These last two types are multipurpose perforating charges used in a variety of tasks, mostly for well perforation in the oil and gas industry. The efficiency of these shaped charges in the destruction of UXOs was evaluated. In some trials (see Tables 8-1 and 8-2), the fuse was kept on the munition for the detonation, but the fuses were usually removed from the munitions for safety reasons.

The explosives included in those munitions and charges were C4, TNT, and Comp B. Comp B was of Type I flakes, Grade A [16]. TNT generally contains up to 1 percent impurities made of a mixture of isomers of TNT and dinitrotoluenes (DNT), especially 2,4-DNT, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene [17]. Military-grade RDX is generally contaminated with 10 to 15 percent HMX [18]. In this project, 12 percent HMX impurity was used for the calculations. Different priming positions were tried during the trials. Figures 8-1 and 8-2 illustrate the lateral priming position and the nose priming position. For the C4 charges detonated alone, two detonator positions were assessed. First, the detonator laid parallel to the ground surface; this orientation was designated as horizontal in Tables 8-1 and 8-2. When the detonator was perpendicular to the ground surface, this orientation was designated as vertical. Finally, ammunition specialists were responsible for the preparation of the rounds and the initiation of the explosives to ensure that all trials were conducted safely and according to standard procedures.

Figure 8-1. 60-mm mortar and 150 g of C4 using a lateral priming position

Figure 8-2. 81-mm mortar and 75 g of C4 using a nose priming position

Site setup

Two sets of experiments were performed at the demolition range of Garrison Valcartier: the first one was conducted in May 2001 and the second one in September 2002. The major requirements for the site were to have proper weather — high winds and heavy rain were considered inappropriate for sampling. Each explosive was placed in the middle of a heavy steel plate 1.34 x 1.77 x 0.1 m. To prevent contamination by residues from prior detonations, the heavy steel plate was raised 0.3 m from the ground as shown in Figure 8-3. Six 3.7- x 5.5-m polyethylene tarps were spread on the soil to avoid contamination from previous demolition activities. Aluminum witness plates, 6 to 24, 1 m x 1 m x 3 mm (Figure 8-4), were placed on the tarps around the steel plate to collect the residues. The distance between the witness plates was 50 cm. To help with sampling, these witness plates were gently bent diagonally, from corner to corner, which created a slightly concave surface. Short aluminum feet were welded at each corner (Figure 8-5). These kept the sampling surface off the ground. Figure 8-6 illustrates the way the witness plates were oriented around the heavy steel plate in accordance with the number of them. The tarps had to be changed regularly, because they sometimes did not resist the heat produced by the fireball and the fragments generated by the detonations. However, the elevated platform preserved the tarp as much as possible from the fireball and avoided flipping of the plates during a detonation.

Figure 8-3. EOD staff install a detonator on a 60-mm mortar; location of the 5-m pressure sensor is shown at the back

Figure 8-4. Witness plates' layout around the heavy steel plate

Figure 8-5. Diagram of an aluminum witness plate used during the trials

The air-blast pressure created by each detonation was recorded using PCB 113B51 sensors (Figure 8-3). Two sensors were used for each trial, and these were installed at 5- and 10-m distances for the smaller munitions, or 10 and 15 m for the larger munitions. These sensors were powered using ports 1 and 2 of a PCB Model 481 current source, and the output was monitored through ports 1 and 2 of a Nicolet Model 440 oscilloscope. The acquisition frequency of the oscilloscope was maintained at 500 kHz for all trials.

No meteorological station was used during the spring 2001 test, but the temperature and the weather conditions were noted. Weather conditions and temperatures are listed in Appendix D. A Weather Monitor II from Davis Instruments meteorological station was used in fall 2002. Atmospheric pressure, temperature, wind direction, and minimum and maximum wind speed were registered.

A Kodak CR2000 and a Sony Betacam camera operating at 1,000 and 30 images per second, respectively, were used to record each trial. The Kodak camera was located about 18 m from the detonation plate and secured in a photo shack, while the Sony was on the roof of the bunker.

Sampling

After each detonation, to avoid degradation of the explosives residues, the plates were sampled as soon as possible. The sampling began approximately 15 min after the detonation to allow site inspection by the EOD specialist to ensure that the area was secure after the detonation. The solid residues, if any, that were projected onto the aluminum plates were first transferred with a clean swab to a 250-mL amber sample bottle. Swabs were 10.2- x 10.2-cm, 4-ply rayon polyester. Each plate was then thoroughly wiped with the acetone-soaked swabs that were placed in a 250-mL amber sample bottle together with the sand already collected (Figure 8-7). The samples were immediately placed in an icebox and kept from direct sunlight. At the end of the day, the samples were transferred in a conditioning chamber and kept at -20 °C until the extraction.

Figure 8-7. Sampling of a witness plate after an event

After sampling, the plates were thoroughly sprayed with acetone and distilled water to remove any residual explosives that might still stick to them (Figure 8-8). The plates were then put back in place for another detonation.

Figure 8-8. Washing of a witness plate after sampling

Extraction and analysis

Into every 250-mL amber sample bottle, about 100 mL of acetonitrile was added, enough to cover the wipes and allow a freestanding solution. Then, the sample bottles were placed on a wrist action shaker table for 18 hr, after which they were transferred to an ultrasonic bath for 1 hr. The samples were grouped together because the number of high-pressure liquid chromatography (HPLC) analyses had to be minimized. The composite pattern is color-illustrated in Figure 8-6. Then, 10 mL of solvent coming from each sample bottle was withdrawn with a pipette and mixed in one container to form a composite solution. For example, the extracts coming from the witness plates represented by the same color in Figure 8-6 were combined in one sole extract. Prior to mixing, the 10-mL extract was filtered with a 0.45-µm filter.

Finally, a precise quantity of the final solution (between 700 and 800 μ L) was transferred with an Eppendorf pipette in a 3-mL Luer-Lok syringe fitted with a 0.45-µm filter. Water was added in different proportions, and the resulting solution was filtered into a 2-mL HPLC amber bottle. Spring 2001 samples were extracted and analyzed by DRDC-Valcartier using reversed-phase HPLC (RP-

HPLC). Analyses were performed on an HPLC equipped with an ultraviolet (UV) diode array detector monitoring at 210, 220, and 254 mm. The column used was a 25 cm x 3 mm x 5 µm Supelcosil LC-8 column eluted with 15:85 isopropanol/water (v/v) at a flow rate of 0.75 mL/min. Standards and solvents were diluted 1:2, acetonitrile to water.

Autumn 2002 samples were extracted and analyzed by CRREL using reversed-phase HPLC. Analyses were performed on a modular system consisting of a P1000 isocratic pump, a UV2000 dual-wavelength absorbance detector set at 210 and 254 mm and an AS3000 autosampler. Analyte separations were performed using the 15-cm x 3.9-mm NovaPac C-8 column eluted with 15:85 isopropanol/water (v/v) , 1.4 mL/min. Standards and solvents were diluted 1:3, acetonitrile to water.

The accuracy of the extraction and the analysis method has been tested. At DRDC-Valcartier, swabs were previously spiked with a standard solution of 25 mg/L and analyzed three times over 10 days. Mean recovery percentages were satisfactory: HMX = 96 ± 2.5 percent, TNT = 96 ± 2.5 percent and RDX = 95±2.7 percent. At CRREL, comparable instruments and the same extraction method were used. Similar mean recovery percentages were obtained: HMX = 97.9 percent, $TNT = 98.7$ percent, and $RDX = 95.5$ percent. CRREL obtained better recovery percentages when swabs were dried before spiking.

The values detected by the RP-HPLC (Appendix A) represented the explosive concentrations of the composites. When the concentration was multiplied by the amount of solvent used for the composites extraction, the results equaled the mass of explosives residues found in a composite. These results must be interpreted carefully because they do not represent the total mass of explosives residues formed by the munition or charge, since only a certain area was sampled. Hence, the results are underestimated.

Results and Discussion

HPLC results obtained after the extraction and analysis of the swipes are reported in Appendix A for both trials. The values in Appendix A are presented by composite using the pattern described in Figure 8-6. In addition, in Appendix A the mass (mg) and the surface concentration $(mg/m²)$ for TNT, RDX, and HMX were added to allow a better comparison. Values for TNT, RDX, and HMX were numerically transformed. The TNT manufacturing impurity, 2,4- DNT, and the TNT by-products, 2-ADNT and 4-ADNT, were proportional to the TNT concentration; therefore, values for these compounds were not numerically transformed. Finally, the transformations of the values were performed using the calculations described in Appendix B.

The values presented in this work are underestimated because they have not been corrected to take into account the full area covered by the blast. Only the residues found on the aluminum plates were included in the calculation. However, the same approach was taken for all the detonation trials. Therefore,

comparison of the results can still lead to the identification of general trends and provide a good idea of the order of magnitude of the environmental impact.

To correctly analyze the results, the effectiveness of the detonation had to be determined. Only results for high-order detonations can be compared between them, because low-order detonations are characterized by very random results. A low-order detonation is either an incomplete detonation or a complete detonation occurring at lower than its maximum velocity. Low-order detonations may be caused by any one or a combination of factors: initiator of inadequate power, deterioration of the explosive, poor contact between the initiator and the explosive, and lack of continuity in the explosive, such as holes or cracks. To determine the order of the detonation, a comparison was made using the Conwep software [19].

Conwep predicts the pressure of a high-order detonation. The experimental pressure values were compared with the theoretical Conwep values (Appendix C) to establish the order of the detonation. When both pressures were similar, the reaction was considered of high order. However, when the experimental values were below 60 percent of the theoretical Conwep values and in agreement with visual observations made during the trial, a decision was made to consider the detonation low order. Because the Conwep software does not offer the possibility to calculate the exact theoretical pressure for complete munitions and charges, the theoretical values were calculated as if the munitions or charges were bare HE. This assumption results in theoretical pressures slightly higher than experimental pressures, since energy is lost to break the casing of the munitions. Finally, when a low-order detonation had occurred for a specific trial, the corresponding results, highlighted in yellow in Tables 8-3 through 8-6, were not compared with high-order detonation trials.

The surface concentration values $(mg/m²)$ were observed to vary between the composites of the same trial (Appendix A). Usually, the concentrations tend to decrease from composite 1 to 3, with increasing distance from the central plate. But for the larger charges like the 60- and 81-mm mortars, the highest concentrations were sometimes obtained for composite 2. The pattern of dispersion was, therefore, heterogeneous. However, the explosive residues were projected farther for larger charges, which is logical.

Trace amounts of TNT, RDX, and HMX were found in some of the six blank samples, but no TNT manufacturing impurities or transformation products were detected. The average amounts were 0.33 mg for TNT, 0.005 mg for RDX, and 0.006-mg for HMX. Blank samples were taken randomly on washed witness plates. Numerous possibilities can explain the presence of background residues: residues from past detonations, particles carried by the wind, and also improper washing of the plates. Sand samples taken around the setup were analyzed to evaluate the potential contribution of the surroundings to the contamination of the plates. Two sand samples showed an average concentration of 1.12 mg/kg of HMX, but no other explosives were detected. Results presented in this paper were not corrected for background residues.

*: Contamination

E: Low-order detonation

1: Performed after a low-order

1: Possible contamination

The results of Appendix A indicate that contamination was found in some trials. In trial 6-5, detonation of a 60-mm mortar with FIXOR™ produced high concentrations of RDX and HMX when none was contained in the charge or in the primer. This result is attributed to FIXOR™ producing sufficiently high blast pressure to project a large quantity of contaminated surrounding sand onto the aluminum plates. This is particularly true considering that FIXOR™ produced a huge fireball that completely burned the tarps around the detonation plate. The trials with FIXOR[™] (B1, C3, 6-5, 6-13, and 6-21) have been highlighted in light green in Tables 8-3 through 8-6. Contamination was also found in some C4 charges detonated alone (Samples F5 to F8). All showed a significant TNT

concentration, but none should have been found because C4 does not contain TNT. This TNT contamination may come from prior detonations. The plates were particularly difficult to wash before trial F5 due to the massive contamination by the preceding low-order detonations (B6, D7, and A6). The TNT contamination suggests that the washing was not adequate to remove all explosives residues from the plates. Thus, because of the possibility of contamination, the results for trials done after a low-order detonation should be considered with caution. The chronological order of the trials was added in Tables 8-3 to 8-6 to point out those trials following low-order detonations. They are highlighted in blue in the tables. The use of clean acetone-soaked rags or clean acetone baths should be considered for future trials.

The mass of explosive found after a detonation was compared with the initial quantities of explosives present in the total charge before the detonation events, giving a percentage of unconsumed explosives (Tables 8-3 and 8-4). The amount of explosive in the primer charge was taken into consideration in all cases. In addition, the residual 12 percent of HMX that comes from the synthesis of RDX was taken into account in the calculations (Appendix B). Then, Tables 8-5 and 8- 6, constructed using the results of Tables 8-3 and 8-4, present the explosive concentration per unit area $(mg/m²)$ after an event. Those values are useful to compare the results of similar trials when different numbers of aluminum plates were used. Theoretically, when more aluminum plates were used, the area covered was larger, and the proportion recovered should be larger.

The results in Tables 8-5 and 8-6 show that the greatest concentrations came from low-order detonations, in agreement with results reported elsewhere. The TNT, RDX, and HMX residues reached as much as 4.98 percent (D6, PMA-1A with LSC), 2.64 percent (D7, PMA-1A with 4-g C4 in a lateral hole), and 1.59 percent (6-12, 81-mm with LSC), respectively. For high-order detonations, the highest TNT concentration was 324 mg/m^2 (1.0 percent) (Appendix B) from a PMA-1A mine detonated with 20-g C4 in the top hole. For RDX, the greatest concentration deposited was 47 mg/m² (0.6 percent) for an M67 grenade detonated with FIXOR™. And finally, for HMX, the greatest value obtained was 4.8 mg/m² (0.5 percent) for an M67 grenade detonated with FIXORTM. Knowing that these concentrations are underestimated, these findings indicate that the BIP of TNT- and Comp B-filled munitions is not always efficient at consuming all the main charge in certain detonation configurations. The results show that the highest amount of residue came from PMA-1A anti-personnel mine imitations. However, some differences exist between real and imitation mines. The plastic casing used in the imitation might not have offered the same confinement as a real mine casing. A lack of continuity in the explosive, which is common to homemade munitions, is also possible. Moreover, the geometry of the mine and the critical diameter of TNT may have caused this situation. The use of more C4 might have given better results; however, the quantities used (4 to 30 g) were those recommended by the EOD personnel for the destruction of PMA-1A mines.

Interestingly, all of the detonations of M67 grenades were high order. The percentage of unconsumed TNT was generally below 0.05 percent. Four trials gave much higher results: C3 (FIXOR™, 0.29 percent), 6-17 (100-g of C4, 0.37 percent), 6-22 (36-g SC, 0.42 percent) and 6-23 (6.5-g SC, 0.66 percent). FIXOR™ was later discovered to have been used in an incorrect configuration for C3 (see below). Tests 6-17 and 6-23 followed low-order detonations and could be contaminated. That leaves only one trial with an inexplicably high concentration of TNT. With the exception of C3 (wrong FIXOR™ configuration), the highest RDX concentration was 0.035 percent for 6-18 (grenade with detonator in Comp B). HMX concentrations were much lower, below 0.02 percent; again, with the exception of C3, the highest concentration was found for 6-18.

For 60-mm mortars, 6 low-order detonations were obtained in 14 trials (B4, B5, B6, 6-3B, 6-4, and 6-7). Results suggest that a 60-mm mortar cannot be destroyed efficiently with less than 100 g of C4 sticking to the casing, or by an LSC, or with a 6.5-g SC; at least 150-g C4 or an SC of 16.5 g are necessary for this operation. With the exception of B1 (wrong FIXOR™ configuration, see below), the worst contaminating trials for TNT were 6-2 (50-g C4 in nose 0.18 percent TNT) and 6-6 (36-g SC, 0.14 percent TNT). This result is surprising for trial 6-2, but it follows a low-order detonation. Besides this, the TNT concentration is below 0.1 percent. RDX concentration is generally below 0.01 percent, the highest value being for sample 6-2. HMX is usually much lower or undetectable, except for sample B3, which was detonated with 150 g of C4 on the side of the casing.

For 81-mm mortars, 4 low-order detonations were obtained over 14 trials; these were observed for samples A4 (75-g of C4 in nose), A6 (100-g of C4 lateral), 6-12 LSC, and 6-15 (6.5-g SC). The occurrence of a low-order detonation for A4 is strange because three similar trials (A1, A5, 6-10) gave high-order detonations. TNT concentrations as high as 0.4 percent were obtained for A1 (75 g of C4 in the nose) and A2 (150 g of C4 lateral). RDX concentrations were generally below 0.1 percent, except for A5 (75 g of C4 in the nose, 0.214 percent), which followed a low-order detonation. RDX, 0.096 percent, was obtained for the 16.5g SC. HMX was usually undetectable, except for A5, which was possibly contaminated.

Differences were noted according to the primer charges used during the trials. When linear shaped charges were used, in four trials, only low-order detonations were obtained. This result is not surprising because LSC are specially designed to give low-order detonations. This kind of detonation is generally characterized by a large amount of residue, and the two cases reported here are no exceptions. Commercial shaped charges, namely the 6.5g RDX SC, also showed a high proportion of low-order detonation: two trials out of three gave low-order detonations, and the third showed a particularly high level of TNT residue (see trials 6-7, 6-15, and 6-23). The destruction of munitions using C4 was more effective when a sufficient amount was used. The required quantity of C4 depends on the type of munition to be destroyed. High-order detonations with low levels of explosives residue were obtained only with the use of at least 150 g of C4 on the side of the munition for the 60- and 81-mm mortars, but 20 g was enough for the grenades.

Extracting information concerning the proper primer position from the results obtained in this work is difficult. The detonation of M67 grenades generally gave high-order detonations and low levels of explosives residue, regardless of the position of the detonator. The BIP of mortar rounds was more influenced by the

quantity and type of primer than by the position of the primer. Of the five trials that were done with 150 g of C4 (A2, B2, B3, 6-1, and 6-9), all gave high-order detonations and mostly low levels of explosives residue. The only exception was sample A2 for which higher levels of TNT were found; however, trial A2 follows a low-order detonation. Five trials (A1, A4, A5, 6-2, and 6-10) were also done with 50 to 75 g of C4 in the nose of the mortar. Trial A4 produced a low-order detonation and the other four trials seem to lead to higher levels of explosives residue than mortars detonated laterally. However, three of these four high-order detonations followed a low-order detonation and could be contaminated. For the PMA-1A anti-personnel mine imitation, the cleanest trials came from detonations with 4 to 30 g of primer in a lateral hole (D2, D3, and D7). Still, more data are needed because one of these trials gave a low-order detonation. The worst contaminating trials came from mines that were detonated with C4 introduced in the top center hole (D4 and D5). This could indicate that the geometry of the mine hinders the propagation of the shock wave when the detonation is initiated by the middle part of the TNT block. Unexpectedly, low levels of explosives residue were obtained for the mine without holes (D1) for which C4 was deposited only on the casing without any direct contact with the explosive. One would think that close contact between the explosive and the primer was necessary to obtain clean detonations. The absence of holes in the plastic casing may have increased the degree of confinement and led to a better detonation. More results are needed to confirm those findings.

The use of a fuse does not seem to influence the type of detonation and the amount of explosives residue, at least for the 60-mm mortars. Indeed, high-order detonations and comparable amounts of residues were obtained for trials B2 through B5, which were detonated under similar conditions, but with and without fuses.

Primer charges were also tested alone to evaluate their potential contribution to the explosive residues. Commercial RDX SC and C4 blocks were detonated. The amount of explosives residues recovered after each detonation was small and similar for SC and C4, around 0.001-0.006 percent for RDX. The greatest recovery was 0.02 percent of RDX for a 20-g block of C4. The percentage of unconsumed HMX in C4 was generally below 0.01 percent, except for the 20-g block of C4, for which as much as 0.015 percent of the initial amount of HMX was recovered. TNT contamination occurred for all C4 and SC charges. For FIXOR™ detonated alone, no data were available, because the detonation was only conducted to generate a reference blast pressure.

When FIXOR™ was used as a primer charge, contamination of RDX and HMX was observed in three trials of rounds containing only TNT: B1 (60-mm), D8 (PMA-1A), and 6-5 (60-mm). No conclusion can be made for the moment. The contamination may come from the high blast pressure of FIXOR™ that might have sprayed residues from the surrounding soil onto the aluminum plates and from the huge fireball that completely destroyed the tarps around the detonation plate for spring 2001 samples, hence increasing the amount of explosives recovered. Nevertheless, two interesting facts were observed. First, only high-order detonations were logged with FIXOR™ in eight trials. This is an important observation considering that high-order detonations seldom show high levels of contamination. The second interesting observation about FIXOR™

concerns the way this initiating charge was used for the destruction of munitions. The amounts of TNT recovered after each detonation in the fall 2002 trial were always lower than those of spring 2001. This may be due to a better positioning of the bottles of FIXOR™ around the munitions; in the first trial they were placed vertically beside the munition, while in fall 2002 the bottles were laid with their bottoms touching the munitions, following the manufacturer's advice. But the possibility of contamination by the surrounding sand in the spring 2001 samples cannot be ruled out. Indeed, the protecting tarps of fall 2002 around the detonation plate were fire retardant and not systematically burned by the fireball, contrary to those of spring 2001. Therefore, the potential for contamination of spring 2001 samples is larger than for those of fall 2002. On the other hand, the HMX and RDX concentrations did not follow the same trend as TNT. More experiments would be needed before drawing final conclusions.

High concentrations of NG were surprisingly found in trials A and B (60and 81-mm mortars) of spring 2001. Since NG was not detected in sand samples, but present only for 60- and 81-mm mortars, it probably comes from the propellant bags and the ignition cartridges, which are the only components of this kind of mortar containing NG. For trial B1, for example, a total of 71.2 mg of NG was found. None was detected in fall 2002 trials because NG analysis was not targeted. The EOD personnel removed the propellant bags prior to the experiments. The ignition cartridge was also supposed to have been removed, but it is hard to verify because these cartridges are inside the mortar rounds. The presence of NG could also come from contamination introduced during the manufacturing or handling of the munitions [20]. The 71.2 mg of NG found in trial B1 strongly suggests that the ignition cartridge was present during some trials. If the presence of the ignition cartridge is assumed, it represents 4100 mg of double-based propellant, which corresponds to 1640 mg of NG (40 percent w/w) present prior to detonation. The 71.2-mg of trial B7 corresponds thus to 4.34 percent of unconsumed NG. In view of this result, apparently NG was less consumed than TNT and RDX.

There are sources of errors in these kinds of trials. The two major ones are the heterogeneous dispersion of the residues on the contaminated surface. There is also the contamination and the adsorption of explosives on soot, which makes extraction of explosives difficult. Brochu et al. [8] have addressed this problem. Soot was not present after all events; it was found mostly after low-order detonation and when FIXOR™ was used.

The variations in weather conditions, such as the wind speed and direction, might also have caused errors. Hot weather has been mentioned as particularly hard to deal with because the witness plates become very hot, which may degrade the explosives faster. Also, in hot weather the plates are difficult to sample and wash with acetone and methanol because of the fast evaporation of the solvent. Considering that the trial of spring 2001 was conducted in very hot and humid conditions, the results may be more uncertain. Measuring the impacts of wind speed and direction was impossible, since composites were used for the analysis. Furthermore, no relationship could be found between the temperature at the time of the detonation or the atmospheric pressure and the amount of dispersed residues (Appendix D).

Conclusion

The first objective of this study was to estimate the quantities and types of residues resulting from the BIP detonation of various munitions. The detonation of munitions using BIP conditions was not always efficient at consuming all of the main charge. For low-order detonations, more residue (up to a few percent) was recovered independently of the configuration. High-order detonations were characterized by much lower explosive residue; the maximum values found were 1.0 percent, 0.6 percent, and 0.5 percent for TNT, RDX, and HMX, respectively. Typical levels of explosives residue, however, were often around 0.05 to 0.4 percent for TNT, 0.035 to 0.1 percent for RDX, and undetectable to 0.02 percent for HMX. To ensure high-order detonations with 60- and 81-mm mortars, 150 g of C4 on the side of the casing should be employed. FIXOR™ and the commercial SCs of 16.5 g and 36 g could also be used. For grenades, all of the configurations tested gave high-order detonations. For the PMA-1A, 4 to 30 g of C4 in a lateral hole or the use of FIXOR™ can lead to high-order detonations. The commercial SCs could probably give similar results, but they have not been tested with the mines.

Unfortunately, identification of general trends is difficult because of the heterogeneous dispersion of the residues and because of the contamination of some samples. This contamination may come from improper washing of the witness plates or from high-pressure blasts that may have sprayed explosive residues onto the witness plates. Moreover, all values are underestimated because the area covered by the plume could not be estimated; only the witness plates were sampled. Conclusions had to be drawn with caution.

TNT residues tended to be higher than RDX residues, while HMX residues were less often found. The cleanest detonations were generally obtained from grenades, while PMA-1A anti-personnel mine imitations released major quantities of explosives residues. As already mentioned, the use of imitation offers a different configuration from real mines, which may explain these results. The geometry and the critical diameter of TNT may also have caused this situation. Concerning the type of primer charge, cleaner detonations were obtained with at least 150 g of C4 for the 60- and 81-mm mortars, but 4- to 20-g charges were enough for the grenades. The linear-shaped charges and the 6.5-g SC gave mostly low-order detonations, and, consequently, a high dispersion of explosives residues. The commercial RDX SC of 16.5 g and 36 g were less of a problem, but more replicates are needed to determine their effectiveness in the field. FIXOR™ gave interesting results only when strictly following the manufacturer's advice.

The priming position influenced the dispersion of residues for PMA-1A mine imitations. Indeed, the cleanest trials came from detonations with C4 introduced in a lateral hole and from mines without holes that were detonated with C4 in the middle of the mine, while the most contaminating ones were initiated with C4 in the top center hole. For the mortar rounds, priming the nose with 75-g C4 was more contaminating than priming the lateral position with 150-g C4. Whether this was due to differences between the priming positions or the quantities of C4 is unclear, however. Detonations of M67 grenades were not influenced by the

position of the detonator. Finally, the BIP of munitions were not affected by the presence of the fuse.

The presence of NG in post-detonation residues of mortar rounds was unexpected, since NG was not supposed to be included in the detonation setups. However, the ignition cartridge may not have been removed as requested, and may thus have contributed to the dispersion of NG. More data are needed to confirm the poor NG consumption during live-fire detonations in order to make recommendations on the potential for NG contamination of the environment.

The second objective of this work was to determine the contribution to the dispersion of explosives residues of many primer charges detonated alone. Past studies have shown that detonation of C4 appeared to increase the amount of RDX residues [6]. So, C4 charges were tested, along with commercial RDX SCs, to determine the potential contribution of the primers. The detonation of various weights of C4 and of commercial RDX SC showed that their contribution was small; the use of C4 led to the dispersion of less than 0.02 percent of RDX and HMX. The performance of commercial SC was even better, with only 0.005 percent RDX dispersed; no HMX was detected.

In general, this study showed that a certain proportion of explosives during a BIP detonation could be sprayed into the environment. The study also demonstrated that the distributions are heterogeneous, and that the amount of explosive residues collected after a detonation strongly depends on the order of detonation. The configuration of the BIP detonation also influences the level of collected residues. For future work, at least six replicates of the same detonation are recommended to be able to generate statistically valid results. Nevertheless, this study has allowed the identification of some problematic cases and some general trends that can be used to make the following recommendations to EOD personnel:

• In BIP operations, the conditions leading to low-order detonations should be avoided whenever possible.

• LSCs and commercial 6.5-g RDX SCs should not be used for BIP detonations of the discussed munitions; charges of 16.5 g and 36 g are required.

• To minimize explosives residues, 150 g of C4 should be used for BIP of 60- and 81-mm mortars.

• The BIP of PMA-1A mine imitations leads to high dispersion of explosives into the environment.

• The BIP of PMA-1A mine imitations is highly dependent on the position of the primer.

The following suggestions are specifically addressed to scientists who perform similar trials:

• Washing of the aluminum witness plates is critical to prevent cross contamination. The use of clean acetone-soaked rags or clean acetone baths is suggested.

• The efficiency of FIXOR[™] should be further evaluated in conditions minimizing contamination from the surrounding soil.

• NG in post-detonation residues should be analyzed whenever NG is present in the munition to be tested.

• Whenever possible, the area covered by the plume should be evaluated to calculate the total amount of explosive residue.

In conclusion, this study demonstrated that BIP operations could spread explosives into the environment, but that the processes involved in controlling a detonation are extremely difficult and complex. More work will be needed to completely understand all the parameters involved in such experiments and to produce applicable solutions for this important activity.

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Appendix A - Analytical Results

Table 8-A2

HPLC Results, Volume Used for Extraction, Mass of Detonation Residues, and Mass of Detonation Residues by Composite for Fall 2002 Trials

Appendix B - Calculations

Calculate the amount of explosives residues in each composite as follows:

For each composite, an amount of explosives residue was calculated. The value was based on the HPLC values previously corrected for dilution and on the total volume of solvent used for extraction. Only TNT, RDX, and HMX values were calculated to simplify the results.

For example, in trial 6-1 composite 6-1-1: $TNT = 21.8$ mg/L and 0.489 L of solvent was used, for a total of 10.9453-mg, which is rounded to one significant figure: 10.9-mg.

This value is listed in Appendix A under mass. It corresponds to the total amount of unconsumed explosives residue found in one composite.

Calculate the total amount released after event

All the composites of a same trial were added together to represent the total mass released for a specific event. For example, $6-1-1+6-1-2+6-1-3 =$ total mass for 6-1. The values were reported in Tables 8-3 and 8-4 under total mass after event.

Calculate the total mass before event (Tables 8-3 and 8-4)

The total explosive weights for the Canadian Forces munitions were obtained from the relevant Canadian Forces Technical Order (CFTO) and from other relevant specifications. The 60-mm mortar and the PMA-1A did not require further calculations, as they are both 100 percent TNT. The 81-mm mortar HE round and M67 grenade were both filled with Composition B, a mixture of 59.5 percent RDX and 39.5 percent TNT, with the remaining 1 percent in wax.

For their part, the C4 demolition blocks are composed of 91 percent RDX. The mass of RDX in the commercial shaped charge explosives is indicated on the product. RDX, however, has between 10-15 percent HMX. No CFTO governs the amount of HMX allowable in RDX (if anything, the presence of HMX increases the explosive effectiveness). Therefore, for the purpose of calculation, an average of 12 percent was used. Here are some examples:

For 150-g C4: $(150 \text{ g x } 0.91)$ x $0.12 = 16.38$ -g HMX $(150 \text{ g x } 0.91)$ x $0.88 = 120.12$ -g RDX

For 81-mm mortar (857-g Comp B) $(857 \text{ g x } 0.395) = 338.5 \text{ g TNT}$ $(857 \text{ g x } 0.595)$ x $0.12 = 61.19$ -g HMX $(857 \text{ g x } 0.595)$ x $0.88 = 448.73$ -g RDX

Calculate the percent explosive remaining after detonation (Tables 8-3 and 8-4)

The percentage in Tables 8-3 and 8-4 is simply the amount of residues found after an event divided by the amount of explosives before the event multiplied by 100.

For example, for trial 6-1, 0.020262 g of TNT was found after the event and 351 g of TNT was present before the event: 0.020262 g / 351 g x 100 = 0.0058%.

The values were reported as "% of unconsumed explosive" in Tables 8-3 and 8-4.

Calculate the concentration of explosive

The concentration of explosives residue by area was calculated from the amounts of residues recovered divided by the number of plates used. Since every aluminum plate was 1 m², then the results gave the concentration in mg/m².

Appendix C - Pressure Data

Table 8-C1

Pressure Sensors Results for Blow-In-Place Detonation Trials of Spring 2001 with Theoretical Conwep Values

Table 8-C2 Pressure Sensors Results for Blow-In-Place Detonation Trials of Autumn 2002 with Theoretical Conwep Values

Appendix D - Meteorological Data

9 Fate and Transport Parameters for Firing Range Residues

Introduction

Background

Solubility is a fundamental parameter for determining the potential fate and transport of energetics residues on firing ranges. However, the solubility of some energetics compounds is not known with certainty. For example, solubility of diphenylamine at 25 °C has been reported to range between 3.6 mg L^{-1} (Kitchens et al. 1978) and 300 mg L^{-1} (Verschueren 1983). For other compounds, the data available may be even more variable. This creates great uncertainty, especially when considering the effects of temperature, which can strongly affect solubility (Lynch et al. 2001). Accurate solubility values are key parameters for describing the fate and transport of propellant residues from firing ranges into groundwater.

The main factors affecting fate and transport of explosives and propellant residues after they dissolve from the solid phase are adsorption, transformation, and irreversible soil binding (Brannon and Myers 1997). Anticipating the movement of energetics residues through soils and into groundwater requires the two fate and transport process descriptors, adsorption coefficients, and transformation rate coefficients. Process descriptors mathematically depict the interactions between soil and water concentrations of energetics. The *adsorption coefficient* mathematically describes the distribution of a chemical between soil and water at equilibrium. When transformation or irreversible sorption is significant, equilibrium is not attainable and the transformation rate coefficient is used to describe the fate and transport of an explosive contaminant. The *transformation rate coefficient* describes the removal of a compound from solution by transformation and subsequent adsorption. The transformation rate coefficients for energetics generally follow first-order kinetics (Brannon and Myers 1997).

Considerable research has been conducted to determine fate and transport process descriptors for explosives. Most of the research has been conducted on TNT, RDX, and HMX (Table 9-1, and Pennington et al. 2001). However, considerable research has been conducted since the publication of the summary table, substantially reducing the data gaps and the need for further study.

Research is still needed on energetic compounds other than explosives, such as propellants, smokes, and illuminants for which descriptors vary greatly (Mirecki, in press).

Fate and transport parameters are used to evaluate the migration of energetics residues from the solid phase into solution during rainfall events and to describe the interactions of energetics residues in solution with firing range soils. This chapter presents new process data leveraged with data obtained in the Army Environmental Quality Technology Program (EQT) work units titled "Fate and Transport of Explosives Contaminants" (A835/309E/RE004), and "Fate and Transport of Propellants, Smokes, and Illuminants" (AF25/309F/HF201), which provided 90 percent of the funding for this effort. Site-specific process data for soil from Fort Bliss, TX, and Jefferson Proving Ground, IN, are also presented.

Objectives

The primary objective of this study was to determine process descriptors for selected energetics residues for which data are lacking. Specifically, fate and transport process parameters were determined for nitrobenzene, perchlorate, nitroguanidine, diphenylamine, N-nitrosodiphenylamine, and ethyl centralite. Nitrobenzene is a 2,4,6-trinitrotoluene (TNT) impurity, and perchlorate, nitroguanidine, diphenylamine, N-nitrosodiphenylamine, and ethyl centralite are propellant components. Another objective was to determine site-specific process descriptors for TNT, RDX, and HMX in soils from Fort Bliss and Jefferson Proving Ground, two sites where soils on live-fire training ranges were characterized for explosives residues earlier in this study (Pennington et al. 2003).

Materials and Methods

Solubility

Distilled-deionized (DDI) water was used as the solvent for the solid propellant compound dissolution experiments with diphenylamine, N-nitrosodiphenylamine, and ethyl centralite. An excess amount of chemical was added to 200-mL of DDI water in a 250-mL Erlenmeyer flask wrapped in aluminum foil to minimize photolysis (Townsend and Myers 1996). A magnetic stir bar was added to the flask, which was then sealed with Parafilm. The solution was stirred at a rate sufficient to maintain a deep vortex. Experiments were performed in triplicate at temperatures of 10, 24, and 30 °C. Samples were taken $\overline{7}$ and 14 days after agitation began. Samples were extracted after adding sufficient DDI water to bring the sample volume to approximately 500 mL (USEPA 1996). The extract was concentrated to 1 mL and analyzed by Method 8270C GC/MS (USEPA 1996b). Nnitrosodiphenylamine was detected by mass spectrometry as diphenylamine because of heat-mediated breakdown to diphenylamine in the gas chromatograph.

Energetics partitioning

Adsorption kinetics. An aquifer soil, LAAP D, and two surface soils with different physical characteristics, Yokena Clay and Grange Hall, were used to measure adsorption kinetics (Table 9-2). Sufficient soil (5 g) and DDI water (20-mls) containing the contaminant of interest were added to 30-ml glass centrifuge tubes to make a soil-to-water ratio of 1:4. The initial concentrations of

nitrobenzene, nitroguanidine, diphenylamine, N-nitrosodiphenylamine, and ethyl centralite were 3, 34.8, 7, 4.15, and 23 mg L^{-1} , respectively. Samples were placed on a reciprocating shaker in the dark at 180 excursions per minute and sampled at 1, 6, 24, 48, 72, 96, and 120 hr. Triplicate tubes were removed and centrifuged at 8,288 RCF for 30 min. A 12-ml water sample was removed and filtered through a 0.45-µm membrane filter. The aqueous samples for diphenylamine, N-nitrosodiphenylamine, and ethyl centralite were prepared by liquid-liquid extraction (SW-846 Method 3510C, U.S. EPA 1996a) after adding sufficient DDI water to bring the sample volume to approximately 500 mL. Diphenylamine, N-nitrosodiphenylamine, and ethyl centralite extracts were concentrated to 1 mL and analyzed by Method 8270C GC/MS (USEPA 1996b); nitrobenzene was analyzed by high-performance liquid chromatography (HPLC) using EPA SW846 Method 8330 (USEPA 1994); and nitroguanidine was analyzed using the HPLC method of Walsh (1989).

Adsorption partitioning. Adsorption partitioning was conducted with an aquifer soil (LAAP-D), a clay soil (Yokena Clay), and a sandy loam soil (Grange Hall) in a 1:4 ratio of soil to water. Nitrobenzene samples were spiked at concentrations of 3, 2.5, 2, 1.5, and 1.11 mg L^{-1} ; nitroguanidine at 33.3, 26.64, 19.98, 13.32, and 6.66 mg L⁻¹; diphenylamine at 8.04, 6.71, 5.03, 3.34, and 1.68 mg L⁻¹; and N-nitrosodiphenylamine samples of 5.16, 3.87, 2.58, 1.29, and 0.52 mg L^{-1} . Triplicate samples for each spike level were shaken for 24 hr on a reciprocating shaker at 180 excursions/min, centrifuged at 8,288 RCF for 30 min, and the aqueous phase removed, filtered, and analyzed as previously described for adsorption kinetics.

Desorption kinetics. The original intention was to determine desorption kinetics on soils already contaminated by training activities on the range. However, due to the extreme heterogeneity in the distribution of explosives in the field (Pennington et al. 2001), no explosives were detected in soils set aside for these tests. Therefore, uncontaminated site soils were spiked with explosives. Contaminant loading of Fort Bliss and Jefferson Proving Ground soil was accomplished by spraying 5 ml of acetone containing $450 \text{ mg } L^{-1}$ of TNT, 400 mg L^{-1} RDX, and 425 mg L^{-1} HMX, respectively, onto 200 g of each dispersed soil in a stainless steel pan. The acetone was allowed to evaporate for 4 hr under a hood, with occasional stirring to ensure that all of the soil was exposed to the air. The soils were then tumbled for 3 days to ensure that the adsorbed

explosives were evenly distributed. Soils were analyzed for TNT, RDX, and HMX (U.S. EPA SW 846 Method 8330). Tests were prepared by loading 4 g of soil and 16 ml of water into 25-ml centrifuge tubes and placing on a reciprocating shaker at 180 excursions per minute. At sampling times (0.5, 1, 6, 24, 48, 72, and 96 hr), triplicate tubes were removed and centrifuged at 8,288 RCF for 30 min. Two ml of the aqueous sample was supplemented with 2-ml acetonitrile, and then analyzed by HPLC for TNT, RDX, and HMX (EPA SW846 Method 8330, USEPA 1994).

Desorption partitioning. Soils (4 g) from Fort Bliss and Jefferson Proving Ground, spiked with TNT, RDX, and HMX as described in the preceding paragraph, were loaded into 25-ml centrifuge tubes in three replicates. Water (16 ml) was added to the centrifuge tubes, the tubes were shaken for 24 hr, and centrifuged for 30 min as described earlier. A 2-ml aqueous aliquot was removed and diluted with 2 ml of acetonitrile before being analyzed for RDX and HMX as previously described. Remaining water was removed from the tests and replaced by 10 ml of fresh DDI water. Testing returned to the shaking and analytical procedures, which were repeated three more times. TNT was not tested because steady-state TNT concentrations were not attained during the desorption kinetics testing for either soil.

Fate of perchlorate under specific Eh-pH conditions. Perchlorate tests with the clay soil (Yokena Clay) were conducted in glass 2800-ml Fernbach culture flasks. Additional organic matter (0.5 percent w/w) from the Atchafalaya Basin, LA was added as an energy source to increase the rate of reduction in the soil by the native microbial community. Sufficient DDI water and soil were added to the flasks to produce a water-to-solids ratio of $18:1 \, (w/w)$. The slurries were kept in suspension using magnetic stirrers and were maintained at room temperature $(\sim 24$ ^oC).

Control of Eh and pH in the slurries was maintained using methods developed by Patrick et al. (1973) with modifications (Brannon 1983). Eh was monitored by platinum and Ag-AgCl electrodes connected to a pH-millivolt meter (Beckman Instruments, Fullerton, CA). The desired Eh was set on a meter relay (Currier and Roser, New Orleans, LA), which, by activating an aquarium pump to introduce air into the system when the set point was reached, prevented the Eh from falling below the preset value. The soil suspensions were incubated and stabilized at the selected Eh-pH values (approximately 2 weeks) before addition of perchlorate.

The study consisted of triplicate tests at two Eh levels (+500 (oxidizing) and -150 mV (highly reducing)), and three pH values (5.5, 7.0, and 10.0). Following stabilization, perchlorate was added in water to bring initial solution concentrations to 10.9-, 9.6-, and 10.7-mg L^{-1} in the pH 5.5, 7, and 10 treatments, respectively. All flasks were covered with aluminum foil prior to spiking to preclude photodecomposition. Slurry samples were withdrawn at 1, 6, 24, 48, 72, 168, 240, and 336 hr. The aqueous phase was analyzed for perchlorate using ion chromatography with a conductivity detector (EPA SW-846 Method 9058, USEPA 1996c). Soils were also analyzed for perchlorate at the end of each incubation.

A set of additional tests was conducted with freshly obtained Lake Park soil to test the hypothesis that a freshly obtained soil would contain a microbial population more capable of degrading perchlorate. This soil was air-dried, sieved to remove large gravel or other trash, then ground. Tests were conducted in duplicate at pH 7 and at two Eh levels (+500 and -150 mV). Sampling was conducted as in the preceding paragraph.

Results and Discussion

Solubility

Temperature strongly affects the solubility of energetics and therefore their fate and transport (Lynch et al. 2001). If ideal conditions are assumed, solubility can be estimated using the equation (Atkins 1982):

$$
\ln x_B = -\left(\frac{\Delta_{fus}H}{R}\right)\left(\frac{1}{T} - \frac{1}{T^*}\right) \tag{1}
$$

where x_B = mole fraction of solute, $\Delta_{\text{fus}}H$ = enthalpy of fusion of solute, $R =$ ideal gas constant, $T =$ absolute temperature, and $T^* =$ solute melting temperature. Aqueous solutions of energetics compounds are not ideal, but the general equation remains similar following the form

$$
\ln S = A - \frac{B}{T} \qquad \text{or} \qquad \qquad S = A * \exp\left(\frac{-B}{T}\right) \tag{2}
$$

where $S =$ solubility, A and $B =$ arbitrary constants, $T =$ absolute temperature.

Figure 9-1 summarizes solubility of diphenylamine, N-nitrosodiphenylamine, and ethyl centralite over a wide temperature range (10-30 ºC). To conform to the format in Equation 2, a linear regression was performed on ln [S] versus T^{-1} , where T is absolute temperature in degrees Kelvin. The solubility of diphenylamine, N-nitrosodiphenylamine, and ethyl centralite increased with temperature. Equations describing the dependence of solubility on temperature are provided in the figure caption. Table 9-3 summarizes mean solubility as a function of temperature. Solubility of diphenylamine was intermediate between the reported values of 3.6 and 300 mg L⁻¹ at 25 °C (Kitchens et al. 1978; Verschueren 1983). Measured N-nitrosodiphenylamine and ethyl centralite solubilities were lower than the reported values of 35.1 mg L⁻¹ at 25 °C (Yalkowsky and He 2002), and 80 mg L⁻¹ at 20 °C (U.S. Army Armament Research and Development Command 1983), respectively.

Figure 9-1. Solubility as a function of temperature for diphenylamine [1n S (mg/L) $= 13.71 - 2957$ T-1, R2 = 0.88]; N-nitrosodiphenylamine $[(1n S (mg/L))]$ $= 12.119 - 2815$ T-1, R2=0.83]; and ethyl centralite [1n S (mg/L) = 13.091-2914 T-1, R2 = 0.75]

Energetics partitioning

Adsorption kinetics. Dissolved nitrobenzene concentrations decreased over time in the two surface soils (Grange Hall and Yokena Clay, Figure 9-2). Halflives were 86.2 and 28.3 hr in the two soils, respectively. The pseudo-first-order transformation rate constant in the aquifer soil (LAAP-D) was not significantly different from zero (Table 9-4). These results are consistent with those summarized in the Hazardous Substance Data Base (HSDB 2002), where rapid to no degradation of nitrobenzene was observed. The current results suggest that nitrobenzene will be rapidly adsorbed and/or degraded in the surface soils, but remain stable in an aquifer soils. However, results are more likely related to the soil properties than to relative depth in the soil profile.

Figure 9-2. Adsorption kinetics of nitrobenzene in LAAP D, Grange Hall, and Yokena Clay soils

Dissolved nitroguanidine concentrations were stable in all three tested soils (Figure 9-3). This is consistent with previously reported lack of susceptibility to aerobic biodegradation in activated sludge (Kaplan et al. 1982). Nitroguanidine would not be expected to degrade in either aerobic surface or aquifer soils, although anaerobic conditions may result in biodegradation (Kaplan et al. 1982). Redox potential exerts a greater influence than soil properties on the fate of nitroguanidine.

Figure 9-3. Adsorption kinetics of nitroguanidine in LAAP D, Grange Hall, and Yokena Clay soils

Diphenylamine rapidly disappeared from solution in Yokena clay soil (Figure 9-4). The disappearance may have been promoted by higher total organic carbon (TOC), CEC, and/or clay content of the Yokena soil. Concentrations also decreased in the Grange Hall soil but were stable in the LAAP-D aquifer soil, which was low in TOC, CEC, and clay content (Table 9-4). These results suggest that diphenylamine will be adsorbed and/or degraded in surface soils, but will be relatively stable in aquifer soils that are similar in composition to the soils tested.

Dissolved N-nitrosodiphenylamine concentrations were present during the entire incubation period for all three tested soils (Figure 9-5). N-nitrosodiphenylamine rapidly degraded or adsorbed to Yokena clay soil, after which solution concentrations remained stable (Table 9-4). In soils where removal occurred, half-lives ranged from 194 to 373 hr (Table 9-4). These results suggest relatively high stability for this compound over a broad range of soil properties.

Solution concentrations of ethyl centralite rapidly reached steady-state condition following exposure to the tested soils (Figure 9-6). After the initial drop in concentration due to adsorption to the solid phase, concentrations remained relatively stable for the remaining 120 hr of the study. Half-lives were indeterminate (Table 9-4). Other than initial adsorption, no discernable processes were removing ethyl centralite from soil solution. Concentrations of ethyl centralite would, therefore, be expected to be relatively stable.

Figure 9-4. Adsorption kinetics of diphenylamine in LAAP D, Grange Hall, and Yokena Clay soils

Figure 9-5. Adsorption kinetics of N-nitrosodiphenylamine in LAAP D, Grange Hall, and Yokena Clay soils

Figure 9-6. Adsorption kinetics of ethyl centralite in LAAP D, Grange Hall, and Yokena Clay soils

Adsorption partitioning. Nitrobenzene adsorption coefficients could be determined for LAAP-D soil only because steady-state conditions were not attained in Yokena Clay and Grange Hall soils. Solution phase concentrations continued to fall until undetectable, indicating degradation. Partitioning of nitrobenzene is controlled by organic carbon (Zhao et al. 2003). Therefore, the measured partitioning coefficient in LAAP-D soil, 0.5 L Kg⁻¹ (Table 9-5) was converted to log K_{oc} (organic carbon normalized partition coefficient) of 2.4 L Kg^{-1} using the equation

$$
K_{oc} = K_d/f_{oc}
$$
 (3)

where K_d is the partition coefficient and f_{oc} is the weight percent fraction of organic carbon in the soil. This value of log K_{oc} was within the range of log K_{oc} values for nitrobenzene (1.48 – 2.57 L Kg⁻¹) summarized by Brannon and Pennington (2002) for five nitrobenzene partitioning studies. The measured K_{oc} value for LAAP-D soil was in close agreement with results of Zhao et al. (2003). These results suggest that nitrobenzene can be transported by groundwater if it reaches the aquifer without undergoing degradation.

Nitroguanidine adsorption coefficients were uniformly low (Figure 9-7), ranging from 0.15 to 0.43 L Kg⁻¹ (Table 9-5). This agrees with previous results showing low K_d (<0.1 L Kg^{-1}) in soil (Haag et al. 1990). The measured partitioning coefficients for nitroguanidine were converted to $log K_{oc}$ using Equation 3 and the measured total organic carbon concentration in the soils. This yielded $\log K_{\text{oc}}$ values of 2.12, 1.71, and 1.25 L Kg⁻¹ for LAAP-D, Grange Hall, and Yokena Clay soils, respectively (Table 9-5). These measured values fall within the range of estimated $log K_{oc}$ values for nitroguanidine reported by others (– 0.356, Burrows et al. 1989, to 2.5 L Kg^{-1} , HSDB 2002). These low K_d values indicate that sorption of nitroguanidine will not impede transport to groundwater.

Diphenylamine adsorption coefficients for LAAP-D and Grange Hall soils were 3.8 and 1.66 L Kg⁻¹, respectively (Table 9-5). McDougal and Jepson (1998) measured and reported an octanol-water partitioning coefficient, K_{ow} , of 3.5 for diphenylamine. Converting the measured diphenylamine partitioning coefficients determined in the current study to K_{oc} using Equation 3 gave log K_{oc} values of 3.28 and 2.76 for LAAP-D and Grange Hall soils, respectively (Table 9-4). Converting McDougal and Jepson's K_{ow} to K_{oc} using the equation of Karickhoff (1981),

 $K_{oc} = 0.411 K_{ow}$ (4)

gave a log K_{oc} of 3.11, comparable to the experimentally derived values. The experimentally derived values were also comparable to an experimental $K_{\rm oc}$ value for diphenylamine of 2.78 and a predicted K_{oc} value of 3.28 derived using molecular topology methods (Meylan and Howard 1992). These results suggest that sorption will not impede transport of diphenylamine to groundwater.

N-nitrosodiphenylamine adsorption coefficients ranged from 0.25 to 11.4 L Kg^{-1} (Figure 9-8). Converting these to K_{oc} yielded 2.85, 1.94, and 2.86 L Kg^{-1} for LAAP-D, Grange Hall, and Yokena Clay soils, respectively. These compare relatively well to estimated 3.1 (HSDB 2002), 2.74 (calculated using Equation 4), and to a log K_{ow} value of 3.13 (HSDB 2002). These results suggest that sorption will impede transport of N-nitrosodiphenylamine only in soils high in organic carbon.

Figure 9-7. Adsorption coefficients for nitroguanidine in LAAP D, Grange Hall, and Yokena Clay soils

Figure 9-8. Adsorption coefficients for N-nitrosodiphenylamine in LAAP-D, Grange Hall, and Yokena Clay soils

Ethyl centralite K_d values were determined from measured solution concentrations and calculated (by difference) soil concentrations at each data point in the adsorption kinetics testing. The K_d values presented in Table 9-5 for ethyl centralite are the mean of seven determinations for each soil. The coefficient of variation (CV) for the three mean ethyl centralite K_d values in Table 9-5 ranged from 19.8 to 21 percent with a mean CV of 20.4 percent. Converting the K_d values to K_{oc} using Equation 3 resulted in log K_{oc} values of 3.66, 3.03, and 2.78 L Kg⁻¹for LAAP-D, Grange Hall, and Yokena Clay soils, respectively. These data were in relatively close agreement with the log K_{oc} value of 3.81 L Kg⁻¹ estimated using Equation 4 and the log K_{ow} of 4.2 reported by McDougal and Jepson (1998).

The partitioning data for ethyl centralite, nitrobenzene, nitroguanidine, diphenylamine, and N-nitrosodiphenylamine indicate that sorption of these compounds can be estimated from K_d , K_{oc} or K_{ow} values. Estimation of sorption reactions for these compounds would require only soil analysis for TOC. Because many of the previously available K_{α} values for these compounds were based on estimates, the experimentally derived values in this report are preferable.

Desorption kinetics and partitioning. Concentrations of HMX desorbed from Jefferson Proving Ground soil and concentrations of HMX and RDX desorbed from Fort Bliss soil reached steady state within 24 hr (Figure 9-9). TNT did not reach steady state and could not be detected after 24 hr of incubation in either soil. These results indicate that TNT, RDX, and HMX are rapidly desorbed and mobilized from the soils. However, the mobilized TNT is rapidly removed from solution, and has a half-life of ≤ 6 hr in both soils. In the Jefferson Proving Ground soils, half-lives of RDX and HMX were 27.5 and 235 hr. Half-lives of RDX and HMX in Fort Bliss soils could not be determined because the transformation rate coefficients did not significantly differ from zero. These results indicate that RDX, HMX in Fort Bliss soil, and HMX in Jefferson Proving Ground soil have the highest potential for transport into groundwater.

Partitioning coefficients were determined only for RDX and HMX in Fort Bliss soils and HMX in Jefferson Proving Ground soil because of the lack of steady-state TNT concentrations in both soils and the lack of steady-state RDX concentrations in Jefferson Proving Ground soil. A slope-derived K_d could be determined only for HMX in Jefferson Proving Ground soil because of rapid desorption of RDX and HMX during testing. The slope-derived K_d was 2.7 L Kg^{-1} with an $r^2 = 0.75$. The slope-derived K_d was in close agreement with the K_d derived from the measured solution concentration and calculated soil concentration following the first desorption step in the kinetic testing ($K_d = 2.43$ L Kg^{-1}). Similarly, derived single-point K_d values for RDX and HMX in Fort Bliss soil were 1.72 and 3.92 L Kg^{-1} , respectively. These results indicate that transport will be greatest for RDX in Fort Bliss soil. However, K_d values for RDX and HMX were low for both soils, indicating extensive transport if degradation does not occur.

Figure 9-9. Desorption kinetics of TNT, RDX, and HMX in Jefferson Proving Ground and Fort Bliss soils

Fate of perchlorate under specific Eh-pH conditions. Perchlorate was stable in Yokena Clay soil under oxidized (+ 500 mV) and highly reduced (- 150 mV) conditions over all tested pH values (Figure 9-10). No decreases in dissolved perchlorate concentrations were observed, even though Yokena Clay soil has been shown to biodegrade both TNT and RDX (Price et al. 1997, 2001). Tipton et al. (2003) reported that perchlorate biodegradation required anaerobic conditions, an adequate carbon source, and an active perchlorate-degrading microbial population. One of these conditions, probably an active perchlorate degrading microbial population, was missing from the Yokena Clay soil, because an adequate carbon source was provided and highly reducing anaerobic conditions were attained.

Figure 9-10. Solution concentrations of perchlorate in Yokena Clay soil slurries under oxidized (+500 mV) and reduced (-150 mV) conditions at pH 5.5, 7, and 10

All conditions necessary for perchlorate biodegradation are evidently not commonly met in the environment because of the many perchlorate detections in surface and groundwaters in the United States (Urbansky 2000). Even though perchlorate-reducing microorganisms are nearly ubiquitous in the environment (Coates et al. 1999) and enriched cultures have been used to completely degrade perchlorate (Kim and Logan 2001), biodegradation in soils has had mixed results (Tipton et al. 2003). Freshly collected soils were observed to degrade perchlorate whereas older soil from the same location showed no biodegradation activity (Tipton et al. 2003). Freshly collected soil tested in this study showed no biodegradation activity under either oxidized or reduced conditions (Figure 9-11). This suggests that the factors affecting perchlorate degradation in soils may be more complex than highly reducing anaerobic conditions, an adequate carbon source, and freshly collected soils with an active microbial population.

Figure 9-11. Solution concentrations of perchlorate in Lake Park soil slurries under oxidized (+500 mV) and reduced (-150 mV) conditions at pH 7

Summary and Conclusions

The solubility of diphenylamine, N-nitrosodiphenylamine, and ethyl centralite increased with increasing temperature. Measured solubility for these compounds was either lower or intermediate in value from the sparse published solubility data. Results of adsorption kinetics and partitioning studies showed that nitrobenzene and diphenylamine were degraded only in surface soils, while Nnitrosodiphenylamine was degraded in the subsurface soil and one of the surface soils. Nitroguanidine and ethyl centralite were not degraded in any of the tested

soils. Perchlorate was not degraded in Yokena clay soil under a wide range of Eh and pH conditions or in freshly collected Lake Park soil under either oxidized or reducing conditions at pH 7.

TNT was rapidly transformed in both Fort Bliss and Jefferson Proving Ground soils. RDX was also rapidly transformed in Jefferson Proving Ground soil. RDX and HMX concentrations in Fort Bliss soil and HMX in Jefferson Proving Ground soil reached steady state within 24 hr. Where not degraded, RDX and HMX were readily desorbed, indicating that transport would be extensive during rainfall events if degradation did not occur. These results indicated that transformation of TNT in both soils and RDX in Jefferson Proving Ground soil was rapid following the introduction of water. RDX partitioned to the Fort Bliss soil less than HMX, indicating that RDX transport would be faster than HMX.

Adsorption of nitrobenzene, diphenylamine, N-nitrosodiphenylamine, nitroguanidine, and ethyl centralite were low and showed generally good agreement with organic carbon-normalized partitioning coefficients (K_{∞}) . These results suggest that sorption of nitrobenzene, diphenylamine, N-nitrosodiphenylamine, nitroguanidine, and ethyl centralite will not generally impede transport of these compounds to groundwater. However, degradation in surface and aquifer soils may preclude transport of these compounds.

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10 Summary and Conclusions

Summary

In addition to increasing the content of the database of munitions constituents in surface soils, FY2003 emphasis was placed on optimizing sampling protocols and defining residues by conducting controlled detonation experiments, including high-order and blow-in-place detonations. Results confirm that the potential for constituent residues in surface soils is munitions-specific, related to weapon system performance (i.e., incidence of low-order detonations and UXO generation), and site-specific (i.e., controlled by the local weather and hydrogeology). Specific findings in FY2003 are summarized below.

Chapter 2

Among the several thousand soil and groundwater samples collected at MMR (Camp Edwards) since the last update (Pennington et al. 2003), no new explosives compounds have been detected. Among the propellants, explosives, and pyrotechnics, the largest proportions observed in soils in decreasing order of frequency were TNT and the ADNTs followed by "Other" (di-n-butyl phthalate, Nnitrosodiphenylamine, white phosphorous), perchlorate, DNTs, and RDX. Perchlorate predominated in groundwater followed by RDX, HMX, and ADNTs in decreasing order of frequency. As perchlorate emerged as a contaminant of concern, previously identified perchlorate plumes were mapped and two new perchlorate plumes, for which the sources are uncertain, were identified.

Chapter 3

The collection and analysis of numerous composite surface samples from different military training ranges established the presence of TNT, RDX, HMX, NG, 2ADNT, 4ADNT, and 2,4DNT on many types of ranges either at the firing position or the impact area. The measured concentrations can be used to predict dermal exposure, ingestion, and migration into surface and subsurface water systems. The concentrations of energetic residues determined on the two Hawaiian ranges were consistent with previous findings at other sites engaged in similar activities. Sampling and analysis protocols must take into account the fact that energetic material residues at both firing and detonation points typically exist as particles. To address the compositional and distributional heterogeneity common to particulate matter, the use of composite sampling strategies is recommended.

Processing of soil samples through a $# 30 (0.6$ -mm) sieve as currently recommended in EPA Method 8330 is not recommended because sieving to this size fraction prior to mechanical grinding removes compounds of interest and results in under-estimation of concentrations.

Chapter 4

Sampling of surface soils at Gagetown artillery, anti-armor, anti-tank, grenade, and small arms ranges identified specific energetic materials related to the various activities. Artillery impact areas exhibited RDX, TNT, amino-DNTs, but also NG and 2,4DNT from propellants. Analyses of surface soil samples from firing positions of anti-armor and anti-tank weapons yielded low to percent concentrations of NG and 2,4DNT from single- and double-based propellants. Impact points for these ranges had low concentrations of TNT and RDX. Firings of Octol-based M72 shoulder-launched anti-tank rockets generated residues of HMX in surface soils, and HMX and TNT at several inches of soil depth. At grenade ranges, residues of TNT, TNT derivatives, and RDX predominated. Detections of NG and 2,4DNT on the grenade ranges may be the result of unknown past use of the area or of burning of unused propellants. In general, explosives residues were detected at lower concentrations on artillery ranges than on antiarmor or anti-tank rocket ranges. Detection of explosives on these Gagetown ranges was typical of similar ranges investigated in Canada and the United States.

Sampling of surface soils for heavy metals was also conducted on Gagetown ranges. Results revealed concentrations of concern for cadmium, copper, lead, and zinc, especially at anti-armor and anti-tank ranges. Grenade ranges exhibited high concentrations of zinc, while small arms ranges exhibited high concentrations of copper and lead (lead up to 0.4 percent by weight). Concentrations of molybdenum, antimony, strontium, and chromium also exceeded background concentrations. Vegetation also exhibited significant concentrations of cadmium, lead, and zinc. Bioaccumulation of these metals is problematic because high concentrations of salts of sodium, calcium, and potassium exist concurrently with the heavy metals. Grazing animals are then specifically attracted to the high salt content and preferentially feed on the contaminated vegetation. Typically, concentrations of heavy metals in the vegetation correlated with concentrations observed in the soils. A pattern of mixed organic/inorganic contamination by explosives and heavy metals was observed on grenade and antitank ranges.

Chapter 5

Results of explosives analyses of surface soil samples on the Cold Lake Air Weapons Range illustrate the difference between residues from artillery ranges and those from air-to-ground ranges. Explosives residue concentrations at the Cold Lake ranges, where only practice bombs are dropped, were significantly lower than concentrations typical of artillery ranges. Of the four ranges sampled, only Shaver range is used for training with HE-containing munitions. This range exhibited high concentrations of explosives residue, predominantly TNT (up to 400 ppm). Other ranges exhibited low concentrations of TNT, RDX, and HMX.

Concentrations tended to be localized around targets. Jimmy Lake range had significant concentrations of propellants, especially NG. Detections of heavy metals on the four ranges were also limited. Notable detections included cadmium, copper, and zinc. The low metals concentrations were attributed to range maintenance practices by which metals are removed on a regular basis. Concentrations of metal in the vegetation were usually higher than in the soil. Since cadmium was a significant detection in vegetation, additional sampling was planned for FY2004. Explosives, propellants, and metals were not detected in the surface water of the lakes.

Chapter 6

Results of residue collection on snow following detonations of artillery projectiles, mortars, and hand grenades demonstrated that high-order detonations consume an average of 99.997 percent of the HE. The unconsumed residue is assumed to occur as fine particles that would result in very low concentrations spread over a large area. These results are consistent with results obtained by sampling ranges where these weapons have been fired repeatedly. The contribution of explosives residues from high-order detonations during live-fire training is concluded to be insignificant. Low-order detonations and blow-in-place demolition are more likely sources of significant residues of high explosives.

Chapter 7

Detonation of unconfined charges represents a worst case scenario by generating greater residues than result when charges are confined by a metal shell case. When explosives are unconfined, detonation pressure is greatly reduced so that detonation is less efficient, and a greater quantity of residues is anticipated. This was demonstrated by detonation of explosives of various sizes and shapes. Results indicated that a relatively low percentage of explosives remained after detonation. Larger charges yielded smaller residues. Cylinders dispersed more TNT residue than other configurations of TNT; however, when the cylinder data were excluded, overall maximum dispersion of TNT was only 0.2 percent. Dispersion of residual RDX tended to exceed residues of the other explosives, especially when the RDX source was C4 blocks. Two insensitive munitions, PBX and XRT, yielded relatively high dispersion. Results of these studies demonstrate that even without the pressure of confinement, explosives residues from high-order detonations are minimal.

Chapter 8

Results of blow-in-place detonations of various munitions demonstrated that the main charge was not always efficiently consumed. For low-order detonations, more residues (up to a few percent) were recovered independently of the configuration tested. High-order detonations were characterized by less residue; the *maximum* values found were 1.0, 0.6, and 0.5 percent for TNT, RDX, and HMX, respectively. However, *typical* levels were less than 0.1 percent for TNT, RDX, and HMX. To ensure high-order detonations of 60- and 81-mm mortars, 150 g of C4 on the side of the casing is recommended. FIXOR and the commercial shaped charges of 16.5 g and 36 g could also be used. All of the configurations of hand grenade detonations produced high-order detonations. For the landmine (PMA-1A), 4 to 30 g of C4 in a lateral hole or the use of FIXOR led to high-order detonations.

Chapter 9

To understand and anticipate the environmental fate and transport of organic compounds such as explosives, fundamental parameters such as solubility, dissolution rate, adsorption, transformation, and irreversible soil binding must be determined. For many of the explosives encountered on ranges, these parameters are unknown. Therefore, emphasis was placed on filling such deficiencies with data based on laboratory determinations of these parameters. In FY2003 fate and transport process parameters were determined for nitrobenzene, perchlorate, nitroguanidine, diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite. Nitrobenzene is an impurity in TNT and a potential photodegradation product. Perchlorate, nitroguanidine, diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite are propellant components that have been detected on firing ranges.

The solubilities of diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite were limited, ranging from approximately 10 to 50 mg L^{-1} over a range in temperatures from 10 to 30 $^{\circ}$ C. Adsorption coefficients of all five compounds were typically less than 20 L Kg^{-1} , suggesting limited attenuation by sorption mechanisms in the soil. However, nitrobenzene and diphenylamine were degraded in surface soils, although not in aquifer soils, while *N*-nitrosodiphenylamine was degraded in the aquifer and one of the surface soils. These compounds are, therefore, subject to degradation in the environment. Nitroguanidine and ethyl centralite were not degraded in any of the tested soils and, consequently, are expected to persist in the environment. Perchlorate, which was tested under a wide range of pH and redox conditions, was recalcitrant to degradation under all conditions, even when fresh soil innoculum was added to the tests.

Conclusions

Pertinent conclusions of the various investigations conducted to date are as follows:

a. Munitions constituents emerging as the principal concern on impact areas of heavy artillery ranges include RDX, TNT, and HMX.

b. Significant contamination potential has been observed at firing points for heavy artillery, where the principal constituents of concern are NG, 2,4DNT, and perchlorate.

c. Energetic material residues at both impact and firing points tend to exist as solid particles having the composition of the munitions prior to firing. Therefore, the potential source contamination is highly distributed, highly heterogeneous in particle size, and often complex in chemical composition. Characterization of such residues requires careful consideration of these properties of the source and careful consideration of sample representativeness during collection and during processing and analyses.

d. Although various constituents present different characteristics, the most important fate and transport processes governing these residues tend to be dissolution and transformation rather than degradation or adsorption to soils. With the exception of TNT, which is often easily attenuated in the surface soils after transformation, explosives residues are slow to dissolve, but readily mobilized once in solution. Therefore, they present a concern for leaching to groundwater slowly over time.

e. Range management practices designed to minimize low-order detonations and UXO generation, remove large observable masses of residues and UXOs, and minimize contamination in blow-in-place disposal will promote control of contamination while maintaining active range use.

Results of this study provide a technical basis for development of rangespecific soil characterization approaches, process descriptors for fate and transport of constituent residues, and for assessing the exposure component of environmental risk assessments. The relationships emerging between various training activities and residues of energetics can form the basis for sound management of training ranges while maintaining environmental stewardship.

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14. ABSTRACT

The characteristics of constituent residues on training ranges, both chemical composition and aerial distribution, vary with the type of range activity and the specific munitions fired. Residues tend to be localized in highly distributed point sources in the vicinity of targets and fixed firing positions. Characterizing these sites requires careful consideration of soil sampling strategies based on site activities and will typically include multi-increment composite sampling. Special care must be taken in laboratory subsampling since residues occur as solid particles of various sizes that are highly heterogeneously dispersed in the soil. For the types of ranges studied, e.g., heavy artillery and hand grenade ranges, RDX is a significant contaminant of concern. TNT, which is typically restricted to surface soil, poses less threat to groundwater than RDX. At firing points, propellant residues can be significant.

High-order detonations, which constitute most of the explosions executed during training, generate undetectable to barely detectable, diffuse surface residuals; however, low-order detonations, the incidences of which are much lower than high-order detonations and which tend to be munitions-specific, are a potentially significant source of residues. Another issue with potential to generate significant residues is clearance of unexploded ordnance by blowing in place. Rendering safe does not always result in complete consumption of explosive charge. Therefore, care must be exercised to achieve complete detonations with secondary changes that do not contribute munitions constituents, especially RDX, to the soil.

Results of fate and transport studies indicate that initial release of energetics from compositions, such as Composition B, into soils tends to be locally very high, approaching temperature-dependent aqueous phase saturation, even though the compositions dissolve more slowly than the solubilities of the individual components would suggest. Furthermore, soil adsorption from solution phase, which is governed to some extent by soil properties, will not significantly limit transport. Therefore, RDX is readily transportable to groundwater. TNT transforms readily to mono-amino products, the transport of which is limited by covalent bonding of these transformation products to soils components.

Results of this study provide a technical basis for development of range-specific soil characterization approaches. Results also provide process descriptors for fate and transport of constituent residues and for assessing the exposure component of environmental risk assessments. The relationships emerging between various training activities and constituent residues provide a sound scientific basis for development of management practices for sustainment of training range activities while maintaining environmental stewardship.

15. SUBJECT TERMS

Detonation residues Dinitrotoluene Explosives HMX Partition coefficients Propellants

RDX Test ranges TNT Training ranges Transformation rates