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Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 1

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Interim report

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Preface

This report was prepared by the U.S. Army Engineer Research and Development Center (ERDC), and represents the collaboration of the ERDC Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, and the ERDC Environmental Laboratory (EL), Vicksburg, MS. The research was sponsored by the Strategic Environmental Research and Development Program, Arlington, VA, Mr. Bradley P. Smith, Executive Director, and Dr. Jeff Marqusee, Technical Director, under Compliance Project Number CP1155. The principal investigator was Dr. Judith C. Pennington, Research Biologist, Environmental Processes Branch (EPB), Environmental Processes and Engineering Division (EPED), EL. Co-principal investigators were Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch (ESB), CRREL, and Dr. James M. Brannon, Geochemist, EPB.

Range soil characterization and snow cover experiments reported in Chapter 2 were conducted by Dr. Jenkins, Ms. Marianne E. Walsh, Research Chemical Engineer, and Mr. Alan D. Hewitt, Research Physical Scientist, ESB; and Ms. Nancy Perron, Physical Sciences Technician, Snow and Ice Branch, CRREL, and Dr. Paul H. Miyares, CRREL. Assistance was received from MAJ Eric Wahlgren, CRREL, Fairbanks, AK; Mr. Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, NH; Mrs. Charolett A. Hayes, Staff Scientist, DynTel, Vicksburg, MS; Dr. Pennington; and Mr. Thomas E. Berry, Jr., Research Physical Sciences Technician, Environmental Systems Branch, Ecosystems Evaluation and Engineering Division, EL. This portion of the study could not have been conducted without the active support and assistance of Mr. Philip Crawford, Environmental Program Manager, and Mr. John Weller, Range Officer, Fort Lewis, WA. The authors also acknowledge SFC Thomas Boylan and SSG Metz Frattarelli, 707 Ordnance Disposal Company (EOD), for assisting in collection of soil samples at Fort Lewis and for identifying the munitions responsible for creating various craters within the artillery impact area. SSG Keith Baker, SGT Adam Bryant, and SGT Timothy Owens, 716th Ordnance Company, are acknowledged for assistance in collecting soil samples at Fort Richardson. Mr. Del Larson, Range Operations, Fort Lewis, is acknowledged for his support, especially in providing information on the usage of the hand grenade range. Mr. Mike Brown and Ms. Jessica Fox, Anteon Corporation, Fairfax, VA, are acknowledged for allowing the authors to assist and collect groundwater samples during one of their routine monitoring efforts at Fort Lewis. Ms. Virginia Lanoue, Range System Administrators Office, is acknowledged for assistance with firing records. COL Jacob McFerren and COL Luke Green were Garrison Commanders at Fort Lewis when these activities were conducted. Mrs. B. Lynn Escalon, Analytical Services, Inc., Huntsville, AL, is acknowledged for conducting the water analyses at EL.

Soil partitioning and explosives dissolution studies reported in Chapter 3 were conducted by Dr. Brannon with the assistance of LTC Jason Lynch and Dr. Joseph J. Delfino of the University of Florida and Mrs. Hayes.

This report was reviewed by Drs. Jeffery A. Steevens, Environmental Risk Assessment Branch, EPED, and Patrick N. Deliman, Water Quality and Contaminant Modeling Branch, EPED. Additional technical reviews of Chapter 2 were provided by Dr. C. L. Grant, Professor Emeritus, University of New Hampshire, Durham, NH, and Martin H. Stutz, U.S. Army Environmental Center, Aberdeen Proving Ground, MD. The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED; Dr. John W. Keeley, Acting Director, EL; Dr. J. C. Tatinclaux, Chief, ESB; and Dr. Barbara J. Sotirin, Director, CRREL.

At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL John W. Morris III, EN, was Commander and Executive Director.

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1 Introduction

Background

Testing and training ranges are essential to maintaining the readiness of the armed forces of the United States. Recently, concerns have arisen over potential environmental contamination from residues of energetic materials at impact ranges. The current state of knowledge concerning the nature and extent of contamination and the fate of residues of energetic materials is inadequate to ensure sound management of ranges as sustainable resources. The potential for environmental impacts, including contamination of drinking water supplies, mandates that the Department of Defense demonstrate responsible management of these facilities to continue testing and training activities.

Regulatory precedent

In January 2000, the U.S. Environmental Protection Agency (USEPA) Region I issued an Administrative Order for Response Action in the matter of “Training Range and Impact Area, Massachusetts Military Reservation” to the National Guard Bureau and the Massachusetts National Guard under authority of Section 1431(a) of the Safe Drinking Water Act, 42 U.S.C.§ 300i(a) (USEPA 2000a). 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 the contamination from past and present activities and sources at and emanating from the Massachusetts Military Reservation (MMR) Training Range and Impact Area.” This is an important precedent for suspension of military training due to environmental contamination of soils and groundwater.

The MMR is an 8,500-ha (21,000-acre) installation on Cape Cod, MA. The Training Ranges and Central Impact Area are approximately 5,700 ha (14,000 acres) located on the Camp Edwards portion of the installation. The Central Impact Area, approximately 810 ha (2,000 acres), has artillery and mortar targets and is surrounded by firing ranges, artillery and mortar positions, and training areas (AMEC Earth and Environment, Inc., 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, explosives-related compounds, pesticides, and other organic contaminants in soils, and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and some organics in groundwater, USEPA ordered the respondents to conduct feasibility studies at several MMR areas including the Central Impact Area (USEPA 2000a). The order also required rapid response actions for contaminated soils at several gun positions and target positions, and for contaminated sediments at a wetland site.

Previous range characterization investigations

Antitank ranges. Extensive range characterization research has been conducted by the Canadian Force Base, Valcartier, Quebec (Thiboutot et al. 1997, 1998, 2000; Ampleman et al. 2000; Dubé et al. 1999). Characterization of light antitank weapon (LAW) rocket ranges at Fort Ord, CA, and at Canadian Force Base Valcartier have also been studied by U.S. scientists (Jenkins et al. 1997, 1998). Results of chemical analyses at the LAW rocket sites indicated explosives residues deposited on the surface soils from high use of the rocket. The main charge in the LAW rockets is octol, which is composed of 60 percent HMX and 40 percent TNT. Accumulations of HMX near tank targets were as high as 1,640,000 $\mu g\ kg^{-1}$ in surface soils at Valcartier, and as high as 587,000 $\mu g\ kg^{-1}$ in surface soils at Fort Ord. However, TNT concentrations were only about 0.01 times that of HMX concentrations at both sites.

Thiboutot et al. (1998) sampled four antitank ranges in addition to the range at Valcartier, two at Western Area Training Center, Wainwright, Alberta, and two at Canadian Force Ammunition Depot, Dundurn, Quebec. Results were similar to those reported for Valcartier, i.e., relatively high levels of HMX in surface soils, but much lower levels of TNT. The highest concentration of HMX detected at these ranges was 3,700,000 $\mu g\ kg^{-1}$ at Range 13, Wainwright. HMX concentrations were much lower at the other ranges due to much lower usage.

Heavy artillery ranges. Thiboutot and Ampleman (2000) collected 87 composite soil samples at Canadian Force Training Range Tracadie, New Brunswick. The range had been used for artillery, gun, and mortar firing, and was heavily contaminated with unexploded ordnance (UXO). Nevertheless, no explosives residues were detected in soils by Standard Method 8330 analysis (USEPA 1994). Ampleman et al. (2000) collected soil samples at several ranges at Canadian Force Base Chilliwack, British Columbia. Soils associated with craters were sampled at the Slesse Range, and concrete, steel, and woodcuttings were sampled at another area. Low concentrations of TNT and RDX were found in both areas. Low levels of RDX and HMX were also found at the Vokes grenade range. However, visual observation at a propellant burning area at Canadian Force Ammunition Depot (CFAD) Rocky Point indicated that the site was littered with partially burned propellant grains. These propellant grains contain nitroglycerin, nitrocellulose, and/or nitroguanidine. The U.S. Army Center for Health Promotion and Preventative Medicine conducted a study at the artillery impact area at Camp Shelby, MS (U.S. Army Center for Health Protection and Preventative Medicine 1999). Analysis of surface soil samples collected in a grid pattern over a large area using Method 8330 (detection limits of about 250 µg kg^{-1}) indicated very little detectable residues of explosives-related contaminants.

Previous fate and transport studies

Important processes affecting environmental fate and transport of explosives include dissolution rate and soil adsorption and desorption. Studies to define dissolution of explosives have been confined to individual explosives compounds (Taylor and Rinkenbach 1923; Verschueren 1983; Spanggord et al. 1983; Hale, Stanford, and Taft 1979; Ro et al. 1996). These studies have limited applicability for dissolution of explosives residues on ranges because explosives are typically formulated with binders, waxes, stabilizer, and other compounds when they are added to munitions. Dissolution of these formulations is likely to proceed more slowly than anticipated on the basis of solubility of pure compound. Extensive studies have been conducted on these processes as listed in the following tabulation:

Fate and Transport Process	Study
Soil adsorption and desorption	Haderlein, Weissmahr, and Schwarzenbach 1996 Pennington and Patrick 1990 Ainsworth et al. 1993 Xue, Iskandar, and Selim 1995 Comfort et al. 1995 Leggett 1985 Selim and Iskandar 1994 Myers et al. 1998 Price, Brannon, and Yost 1998 Brannon, Price, and Hayes 1997
Transformation	McCormick, Feeherry, and Levinson 1976 Kaplan and Kaplan 1982 Townsend, Myers, and Adrian 1995 Price, Brannon, and Hayes 1997 Comfort et al. 1995 Selim, Xue, and Iskandar 1995 Xue, Iskandar, and Selim 1995 Haderlein, Weissmahr, and Schwarzenbach 1996 Myers et al. 1998 Riefler and Smets 2000
Degradation	McCormick, Feeherry, and Levinson 1976 McCormick, Cornell, and Kaplan 1981, 1985 Lewis et al. 1996 Funk et al. 1993 Crawford 1995 Pennington et al. 2001 Regan and Crawford 1994 Coleman, Nelson, and Duxbury 1998 Kaplan 1993 Hawari et al. 2000 Spanggord et al. 1983
Chemical reactions with soil components	Kaplan and Kaplan 1982 Caton et al. 1994 Pennington et al. 1995a, 1997, 1998 Thorne and Leggett 1997 Thorn 1997 Haderlein, Weissmahr, and Schwarzenbach 1996

These studies have focused on the principal high explosives contamination typically resulting from manufacturing and from loading, assembling, and packaging of explosives into casings. The primary difference between fate and transport of explosives residues on ranges and contamination associated with loading, assembling, and packaging facilities is the integrity of the delivery system, the transport of explosives from the munitions, and the environment (aquatic, terrestrial, wetland) in which the delivery system comes to rest. Instead of solubilized explosives concentrated in lagoons and washout areas as has been observed at loading, assembling, and packaging facilities, firing ranges present more diffuse sources that are less readily characterized. In addition to contaminated soil, explosives are also present in munitions at various states of integrity (solid formulations) that may completely or partially confine the explosives. Since fate and transport processes have not been studied in the context of range contamination, data for process descriptors are incomplete or lacking for some relevant explosives compounds, propellants, and detonation by-products.

Related Ongoing and Leveraged Studies

Range characterization

The Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, U.S. Army Engineer Research and Development Center (ERDC), has an agreement with the U. S. Army Alaska Public Works to conduct site investigations at four firing ranges: Range Alpha and Stuart Creek at Fort Wainwright and Washington and Delta Creek Ranges at Fort Greeley. These site investigations will be leveraged to provide additional data on concentrations of explosives residues in surface soils due to training range activities.

Fate and transport studies

Two studies are currently under execution at the Environmental Laboratory, Vicksburg, MS, ERDC, concerning fate and transport processes for explosives. The studies are funded under the Installation Restoration Research Program of the Army Environmental Quality Technology Program. One work unit, A835/301X/UX001, “Characterization and Mobilization of Unexploded Ordnance,” is quantifying chemical signatures emanating from UXO under various environmental and geophysical conditions. The purpose of the study is to provide the technical basis for chemical sensor development, for discrimination between UXO and innocuous clutter, and for refinement in classification of detected UXO. The other work unit, A835/309E/RE004, “Fate and Transport of Explosives Contaminants,” is developing screening level and comprehensive fate and transport models and process descriptors for UXO in soil, aquifer, and aquatic environments for use in the exposure phase of risk assessments. These work units are concerned with explosives 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 this project to ensure a comprehensive and unified database. Approximately 10 percent of the funds for defining fate and transport parameters will be contributed by the Strategic Environmental Research and Development Program.

Scope of Project

This project was designed to develop techniques for assessing the potential for environmental contamination from energetic materials on testing and training ranges. Techniques will be 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 offsite transport in surface runoff or as a component of airborne dust, are also important, but are beyond the scope of the project.

The study will be executed in the following two parts: range characterization and fate and transport parameters for explosives residues. To characterize ranges, heavy artillery impact and firing points and hand grenade ranges will be sampled. Where possible, groundwater associated with the ranges will also be sampled. Chemical residues from live fire or demolitions of specific rounds will be assessed by detonations on snow cover. To fill data gaps in transport parameters, such as dissolution kinetics and partitioning coefficients, laboratory scale batch tests will be conducted.

Objectives

The primary objective of the study is to provide the Department of Defense 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 management decision making, minimize environmental impacts of testing and training, and contribute to continued operation of ranges.

Specific objectives include the following:

a. Provide a unified database system that will include (1) a listing of the energetic materials used in current and past munitions systems that are known or expected to be present in UXO items on testing and training ranges and whose use may have resulted in diffuse low-level contamination of soils, and (2) a specific protocol that can be used to determine the nature and extent of surface soil contamination around impact areas to include the sampling strategy and analytical methods best suited to this application.

b. 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. Provide new data for the relevant environmental processes controlling the fate and transport of residues of high explosives on ranges.

2 Characterization of Explosives Contamination at Military Firing Ranges

Introduction

Background

Little information is currently available on explosives residues in soils at artillery or bombing ranges. Soil contaminants at MMR include the following explosives (highest concentration in ppm): RDX (43), HMX (10), TNT (2.1), 2,4-dinitrotoluene (2,4DNT) (18), 2,6DNT (0.96), nitroglycerin (130), 2-amino-4,6-dinitrotoluene (2ADNT) (0.8), 4-amino-2,6-dinitrotoluene (4ADNT) (0.4) (USEPA 2000a). The source of such explosives contamination potentially arises from artillery firing, explosives disposed of by burial, or residues where explosives were burned.

Some data from the MMR and results of a study conducted by the Army Environmental Hygiene Agency at Aberdeen Proving Ground, MD (Phillips and Bouwkamp 1994), have addressed the levels of propellant residues from firing activities near gun positions. Analysis of several soil samples collected near firing positions at MMR showed residues of 2,4DNT (as high as 17 ppm) as well as one of its manufacturing impurities, 2,6DNT (as high as 0.96 ppm), and nitroglycerin (as high as 130 ppm) (USEPA 2000a). Other contaminants in surface soils included *n*-nitrosodiphenylamine (0.93 ppm), pentachlorophenol (0.18 ppm), arsenic (0.17 ppm), and di-*n*-butyl phthalate (16 ppm). Results from Phillips and Bouwkamp (1994) indicated that 2,4DNT, nitroglycerin, HMX, RDX, dibutyl phthalate, nitrosodiphenylamine, and several polyaromatic hydrocarbons were present in surface soils in the immediate vicinity of weapons firing positions. While propellant residues can be an isolated issue at firing ranges, the rate of migration of the components of these formulations in the surface soils will be very slow compared with the rate of migration of several common components of military high explosives, particularly HMX, RDX and ammonium picrate. Therefore, the possibility of groundwater contamination from propellants may not be a significant compliance issue associated with ranges.

Objectives

The objective of this portion of the study was to assess the potential for contamination of groundwater with explosives-related contaminants on military training ranges. Specific objectives include development of a protocol that can be used to determine the nature and extent of surface soil contamination around impact areas. This protocol will include the sampling strategy and analytical methods best suited to this application. Data generated with this protocol can be used to estimate a source term for post-blast residues based upon the extent of surface soil contamination at a specific site. To address these objectives, the composition and extent of post-blast residue accumulation on two different types of firing ranges, heavy artillery and hand grenade, were determined during the first year of the project. Ranges were sampled at Fort Lewis, WA, and at Fort Richardson, AK.

Fort Lewis, WA

Location

Fort Lewis is located approximately 16 km (10 miles) east of Olympia, WA, and adjacent to McChord Air Force Base (Figure 1). Fort Lewis, part of Forces Command, is the home of First Corps, one of 15 U.S. power projection platforms. The Corps' primary focus is Pacific Rim. Fort Lewis includes 115 live fire ranges and encompasses 34,803 ha (86,000 acres).

Approach

Surface soils were sampled at three functional areas: a hand grenade range impact area, a firing point for heavy artillery, and an artillery impact area. Groundwater was sampled from monitoring wells and seepage areas around the periphery of the heavy artillery range. Historical firing records from an electronic database were reviewed to determine the kinds of munitions that have been fired on the heavy artillery range over time.

Hand grenade range

The hand grenade range is divided into four launching and impact areas separated by concrete and wooden walls. The range has been actively used for at least 30 years.[1] Currently, about 95 percent of the detonations on this range are M67 fragmentation grenades, which are widely used by the U.S. Army. The other 5 percent are manufactured in Canada and Britain, and are used by Canadian and British troops who train regularly at Fort Lewis. The Canadian hand grenade is

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[1] Personal Communication, Mr. Del Larson, Range Operations Specialist, Fort Lewis, WA, 2000.

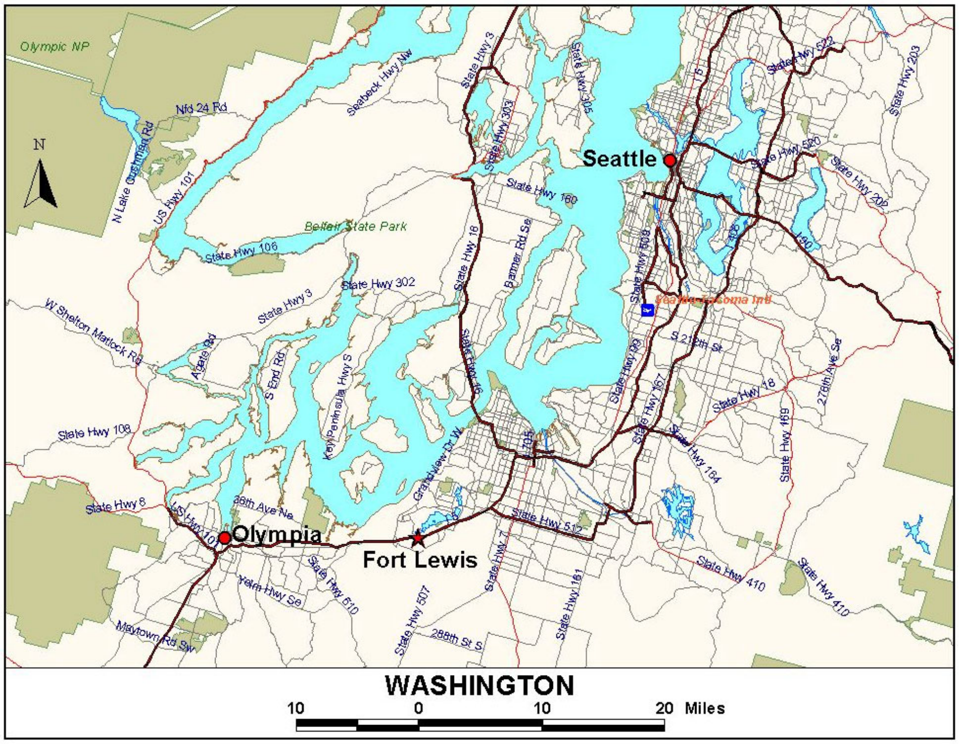

Figure 1. Location of Fort Lewis

model C7, but is manufactured to the same specification as the U.S. M67. The current British hand grenade is the Model L2, which is based on the older U.S. M26 hand grenade.

The M67 and C7 grenades contain 186 g of Composition B as the main charge. Composition B is composed of 60 percent military grade RDX and 39 percent military grade TNT. Military grade RDX generally contains HMX as a major impurity with concentrations of HMX ranging from 8 to 12 percent (U.S. Army 1984). Military grade TNT is about 99 percent 2,4,6TNT with the remainder made up of other isomers of TNT, the various isomers of dinitrotoluene (2,4DNT being the most abundant), 1,3-dinitrobenzene, and 1,3,5-trinitrobenzene (TNB) (Leggett, Jenkins, and Murrmann 1977; George et al. 1999). Thus, each grenade contains about 100.4 g of RDX, 11.2 g of HMX, and 71.8 g of TNT in the main charge. The detonator in the M67 also contains 1.3 g of RDX; thus, each grenade contains a total of about 101.7 g of RDX, 11.2 g of HMX, 72.5 g of 2,4,6TNT, with less than a gram of 2,4DNT, TNB, and other impurities. The M26 grenade contains about 84.2 g of RDX, 9.4 g of HMX, 60.1 g of TNT, and 0.6 g of 2,4DNT and other impurities.

The soil in the grenade impact area is coarse gravelly sand with stones as large as 15 cm (Table 1). Grass sparsely covers areas not recently affected by range use. The four impact areas are consecutively numbered, and judging from the numbers of craters in each, have been used to a similar extent. Range 3, which was selected for extensive soil sampling, is approximately 11 m wide at the launch end (Figure 2). The sidewalls that enclose the impact area widen to

Table 1
Physical Characteristics of Fort Lewis Soils[1]

Sample Location	TOC[2] %	CEC[3] meq 100 g^{-1}	Total Fe[4] mg kg^{-1}	Total Inorganic N[5] mg kg^{-1}	pH	Particle Size Distribution, % Sand	Silt	Clay
Artillery range								
Firing point	11.3	47.4	1,530	1,530	5.6	63.2	17.5	19.3
Impact area	7.38	38.0	1,960	3,484	5.7	64.7	19.2	16.1
Hand grenade range								
Surface	0.26	6.8	3,030	175	6.8	82.3	7.8	9.9
Subsurface	0.12	6.8	2,010	151	7.0	84.6	4.5	10.9

[1] Values represent a single composite of samples from each location.
[2] Total organic carbon.
[3] Cation exchange capacity.
[4] Total iron.
[5] Total inorganic nitrogen.

Figure 2. Hand grenade range at Fort Lewis. Tape extends perpendicular from launch area. Note sample jars in rows perpendicular to tape at 15, 20, and 25 m from launching areas

approximately 25 m where they end some 25 m from the launch bunker. The presence of craters indicated that grenades had landed well beyond this 25-m distance. The range was heavily cratered indicating extensive use. Over the last 4 years explosives ordnance demolition (EOD) (detonation of duds and low-order detonations) used C-4 explosive (RDX). In prior years TNT was used.

Within Range 3, three lanes perpendicular to the launching bunker were laid out for soil sampling. These lanes were located at 15, 20, and 25 m from the launching area (Figures 2 and 3). At 15 m from the launch site, soil samples were collected at 6.2, 7.4, 8.8, 10.1, and 11.3 m from a reference wall that separated Range 2 from Range 3. At 20 m, samples were collected at 6.2, 7.8, 9.1, and 10.2 m from the reference wall in a similar manner. Also at 20 m, a set of seven surface samples was collected in a wheel pattern at 11.5 m from the wall. At 25 m, samples were collected at 6.3, 7.7, 8.6, 10.0,11.2, 12.0, and 13.4 m from the reference wall. At each sampling location a surface sample (0 to 1.0 cm) and a discrete depth sample (at 10 cm) were collected, except for the samples collected in the wheel pattern, where only surface samples were collected. All soil samples were collected using stainless steel trowels, which were carefully wiped with a clean paper towel, washed with acetone, and air dried between samples.

Figure 3. Launching area of hand grenade range at Fort Lewis

A deep (approximately 93-cm) crater was observed approximately 30 m from the launch bunker. Multiple impacts or EOD activity may have created the crater. The bottom of the crater appeared to be undisturbed native subsoil, its finer grain being much different from the overlying gravel. A surface sample was collected at the bottom of the crater and at 10-, 15-, 23-, and 30-cm depths below surface. The overlying soil was carefully removed to prevent contamination of lower levels. The samples taken from the bottom of this crater were moist, whereas the surface samples were quite dry.

The most distant crater from the launch area, at approximately 45 m, was selected for sampling to represent the effect of minimal range use. One composite surface soil sample was collected from the rim of the crater, one surface sample at the bottom of the crater, and a discrete depth (10-cm) sample from the bottom of the crater. A total of 48 samples were collected within the Fort Lewis hand grenade range impact area.

During sampling of the grenade range, evidence of several low-order detonations was observed, where large portions of the grenade casings were intact. These grenade casings were collected and returned to the laboratory for explosives residue analysis.

Artillery range firing point

The day before and during the previous 6 weeks, National Guard units had been firing eight 105-mm howitzers at Fort Lewis Range R74. Approximately 600 rounds had been fired through each of the howitzers prior to soil sampling. The container in which the rounds had been stored was labeled as follows: (Comp B, C445, M2A2, M 103, Cart 105, HEM1, dual grain with supply charge without fuse for HOW[1]). The propellant used for these rounds was composed of 85 percent nitrocellulose, 9 percent DNT, 5 percent dibutyl phthalate, and 1 percent diphenylamine. The area in front of two of the howitzers, Gun 1 and Gun 2, was chosen for firing point sampling. Both guns were aimed approximately 200 deg true into the 91st Division Prairie Artillery Impact Area. The firing area was grass covered with various shrubs and low trees. Dirt access roads passed in front of the guns and were sampled when these were within the sampling scheme. All surface soil samples included the top 0.5 cm as well as the associated surface organic matter and shallow roots when present. One surface soil sample was collected approximately 400 m to the east from the nearest gun (Gun 1) to serve as an estimate of background contamination.

Gun 1. A measuring tape was laid out on the ground extending from the front of Gun 1 and in the direction of fire. Surface soil samples (about 10 cm^2) were collected using a putty knife along the measuring tape at the following distances from the muzzle: 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 and 10.0 m (Figure 4). Similar samples were collected perpendicular to the muzzle of the gun on both sides at 1.5 and 3.0 m. Surface soil samples were also collected 3.0 m on both sides perpendicular to the direction of fire at 5.0 m and 10.0 m. The final soil sampling, 2 m in front of the muzzle, took place as follows. A wheel-shaped 1.2-m-diameter sheet of plastic was placed on the ground. Six equally spaced surface soil samples were collected around the circle, and one surface soil sample was collected in the middle of the circle. Additionally, two depth samples, 0-5 cm and 5-9 cm, were collected in the center of the circle. This sampling scheme produced a total of 22 surface and 2 different depth soil samples at Gun 1 (Figure 4).

Gun 2. A measuring tape was laid out on the ground in front of Gun 2 and in the direction of fire. Surface soil samples were collected using a putty knife along the measuring tape at the following distances from the muzzle: 0.5, 1.0, 1.5, 2.0,

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[1] HOW probably indicates "howitzer."

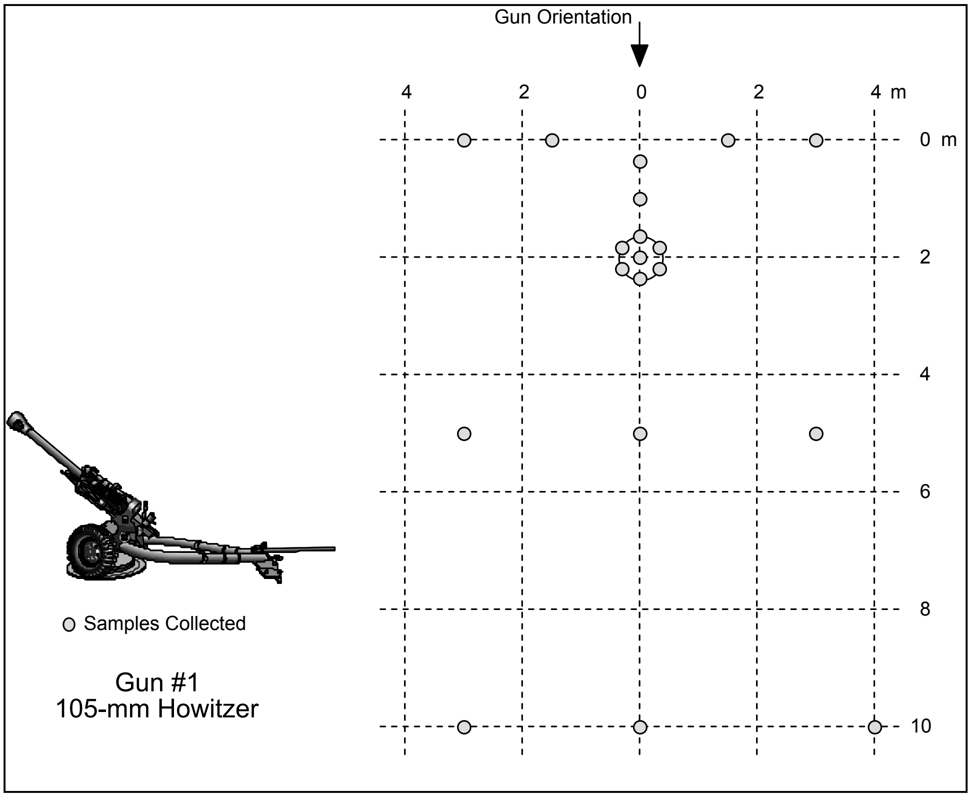

Figure 4. Template for sampling at Gun 1 firing point, Fort Lewis

2.5, 5.0, 10.0, 15.0, and 20.0 m (Figure 5). Surface soil samples were also collected perpendicular to the muzzle of the gun on both sides at distances of 1.5, 3.0, and 6.0 m. Surface soil samples were also collected 3.0 m perpendicular to the direction of fire on both sides at distances of 5.0, 10.0, 15.0, and 20.0 m from the muzzle. This sampling scheme produced a total of 23 soil samples at Gun 2 (Figure 5).

Artillery range impact area

The artillery impact area (91st Division Prairie) at Fort Lewis consists of approximately 3,800 ha. The portion of the impact range chosen for sampling was approximately 1 km in diameter and was centered at the approximate impact point for the 105-mm howitzers described earlier. Two EOD technicians from the 707 Ordnance Disposal Company at Fort Lewis assisted in matters of safety, in determining the type of round that had created specific craters, and in estimating the age of each crater. Soil from the impact area was characterized (Table 1). Vegetation consisted mainly of grasses and low shrubs and a few, widely scattered, small evergreen trees. Samples were collected throughout this area around various points of interest. The most recent craters were produced the day before sampling from the impact of the 105-mm howitzer rounds. Several mortar craters from variously sized rounds were considered recent, within the last

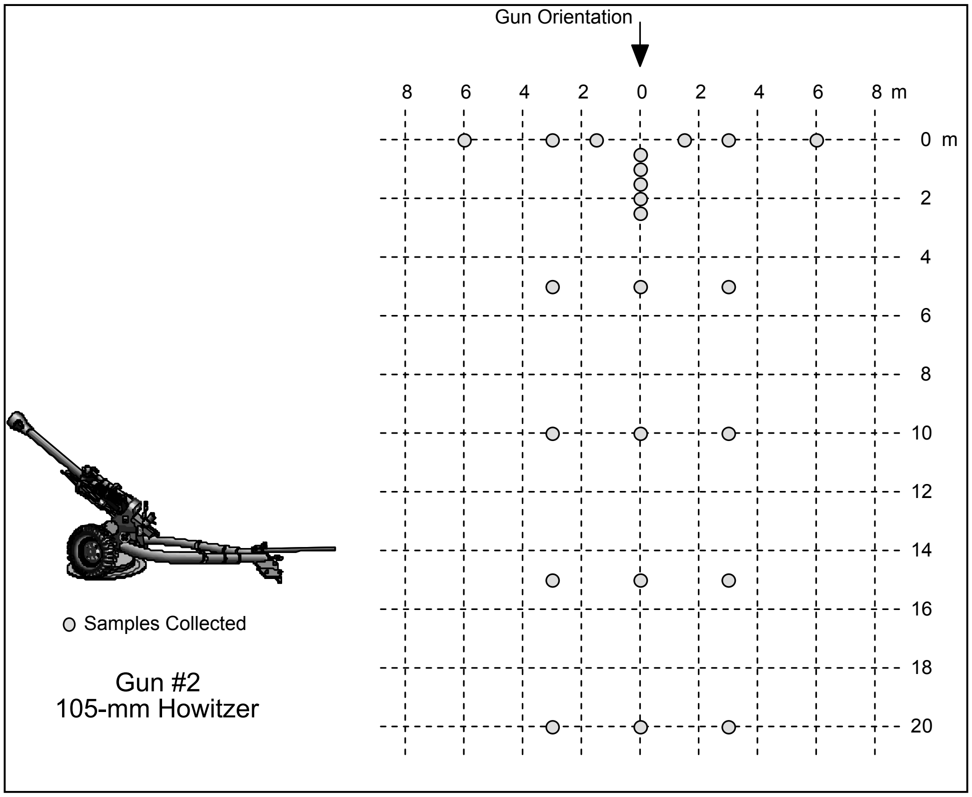

Figure 5. Template for sampling at Gun 2 firing point, Fort Lewis

month. Several older craters varying in age from months to years and produced by variously sized artillery and mortar impacts were also sampled.

The sampling of craters generally consisted of collecting surface soil randomly around the rim, around the inside sloping surface, and at the bottom. With the assistance of the EOD team, several soil samples were collected around and below a low-order detonation of a 155-mm artillery round. Three surface soil samples were collected around a low-order 120-mm mortar round. Several samples and the associated surface organic matter were collected in areas that were overgrown with vegetation and had no apparent disturbance within several meters. Numerous surface soil samples and some depth samples were collected as deemed appropriate. Five areas were sampled using the wheel sampling scheme described earlier. Some of these areas were centered over a crater and some were between craters. A total of 70 samples were collected within the artillery impact area.

Fort Richardson, AK

United States Army Garrison Alaska consists of the three posts of Fort Richardson (Anchorage), Fort Wainwright (Fairbanks), and Fort Greely (Delta Junction). Fort Richardson borders Anchorage, AK, to the west and north. The garrison headquarters is located at Fort Richardson, as is the headquarters of the United States Army Alaska (USARAK). The garrison supports rapid deployment of the 172nd Separate Infantry Brigade and elements of the Arctic Support Brigade within the Pacific theater, and worldwide as directed in support of Pacific Command's (USARPAC) objectives, U.S. national interests, and contingency operations. The fort encompasses 25,091 ha (62,000 acres), with 19,020 ha (47,000 acres) available for training. Military assets within that area include a heliport, a drop zone suitable for airborne and air-land operations, firing ranges, and other infantry training areas.

Sampling at Fort Richardson was limited to the hand grenade range that is located in the small arms complex near Glenn Highway. The grenade range is not divided into individual bays, but is a single open area with six launching bunkers and a large rubber tire 35 m downrange of each to serve as a target. The surface soil is mainly gravel. The top surface of the soil was frozen (20 October), but the soil just beneath the surface was thawed at the time of collection. The area between targets 1 and 2 was selected for sampling. No clues to the intensity of use of each area were visible, since surface craters are filled in with gravel after each exercise. However, the protocol for use of the range suggested that the six areas were equally used.

At one sampling point a set of four soil samples was collected 27 m from a line connecting the pits, or the launching points, and at depths of surface, 15, 30, and 45 cm (Figure 6). A second set of four samples was taken at the same depths and 27 m from the launch line, but 1 m to the left of the first set. Additional sets of four samples were collected in an identical manner at distances of 30, 32 and 33 m from the launch line. A set of 15 surface soil samples 1 m apart was collected at 35 m on the line between the two target tires (Figure 6). A seven-sample wheel of surface soil samples, like that described for samples at Fort Lewis, was centered at the 35-m line, 10 m left of tire 2 (Figure 6). At the center of the wheel, three samples were collected at depths of 15, 30 and 45 cm. A total of 48 soil samples were collected at the Fort Richardson grenade range. Samples were collected using shovels because of the gravelly consistency of the surface soil.

Methods

Soil sampling and analysis

Shovels used for sampling at Fort Richardson were carefully wiped with clean towels, washed with acetone, and air-dried between samples. Samples were placed into precleaned, straight-walled jars. Each jar was sealed in a zip-lock bag before shipping to the laboratory in ice-filled coolers (Federal Express, overnight). Upon arrival at CRREL the samples were frozen at -30 °C, and extracted and analyzed within 2 weeks.

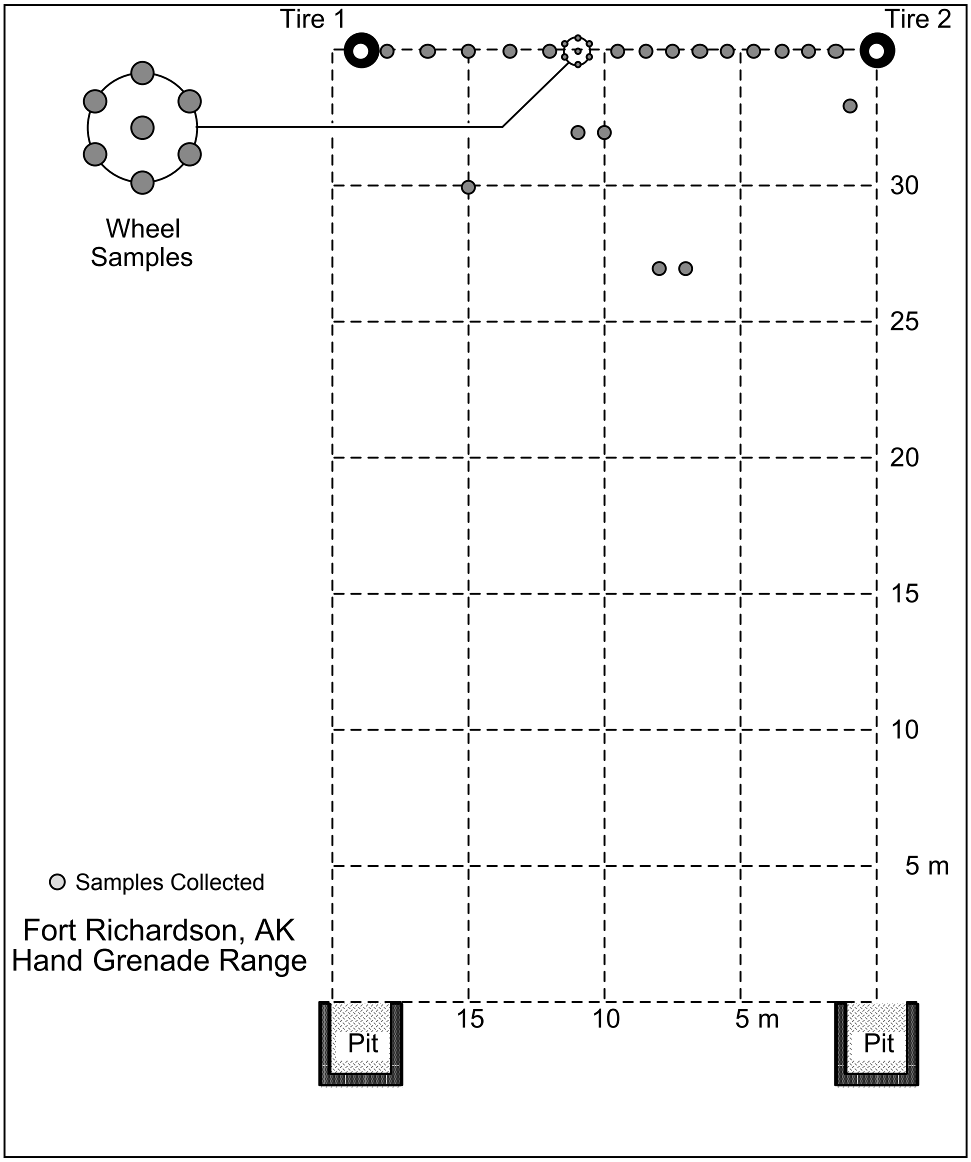

Figure 6. Template for sampling hand grenade ranges at Fort Richardson

Prior to extraction, soil samples were allowed to thaw at room temperature, and homogenized thoroughly using a spatula. The samples sometimes consisted of soil only, but typically contained both soil and organic matter. A 2.00-g portion of undried sample was placed into a 22-mL scintillation vial. A 5.00- or 10.0-mL aliquot of acetonitrile (AcN) was added, depending of the amount of organic matter present. The vials were placed on a vortex mixer for 30 sec to suspend the soil particles, and into an ultrasonic bath for 18 hr. The temperature of the bath was maintained at less than 25 °C with cooling water. The vials were removed from the bath and allowed to stand undisturbed for 30 min. A 2.5-mL aliquot of each extract was removed using a glass syringe and filtered through a 25-mm Millex-FH (0.45-µm) disposable filter, discarding the first mL and collecting the remainder in a clean auto sampler vial. The extracts were kept cold prior to and during analysis.

The vials containing the extracts were placed into gas chromatography (GC) auto sampler trays that were continuously refrigerated by circulating 0 °C glycol/ water through the trays. Extracts were analyzed by GC using a microelectron capture detector (GC-ECD). Results were obtained on a Hewlett-Packard 6890 GC equipped with a microcell ^{63}Ni detector at 280 °C according to the general procedure outlined in USEPA SW-846 Method 8095 (USEPA 1999). Direct injection of 1 µL of soil extract was made into a purged packed inlet port, at 250 °C, that was equipped with a deactivated Restek Uniliner (Restek, Belleforte, PA). Primary analysis was conducted on a 6-m × 0.32-mm-ID fused silica column, with a 1.5-µm film thickness of 5 percent (phenyl)-methylsiloxane (RTX-5 from Restek). The GC oven was temperature programmed as follows: 100 °C for 2 min, 10 °C min^{-1}, ramp to 260 °C, 2-min hold. The carrier gas was helium at 10 mL min^{-1} (linear velocity of approximately 90 cm sec^{-1}). The ECD makeup gas was nitrogen flowing at 40 mL min^{-1}. If a peak was observed in the retention window for a specific signature compound, the extract was reanalyzed on a confirmation column, 6 m × 0.53 mm ID having 0.1-µm film thickness of 50 percent cyanopropylmethyl–50 percent phenylmethyl-polysiloxane (RTX-225 from Restek). Further details of the procedure may be found in SW-846 Method 8095 (USEPA 1999). If analyte concentrations were within the linear range of the ECD, concentrations were reported from the determination on the primary column, unless coelution with another compound was apparent. In such cases, concentrations were reported from the determination of the confirmation column. Detection limits for the GC-ECD analysis were about 1 µg kg^{-1} for dinitro and trinitro aromatics, and 3 µg kg^{-1} for RDX (Table 2).

Extracts were also analyzed by reverse phase-high-performance liquid chromatography (RP-HPLC) according to SW-846 Method 8330 (USEPA 1994). When concentrations were above 500 µg kg^{-1}, the reported concentrations were taken from the HPLC analysis, which had a higher range of linearity. The response of the GC-ECD was inadequate for the reduction products of 2,4DNT (4-amino-2-nitrotoluene (4A2NT) and 2-amino-4-nitrotoluene (2A4NT)). Data reported for these analytes were obtained by RP-HPLC. RP-HPLC analysis was conducted on a modular system composed of a Spectra-Physics Model SP8800 ternary HPLC pump, a Spectra-Physics Spectra 100 variable-wavelength ultraviolet (UV) detector set at 254 nm (cell path 1 cm), a Dynatech Model LC241 auto sampler equipped with a Rheodyne Model 7125 sample loop injector, and a Hewlett-Packard 3393A digital integrator set to measure peak heights. Extracts were diluted with reagent grade water (one part extract and four parts water). Separations were conducted on a 15-cm × 3.9-mm NovaPak C-8 column (Waters Chromatography Division, Milford, MA) eluted with 85/15 water/isopropanol (v/v) at 1.4 mL min^{-1}. Samples were introduced by overfilling a 100-µL sampling loop. Concentrations were estimated against standard analytical reference material (SARM) multianalyte standards from peak heights. Detection limits for 4A2NT, 2A4NT, and 3,5-dinitroaniline (3,5DNA) were about 250 µg kg^{-1}.

Table 2
Method Detection Limits of Nitroaromatics, Nitramines, and Nitrate Esters in Soil Determined by GC-ECD (Walsh and Ranney 1999)

Analyte	Limits, μg kg-1
1,3-Dinitrobenzene	0.8
2,6-Dinitrotoluene	0.8
2,4-Dinitrotoluene	0.8
1,3,5-Trinitrobenzene	3
2,4,6-Trinitrotoluene	1
RDX	3
4-Amino-2,6-dinitrotoluene	1.5
2-Amino-2,4-dinitrotoluene	2.5
Tetryl	20
HMX	25
3,5-Dinitroaniline	2
Nitroglycerin	20
PETN	25
o-Nitrotoluene	15
m-Nitrotoluene	12
p-Nitrotoluene	10

Analysis of fragments from low-order hand grenade detonation

A casing from a low-order detonation of a hand grenade was recovered at the Fort Lewis hand grenade range. Residual Composition B, the main charge for M67 grenades, was evident on the surface of the metal casing. Small portions of the hand grenade case were placed into 5.0 mL acetone and allowed to dissolve for 5 min, after which time an aliquot was removed for analysis. After an additional 15 min of soaking, a second aliquot was removed for analysis. Both acetone extracts were diluted 1:100 with 25 percent acetone and 75 percent acetonitrile. The resulting solutions were analyzed using the separations described in SW-846 Method 8330 (USEPA 1994).

Sampling and analysis of water samples from monitoring wells and seeps

Water samples were collected from five groundwater monitoring wells (MW01 through MW04 and MW07) and five seeps (A1ASPO1 through A1ASPO5) (Figure 7). The wells were sampled by micropurge (low-flow) techniques using a low-flow pump. Groundwater was discharged via Teflon-lined

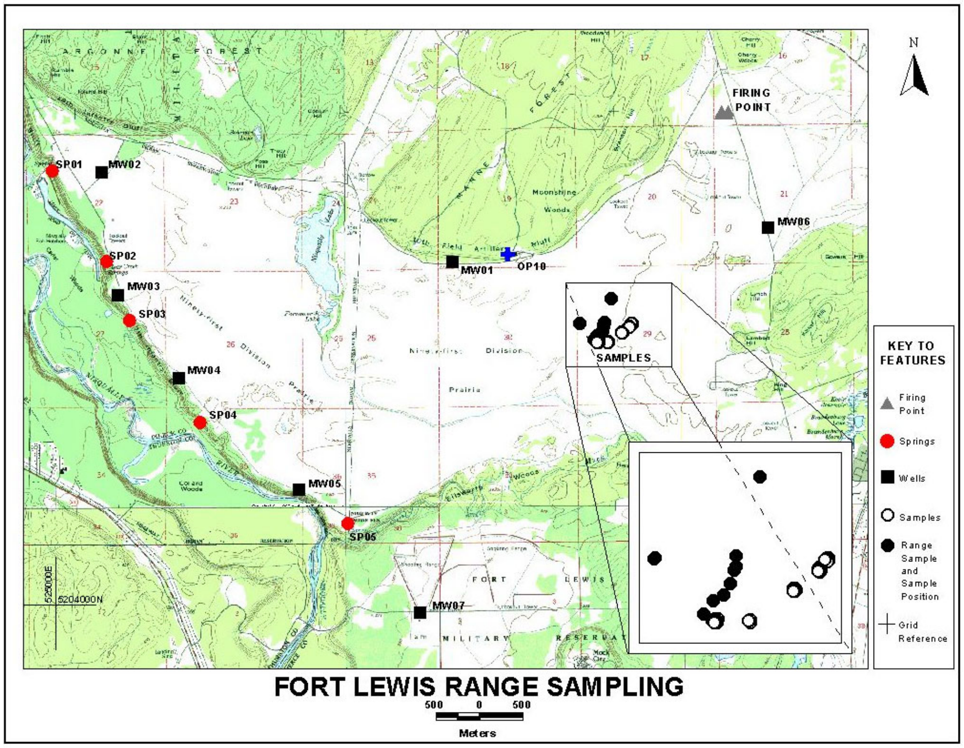

Figure 7. Sampling locations on the heavy artillery range at Fort Lewis. Locations with solid circles were determined by global positioning system

tubing. Tubing was dedicated to each well to prevent contaminant carry-over from one well to the next. The sampling pump was decontaminated between wells by purging with a mild detergent and clean water. Samples were collected in a single 4-L brown glass bottle, thoroughly mixed, and subdivided into separate bottles already containing appropriate preservatives for the specific analyses (analytical chemistry described in the following paragraphs). The collection bottle was rinsed three times with deionized water between samplings. The subsamples were distributed as follows: two 1-L samples for explosives; a 500-mL sample for nitrate/nitrite, total organic carbon, total iron, calcium, magnesium and manganese; and a 100-mL sample for sulfate and chloride. Seepage areas were sampled by placing the sample container into the stream of discharge. Field parameters were measured with a hand-held monitoring unit (Horiba U10, Horiba Instruments, Irvine, CA). Field parameters included pH, conductivity, dissolved oxygen (DO), and temperature. Samples were obtained when consecutive DO readings were within 10 percent of each other. The samples were split by Environmental Laboratory (EL) personnel, one aliquot of each sample going to the contractor, Anteon Corporation, Fairfax, VA, and the second going to CRREL. Three of the samples were also split and sent to the EL analytical chemistry laboratory. Samples for explosives were preserved with 1.2 g of $NaHSO_4$ to 1 L water (Jenkins et al. 1995).

At CRREL the water samples for explosives analyses were extracted using solid-phase extraction as described in SW-846 Method 3535A (USEPA 2000b). Specifically, 500 mL of each sample was passed through a 500-mg Sep-Pak

Porapak RDX cartridge (Waters), and the retained analytes were eluted using 5.0 mL of acetonitrile. The extracts were analyzed by GC-ECD as described in the section “Soil sampling and analysis.” At EL the water samples were extracted using solid-phase extraction as described previously. Analyses were conducted by RP-HLPC with a UV detector according to SW-846 Method 8330 (USEPA 1994) on a Waters system composed of a 610 Fluid Unit pump, a 717 plus auto sampler with a 200-µl loop injector, a 486 tunable UV absorbance detector monitored at 245 nm, and Millennium 2.1 chromatography software (Waters). Separations were obtained on a Supelco LC-18 RP-HPLC column 25 cm by 4.6 mm (5 µm) with second column confirmation on a Supelco LC-CN reverse phase column (25 cm by 4.6 mm, 5 µm). At the contract laboratory, the samples were also analyzed by RP-HPLC according to SW-846 Method 8330 (USEPA 1994). Laboratory analyses included the following, which are target analytes for Method 8330: HMX, RDX, TNB, 1,3-dinitrobenzene (DNB), tetryl, TNT, nitrobenzene (NB), 4ADNT, 2ADNT, 2,4DNT, 2,6DNT, o-nitrotoluene (2NT), m-nitrotoluene (3NT), and p-nitrotoluene (4NT). Additional transformation products of TNT and TNB assayed by the EL laboratory included DNA, 2,4-diamino-6-nitrotoluene (2,4DANT), 2,6-diamino-4-nitrotoluene (2,6DANT) and 2,2′,6,6′-tetranitro-4,4′-azoxytoluene (44′AZOXY). Additional transformation products of RDX assayed by the EL laboratory included 1,3,5-hexahydro-1-nitroso, 3,5-dinitrotriazine (MNX), 1,3,5-hexahydro, 1,3,5-trinitrosotriazine (TNX), and 1,3,5-hexahydo-1,3-dinitroso-5-nitrotriazine (DNX).

Laboratory analyses for geochemical parameters included total iron, calcium, magnesium, and manganese (Method 6010, USEPA 1988a), total organic carbon (Method 505C, American Public Health Association 1985), nitrate-nitrite nitrogen (Method 353.2, USEPA 1982), sulfate (Method 375.2, USEPA 1982), and chloride (Method 325.2, USEPA 1979). Samples for total iron, calcium, magnesium, manganese, total organic carbon, and nitrate-nitrite nitrogen were preserved with 0.4 g $NaHSO_4$ to 250 mL of water. Samples for sulfate and chloride were not preserved. Iron speciation was achieved by ion chromatographic separation (Dionex Corporation, Sunnyvale, CA) of samples preserved with 1 percent HCl followed by analysis according to Method 6020 (USEPA 1988a) on a Perkin Elmer (Norwalk, CT) inductively coupled plasma mass spectrometer.

Historical firing records

Historical firing records contained in an electronic database at Fort Lewis were reviewed to understand the major components potentially contributing to an explosives contamination source term on the heavy artillery impact range. These records were available from 1997 through the time of sampling, July 2000. Only munitions items identified by the Fort Lewis Range Operations Office as high use were included. These were 81-, 120-, and 107-mm mortars and 105- and 155-mm howitzers. The database provided the number of rounds by Department of Defense Identification Code (DODIC) number and date when and location where firing was scheduled to occur. Composition of these rounds was determined by consulting the Munitions Items Disposition Action System (MIDAS) and Picatinny Arsenal, NJ.[1] The dud and low-order detonation rates for these munitions were extracted from the data generated by the U.S. Army Defense Ammunition Center, McAlester, OK (Dauphin and Doyle 2000).

Results and Discussion

Hand grenade ranges, Fort Lewis and Fort Richardson

The results from the analysis of the soil samples collected from the Fort Lewis hand grenade range are presented in Table 3. Of the 19 target analytes of the method, RDX, TNT, HMX, 2,4DNT, 2ADNT, 4ADNT, 1,3,5TNB and 3,5DNA were found at concentrations exceeding 10 $\mu g\ kg^{-1}$ (10 parts per billion) in at least one sample. RDX, TNT and 4ADNT were detected in every sample analyzed from the grenade range. RDX, TNT and HMX were consistently found at the highest concentrations with maximum values of 51,200, 75,200, and 10,100 $\mu g\ kg^{-1}$, respectively. Diagrams showing the concentrations of RDX, TNT and HMX for these samples are shown in Figures 8, 9, and 10, respectively.

For the surface/10-cm-depth sample pairs, concentrations were consistently higher in surface samples than in samples collected at the 10-cm depth. In neither case were the values normally distributed. Therefore, for the following discussion, ranges and median values for each analyte rather than means and standard deviations will be used as listed in the following tabulation:

Analyte	Surface, $\mu g\ kg^{-1}$		10 cm, $\mu g\ kg^{-1}$	
	Range	Median	Range	Median
RDX	316 to 51,200	1,560	76 to 7,390	195
TNT	51.1 to 75,100	543	11.9 to 2,060	56.0
HMX	172 to 10,100	728	<1 to 1,540	53.4

The ratio of TNT to either 4ADNT or 2ADNT was generally higher at the surface than at the 10-cm depth, probably because the soil remained wetter at depth, thereby creating a condition more favorable to transformation. Detonations in the sandy soil in this range probably mix the soil profile to some extent. Therefore, one 10-cm-depth sample had concentrations of RDX and TNT of 7,390 and 2,060 $\mu g\ kg^{-1}$, respectively.

For the surface samples collected in the wheel pattern 11.5 m from the launching area, RDX concentrations ranged from 424 to 28,000 $\mu g\ kg^{-1}$. A chromatogram of the extract from the center sample of the wheel analyzed on the RTX-5 column is presented in Figure 11. Likewise, TNT concentrations ranged from 126 to 40,600 $\mu g\ kg^{-1}$, and HMX concentrations from 455 to 3,900 $\mu g\ kg^{-1}$.

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[1] Personal Communication, March 2000, Mr. Mark Serben, Office of the Product Manager for Mortar Systems, TACOM, Picatinny Arsenal, NJ.

Table 3
Explosives in Soils[1] from Fort Lewis Hand Grenade Range, µg kg^{-1}

	Location[2]										
Sample	From Reference m	Depth cm	RDX	HMX	TNT	2,4DNT	2,6DNT	4ADNT	2ADNT	1,3,5TNB	3,5DNA
15 m from Launch Point											
137	6.2		689	365	329	38.2	2.2	147	140.8	89.4	28.2
138	6.2	10	86	t[3]	128	22.5	<0.8[4]	150	274	<3	56.8
139	7.4		11900	1120	4230	16.9	2.2	180	163	<3	44.6
140	7.4	10	76	<25	33.9	7.5	<0.8	63.5	58.7	<3	18.0
141	8.8		990	172	79.9	18.7	1.7	95.2	91.3	55.2	20.2
142	8.8	10	235	<25	61.1	<d	<0.8	23.8	13.7	22.4	2.85
143	10.1		1730	1590	374	92.0	2.3	322	273	56.8	11.5
144	10.1	10	385	60.9	33.8	11.5	1.0	38.7	43.9	33.9	15.8
145	11.3		1640	813	51.1	13.7	2.4	146	128	50.4	23.3
146	11.3	10	369	77.8	263	5.5	1.7	75.6	83.4	16.0	24.3
20 m from Launch Point											
129	6.2		316	232	17700	18.1	1.6	74.1	51.5	<3	<2
130	6.2	10	107	<25	67.4	5.7	1.6	35.7	<2.5	<3	<2
131	7.8		1660	332	941	17.7	5.0	95.5	68.8	<3	<2
132	7.8	10	117	60.3	74.8	11.5	1.1	71.8	89.4	33.4	37.7
133	9.1		6230	294	75100	78.3	3.1	130	130	<3	34.5
134	9.1	10	97	66.0	42.0	8.1	0.8	28.1	37.6	25.4	7.2
135	10.2		503	239	264	30.6	1.7	149	167	98.0	24.1
136	10.2	10	202	49.7	21.0	7.1	<0.8	37.8	46.5	11.4	24.7
122	11.5 C[5]		1940	1210	293	19.2	3.1	94.1	23.3	<3	<2
123	A		424	455	126	16.6	3.0	80.3	60.8	<3	<2
124	B		28000	3900	40300	24.3	2.8	250	231	<3	<2
125	C		1260	625	40600	31.3	2.2	83.7	14.7	<3	<2
126	D		1100	761	379	32.0	2.8	111	88.0	<3	<2
127	E		1630	1030	333	9.4	2.0	66.6	55.5	<3	<2
128	F		1750	1170	4470	11.6	1.2	83.1	64.0	<3	<2
25 m from Launch Point											
147	6.3		1030	642	563	17.5	3.1	153	138	124	26.5
148	6.3	10	187	45.2	72.2	6.1	0.9	75.0	97.3	36.1	32.4
149	7.7		1050	436	1050	69.2	2.2	125	132	126	32.3
150	7.7	10	261	91.3	45.2	7.8	110	47.6	57.5	44.5	20.4
151	8.6		1380	2330	95.3	17.5	2.6	80.2	74.8	149	29.5
152	8.6	10	186	82.7	22.1	4.6	1.0	25.7	31.4	36.0	14.0
153	10		2530	1450	255	37.8	2.7	144	164	134	37.8
154	10	10	179	<25	11.9	5.2	1.8	29.6	31.6	15.4	15.0
155	11.2		27700	5810	10800	26.6	4.7	173	196	<3	16.7
156	11.2	10	7390	1540	2060	28.3	2.1	258	245	<3	19.6
157	12.0		51200	10100	15800	33.0	33.2	388	298	<3	67.5
158	12.0	10	864	57.1	29.9	3.9	1.5	26.0	35.5	<3	16.1
159	13.4		24700	5220	522	39.6	5.1	279	281	214	34.3
160	13.4	10	243	42.5	80.2	5.8	1.4	32.8	55.1	38.5	18.1
Deep 93-cm-diameter Crater 30 m from Launch Point											
161	Bottom surface		1690	329	153	10.1	1.6	96.3	98.0	69.6	9.2
162		10	684	230	120	10.1	<0.8	109	113	39.6	6.5
163		15	626	346	214	8.8	1.3	126	116	31.1	<2
164		23	775	197	197	10.1	1.6	111	115	38.5	<2
165		30	234	91.0	99.4	8.7	1.4	51.8	67.4	31.9	4.4
Approximately 45 m from Launch Point											
166	Crater c/B[6]		18.1	t	5.65	2.9	1.2	21.3	25.5	t	3.7
167	Crater R/cp[7]		70.5	t	5.63	<0.8	1.4	24.4	27.7	<3	5.0
168	Crater c[8]	10	25.0	t	5.58	1.5	<0.8	28.9	38.0	<3	3.7

[1] Values given are for surface soils except where noted. The following undetected analytes were excluded from the table: 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 1,3-dinitrobenzene, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

[2] Locations give distance from reference wall separating impact areas for each range and depth in cm if sample was not taken at the surface.

[3] Trace detected below mean detection limit.

[4] Less than detection limits.

[5] Wheel pattern of sampling, C = center of wheel; A-F clockwise around wheel circumference.

[6] Center, bottom of crater.

[7] Rim, composite.

[8] Center.

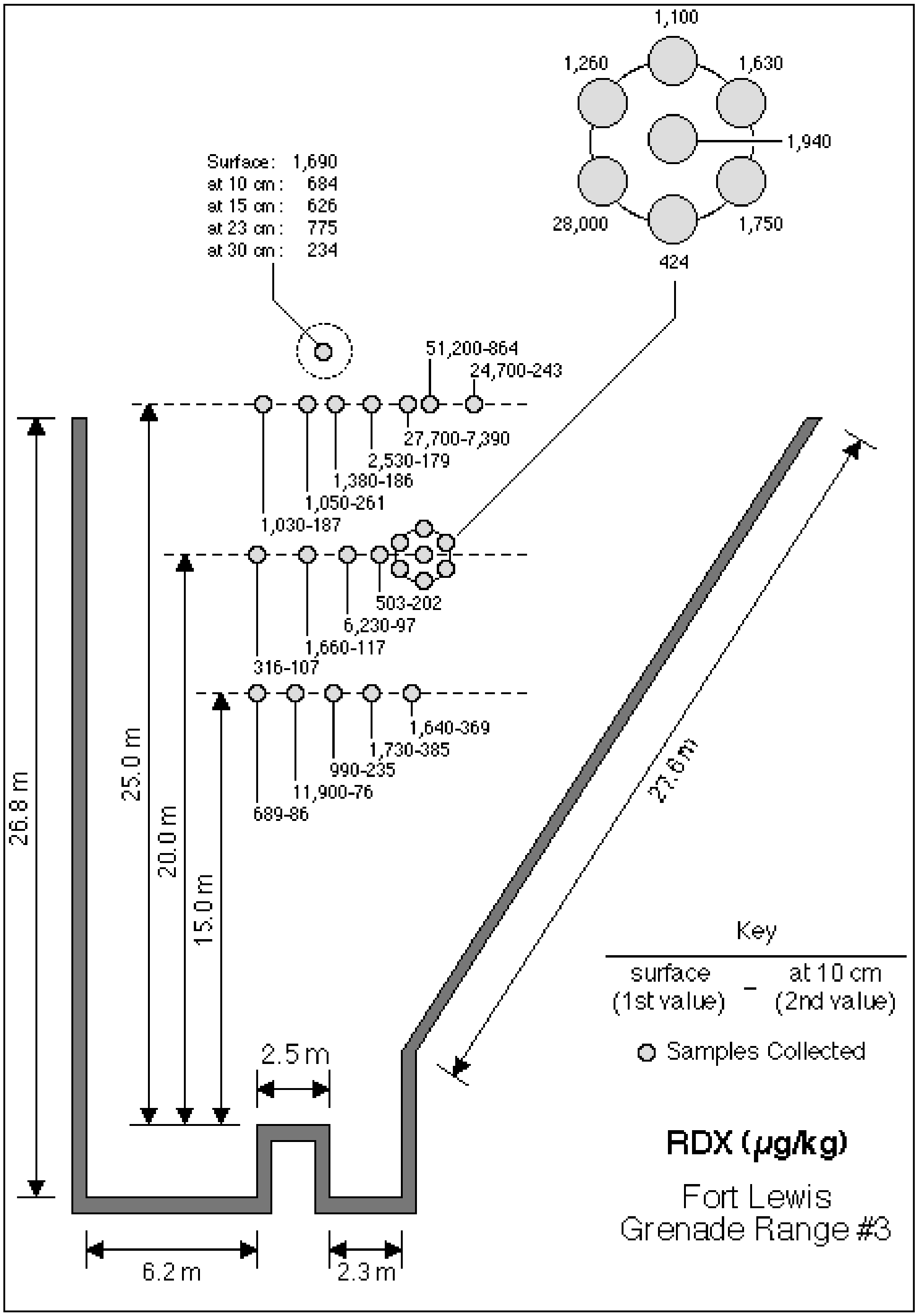

Figure 8. Distribution of RDX in surface soils at hand grenade range 3, Fort Lewis

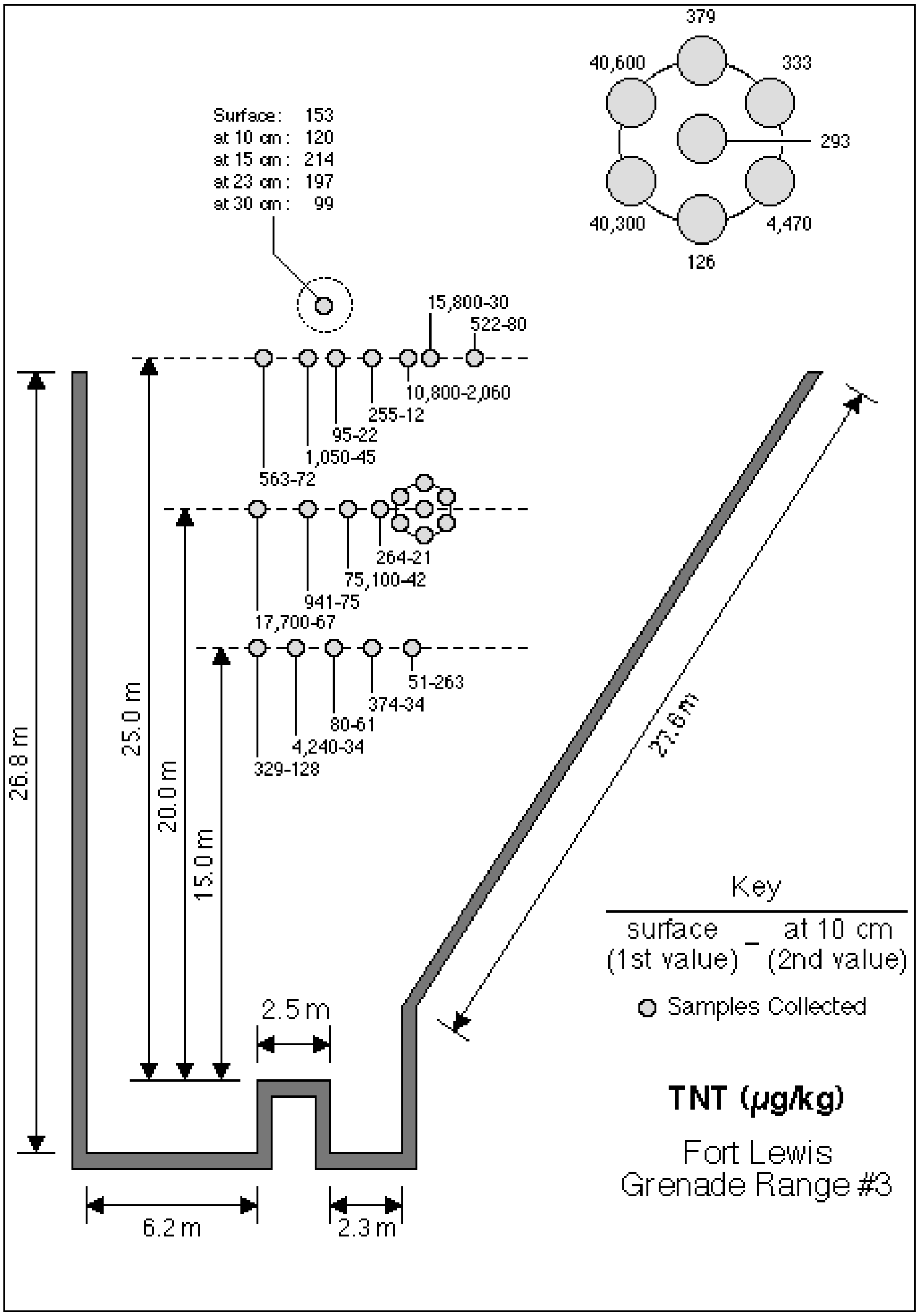

Figure 9. Distribution of TNT in surface soils at hand grenade range 3, Fort Lewis

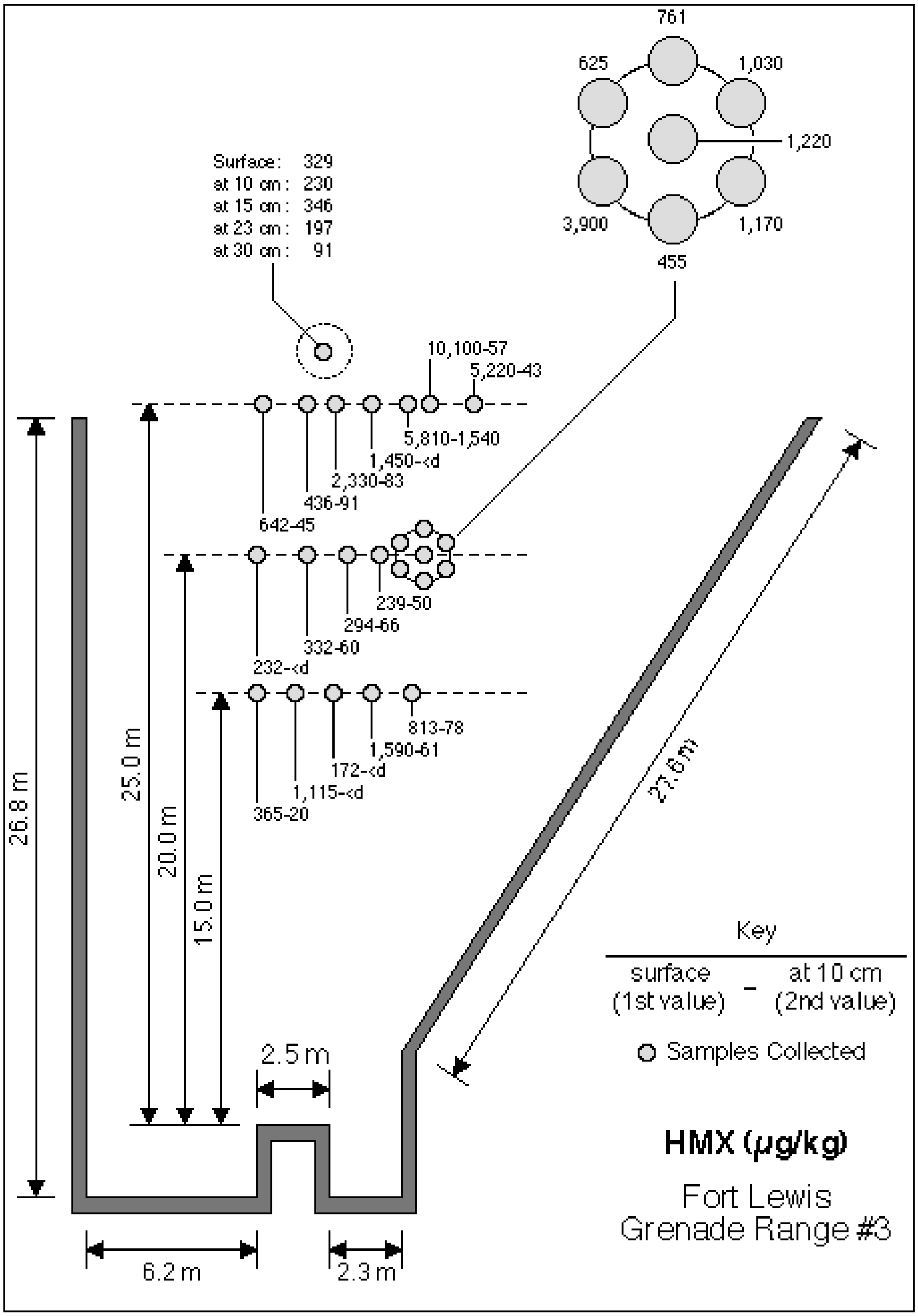

Figure 10. Distribution of HMX in surface soils at hand grenade range 3, Fort Lewis

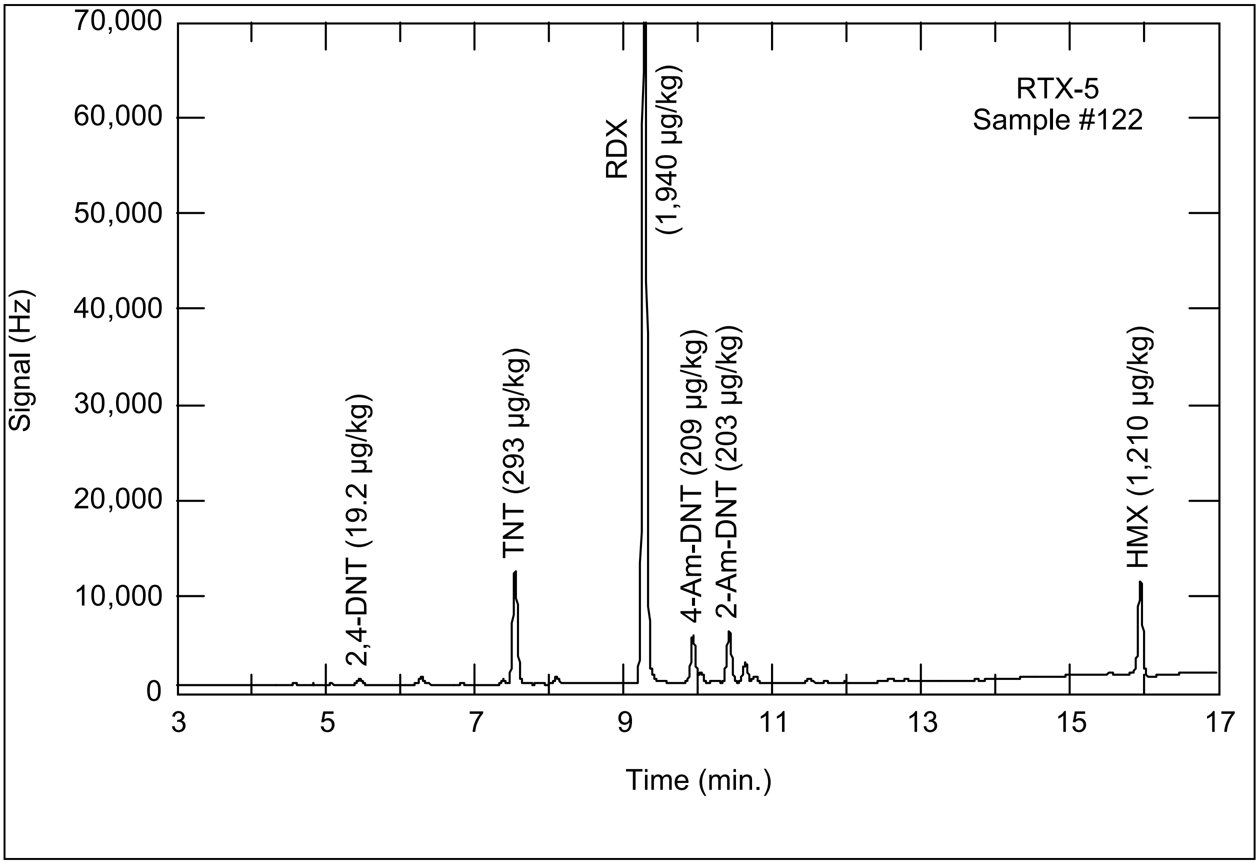

Figure 11. GC-ECD chromatogram of extract from surface soil collected from Fort Lewis hand grenade range

Therefore, as found elsewhere (Jenkins et al. 1997, 1998), explosives concentrations in surface soils are spatially very heterogeneous within this range, even over short distances. Obtaining representative samples for establishing a mean concentration using discrete soil samples would be difficult.

As stated previously, results from the analysis of a hand grenade casing remaining after a low-order detonation at Fort Lewis revealed the presence of residual Composition B. The ratio of RDX to HMX in the sample removed from the casing was 7.61. The ratios of RDX to HMX from analysis of individual soil samples varied tremendously, but the ratio obtained using the median values was 2.14 for the surface soil and 3.65 for soil collected at the 10-cm depth. These reduced ratios are interpreted to indicate that RDX has preferentially leached deeper into the soil profile because of a higher thermodynamic solubility and a faster rate of dissolution.[1]

Results from the analysis of soil samples from the Fort Richardson hand grenade range indicated detectable concentrations of RDX, TNT, 4ADNT, and 2ADNT in most surface soil samples (Table 4). Diagrams for RDX and TNT are presented in Figures 12 and 13, respectively. As found for the Fort Lewis range,

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[1] Personal Communication, 2000, Dr. Paul H. Miyares, Chemist, Micromass Corporation, Beverly, MA.

RDX was the explosives-related analyte found at highest concentration in the 27 surface soils, although the concentrations found at the Fort Richardson range were generally an order of magnitude lower than those found at Fort Lewis. The reason for this difference may be the practice at Fort Richardson of filling in the craters with clean gravel after each training session, or a lower usage of the range in terms of total grenades thrown than at the Fort Lewis range. Several RDX concentrations exceeded 100 $\mu g\ kg^{-1}$ at the Fort Richardson range, but most of the values were below 30 $\mu g\ kg^{-1}$, indicating that the distribution of these data was also nonnormal. Overall, RDX concentrations in the surface soil ranged from 1.7 to 518 $\mu g\ kg^{-1}$ with a median value of 28.9 $\mu g\ kg^{-1}$.

RDX was detected in all of the 21 subsoil samples collected at Fort Richardson with concentrations ranging from 1.8 to 193 $\mu g\ kg^{-1}$ (Figure 12). Median values for soil samples collected at 15-, 30- and 45-cm depths were 15.0, 5.2, and 4.3, $\mu g\ kg^{-1}$, respectively. These results suggest that RDX is leaching downward into the soil profile at the hand grenade range, but the concentrations must be very low. These residual concentrations in subsurface soils are often barely detectable, even using the new GC-ECD method with much lower detection limits than the method that had been used traditionally, RP-HPLC Method 8330. Had Method 8330 been used to analyze the soils samples at Fort Richardson, explosives analytes in most samples would have been below detection.

The distribution of TNT concentrations in surface soil samples at Fort Richardson was similar to that of RDX. Several values were above 50 $\mu g\ kg^{-1}$, but most of the values were less than 20 $\mu g\ kg^{-1}$ (Figure 13). As observed previously, concentrations were an order of magnitude or more lower than found at Fort Lewis. In surface soil samples TNT concentrations ranged from 0.9 to 134 $\mu g\ kg^{-1}$ with a median value of 9.7 $\mu g\ kg^{-1}$. The two environmental transformation products of TNT, 4ADNT and 2ADNT, ranged from <1 to 48.8 $\mu g\ kg^{-1}$ and <1 to 28.0 $\mu g\ kg^{-1}$, respectively, with median values of 10.1 and 7.3 $\mu g\ kg^{-1}$. Concentrations of TNT in 16 of the 21 subsoil samples were <1 $\mu g\ kg^{-1}$. Concentrations of 4ADNT and 2ADNT were also generally <1 $\mu g\ kg^{-1}$ indicating that neither TNT nor its daughter products were leaching at detectable concentrations below the surface soil. The behavior of TNT relative to RDX is not surprising, since TNT and its daughter products are known to adsorb to soils to a much greater extent than RDX (Brannon et al. 1999).

Concentrations of HMX in surface soils at Fort Richardson ranged from <1 to 80.4 $\mu g\ kg^{-1}$ with a median value of 6.9 $\mu g\ kg^{-1}$ (Figure 14). A ratio of the median values for RDX/HMX in these soils is 4.2 compared with a mean ratio of 7.6 for the Composition B extracted from a low-order hand grenade. Concentrations of HMX in the subsoil were <1 $\mu g\ kg^{-1}$ in 14 of the 21 samples. The lower solubility and rate of dissolution of HMX compared with RDX are probably responsible for a lower residual concentration ratio of RDX to HMX in surface soil than present in Composition B, and for the higher ratio of RDX to HMX found in the subsoil samples.

Table 4
Concentrations, µg kg^{-1}, of Explosives in Soils from Fort Richardson Hand Grenade Range[1]

Sample Number	Location[2]			TNT	4ADNT	HMX
	From Reference, m	From Launch, m	Depth cm			
1	27	7		56.1	26.3	t[3]
2	27	7	15	<1[4]	t	t
3	27	7	30	t	t	t
4	27	7	45	t	<1.5	t
5	27	8		2.9	2.1	t
6	27	8	15	<1	<1.5	t
7	27	8	30	<1	<1.5	<25
8	27	8	45	<1	<1.5	<25
9	33	1		52.0	4.1	36.9
10	33	1	15	3.4	1.9	t
11	33	1	30	<1	<1.5	<25
12	33	1	45	2.7	<1.5	<25
13	32	10		1.5	4.1	t
14	32	10	15	<1	<1.5	<25
15	32	10	30	<1	<1.5	<25
16	2	10	45	<1	<1.5	<25
17	W[5]	35	10	50.2	43.6	t
18	Wheel	35		9.7	12.8	t
19	Wheel	35		5.9	9.4	t
20	Wheel	35		20.4	17.3	t
21	Wheel	35		6.7	8.2	t
22	Wheel	35		3.9	6.9	t
23	Wheel	35		27.0	12.4	t
24	W	35	15	<1	<1.5	<25
25	W	35	30	<1	<1.5	<25
26	W	35	45	11.2	17.9	t
27	32	12		2.5	2.1	<25
28	32	12	15	<1	<1.5	<25
29	32	12	30	<1	<1.5	<25
30	32	12	45	<d	<1.5	<25
31	30	15		8.2	11.7	t
32	30	15	15	<1	<1.5	t
33	30	15	30	<1	<1.5	<25
34	30	15	45	<1	<1.5	<25
35	35	1		42.8	5.3	66.6
36	35	2		t	<1.5	<25
37	35	3		19.9	8.3	t
38	35	4		29.9	10.6	27.4
39	35	5		93.9	48.8	56.4
40	35	6		28.7	20.2	30.
41	35	7		9.3	9.2	t
42	35	8		7.2	10.1	t
43	35	9		70.6	11.6	t
44	35	11		6.8	7.3	56.9
45	35	12		6.8	10.6	80.4
46	35	13		8.5	9.0	t
47	35	14		13.8	14.5	t
48	35	15		134	47.5	t

[1] Values are for surface soils except where noted. The following undetected analytes were excluded from the table: nitrobenzene, *o*-nitrotoluene, *m*-nitrotoluene, *p*-nitrotoluene, nitroglycerin, 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene, PETN, 3,5-dinitroaniline, tetryl.

[2] Locations give distances from reference wall followed by distance from launch in meters. Depth in cm is also given for samples not taken from the surface.

[3] Values are trace below the mean detection limit.

[4] Less than detection limits.

[5] W = west.

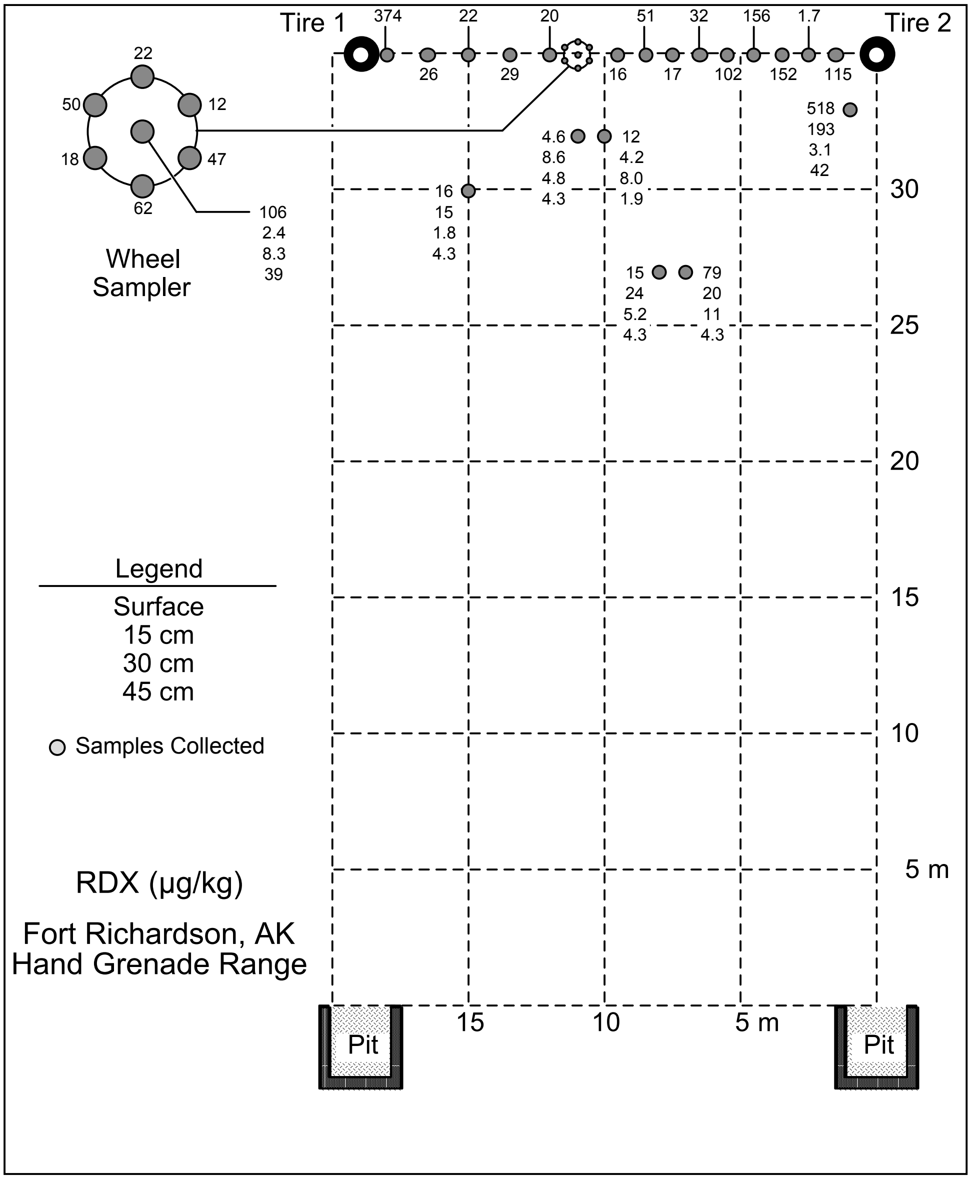

Figure 12. Fort Richardson hand grenade range distribution of RDX

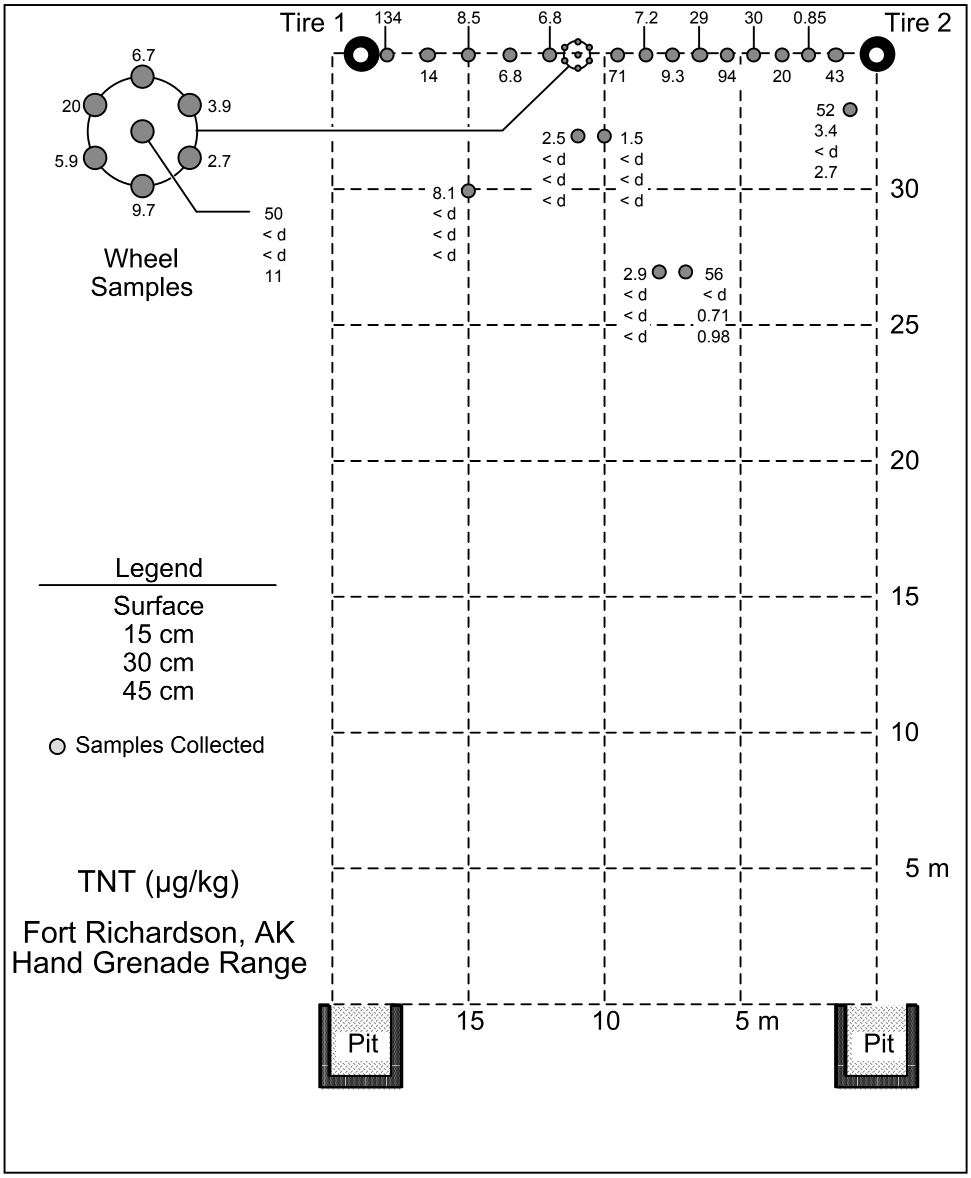

Figure 13. Fort Richardson hand grenade range distribution of TNT

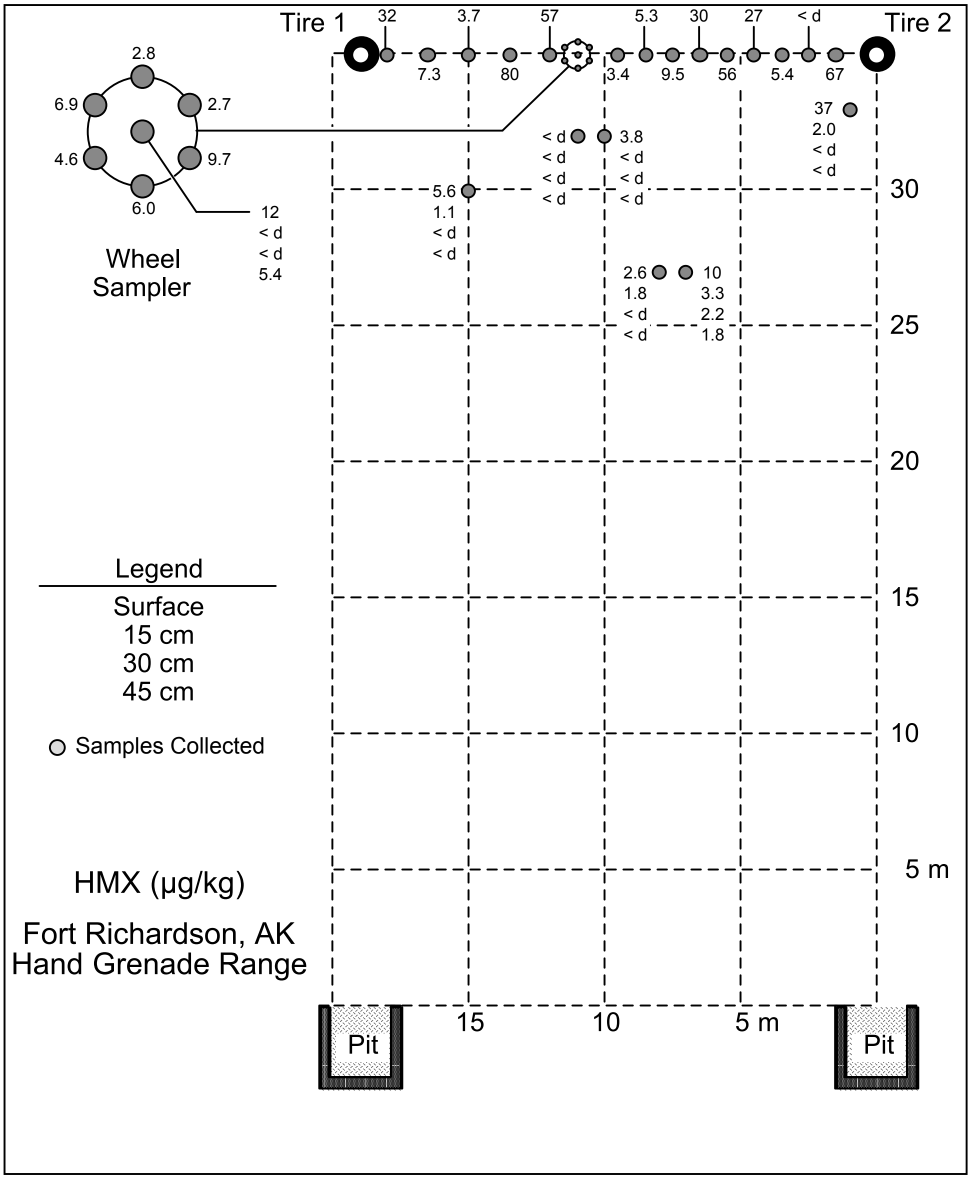

Figure 14. Fort Richardson hand grenade range distribution of HMX

Overall, subsurface concentrations of these explosives-related analytes decline rapidly below the surface soil at Fort Richardson. Because this grenade range has a much harder surface than the range at Fort Lewis, much less mixing of the soil profile is likely. Analytes found at depth were more likely to have arrived there by leaching than by remixing due to heavy activity as observed at Fort Lewis.

Artillery range firing point

Results from analysis of the 48 surface soil samples from the artillery firing point for Guns 1 and 2 at Fort Lewis (Tables 5 and 6, respectively) show the following major propellant-related compounds: dinitrotoluenes (2,4DNT, 2,6DNT, 2,5DNT, and 3,4DNT); the two isomeric environmental transformation products of 2,4DNT, 4A2NT and 2A4NT; and 2,4,6TNT, presumably a manufacturing impurity in dinitrotoluene. Of these compounds 2,4DNT was present at the highest concentration in all samples from both guns. Concentrations of 2,4DNT varied from 982 to 175,000 µg kg^{-1} (median value = 31,500 µg kg^{-1}) for surface samples collected in front of Gun 1 and from 1,030 to 237,000 µg kg^{-1} (median value = 40,900 µg kg^{-1}) in front of Gun 2. While these numbers appear quite large, they are in µg kg^{-1}, or parts per billion, and the guns had fired approximately 610 rounds from the same position over the previous several months.

The propellant-related compounds detected at the next highest concentrations were 4A2NT and 2A4NT. These two compounds ranged in concentration for surface soil from below detectable limits <d to 3,000 µg kg^{-1} and from <d to 1,340, µg kg,$^{-1}$ respectively. Concentrations in the surface soil were typically about two orders of magnitude lower than concentrations of 2,4DNT. Concentrations of 2,6DNT, 3,4DNT, and 2,4,6TNT were also at least two orders of magnitude lower than 2,4DNT; concentrations of 2,5DNT were generally three orders of magnitude lower than 2,4DNT.

Gun 1. The distribution of 2,4DNT in the soil samples collected in front of Gun 1 is shown in Figure 15. All but two of these samples were collected from surface soil. Samples were collected as far as 10 m beyond the muzzle of the gun. The mean concentration of the three samples at 10 m was 19,500 µg kg^{-1}. A seven-sample set of surface soils was collected in a wheel pattern in front of Gun 1, 2 m from the muzzle. This was done to assess the short-range spatial heterogeneity of analytes in the surface. Results indicated that concentrations of 2,4DNT ranged from 4,400 to 99,200 µg kg^{-1} (Figure 15). Thus as found elsewhere, the distribution of munitions-related analytes was spatially very heterogeneous, even over short distances. Only two subsurface soil samples were collected in the area in front of Gun 1. These samples were collected on the center line, 2 m in front of the gun, below the center of the samples collected in the wheel pattern. The concentrations of 2,4DNT in the surface soil, in the soil segment from 0.5 to 5 cm, and from 5 cm to 9 cm were 66,900, 955, and 458 µg kg^{-1}, respectively. Therefore, some downward migration of 2,4DNT is possible, but cannot be confirmed with only one set of samples.

Gun 2. The distribution of 2,4DNT in the soil in front of Gun 2 is shown in Figure 16. Concentrations of 2,4DNT, the two amino transformation products of 2,4DNT, 2,4,6TNT, and the other isomers of DNT were very similar to those found for samples collected in front of Gun 1. For Gun 2, samples were collected at distances as far as 20 m from the muzzle of the gun on the center line and 3 m to the left and right of the center line. A chromatogram for the extract of one of the samples collected 20 m from the muzzle is shown in Figure 17. Even at this range, the mean concentration was 4,060 µg kg^{-1}. Thus propellant residues were

Table 5
Explosives Concentrations in Soils, µg kg^{-1}, at 105-mm Gun 1 Position, Fort Lewis[1]

Sample Number	Location[2]		TNT	2,4DNT	2,6DNT	4A2NT	2A4NT	NG	2,5DNT	3,4DNT
	From Muzzle m	Depth cm								
1	1.5 R		<1[3]	8.15e3	360	631	250	299	6.7	30.1
9	3.0 R		336	1.75e5	4840	1600	666	<20	158	696
2	1.5 L		28.3	3.47e4	999	515	290	<20	23.7	123
10	3.0 L		81.6	3.18e4	211	t[4]	t	t	14.2	122
3	0.5 C		47.1	2.89e4	1000	745	300	t	23.9	151
4	1.0 C		142	4.37e4	420	677	302	<20	25.4	175
5	1.5 C		397	1.44e5	743	1230	451	<20	71.0	503
6	2.0 C		442	1.15e5	133	3000	1340	<20	44.7	380
7	2.5 C		215	1.4e5	1314	666	372	<20	73.5	456
8	5.0 C		158	9.1e4	1330	791	272	<20	60.2	327
11	5.0 C 3.0 R		167	1.62e5	3840	1500	762	254	134	637
12	5.0 C 3.0 L		<1	982	4.8	t	t	<20	<d	<d
13	10 C		9.7	2.21e4	455	303	t	<20	20.8	108
14	10 C 3 R		5.5	5.15e4	39.5	t	t	<20	1.9	18.1
15	10 C 3 L		106	3.11e4	63.4	351	297	<20	10.3	107
16	2 C[5]		85.2	6.69e4	300	<d	<d	<20	23.7	209
23	2 C	0.5-5	<1	955	16.3	t	t	<20	<d	1.78
24	2 C	5.1-9	<1	458	6.6	<d	<d	<20	<d	<d
17	2 A		125	6.19e4	1160	687	257	<20	51.0	249
18	2 B		188	9.92e4	1260	1070	398	<20	51.6	323
19	2 C		63.5	1.96e4	340	480	385	<20	16.1	88.7
20	2 D		13.6	6.27e3	7.1	300	t	<20	<d	16.5
21	2 E		20.5	2.63e4	65.8	508	t	<20	9.7	82.7
22	2 F		1.7	4.4e3	10.0	t	t	<20	<d	22.8
48	Bkg[6] ~400		<1	33.5	0.9	<d	<d	<20	<d	<d

[1] Values are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, 3,5-dinitroanaline, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

[2] Locations are distances relative to the muzzle of the gun: R = to the right, L = to the left, C = directly in center front. Depth in cm is also given for samples not taken from the surface.

[3] Less than detection limits.

[4] Values are trace below mean detection limits (see Table 2).

[5] Wheel pattern of sampling: C = center of wheel; A-F = clockwise around wheel circumference.

[6] Background, soil across road from Gun 1.

Table 6
Explosives Concentrations in Soils at 105-mm Gun 2 Position, Fort Lewis (µg kg^{-1})[1]

Sample Number	Location[2]	TNT	2,4DNT	2,6DNT	4ANT	2ANT	NG	2,5DNT	3,4DNT
25	1.5 R	168	9.68e4	275	1,000	334	<d[3]	27.7	270
26	3.0 R	173	7.9e4	236	1,220	307	344	26.0	247
46	6.0 R	13.3	1.03e4	3.33	510	t[4]	<d	<d	2.59
27	1.5 L	331	8.94e4	93.0	603	t	158	46.4	490
28	3.0 L	120	5.77e4	341	830	326	<d	24.0	206
47	6.0 L	206	5.84e4	108	t	t	324	23.1	288
29	0.5 C	85.2	4.09e4	132	573	t	12.0	12.4	123
30	1.0 C	77.0	3.81e4	279	502	t	<d	<d	127
31	1.5 C	71.8	4.85e4	97.5	596	t	<d	12.2	131
32	2.0 C	513	2.37e5	235	489	475	<d	67.1	732
33	2.5 C	406	1.07e5	198	1,320	602	<d	60.0	657
34	5.0 C	513	2.12e5	106	1,050	481	<d	58.3	640
35	5.0 C, 3 R	27.7	2.04e4	168	1,490	493	<d	9.0	77.0
36	5.0 C, 3 L	17.0	2.06e4	382	263	t	<d	22.2	149
37	10 C	54.1	1.6e4	8.05	497	t	84.9	4.0	44.1
38	10 C, 3 R	219	5.27e4	41.6	277	t	<d	30.2	324
39	10 C, 3 L	207	1.01e5	83.8	<d	<d	<d	26.5	296
40	15 C	82.4	3.53e4	30.3	t	t	<d	8.0	102
41	15 C, 3 R	11.1	2.45e3	22.5	<d	<d	<d	<d	16.3
42	15 C, 3 L	7.9	6.08e3	30.6	<d	<d	<d	1.8	21.5
43	20 C	<1	4.63e3	129	<d	<d	<d	3.7	19.8
44	20 C, 3 R	3.0	3.13e3	70.0	<d	<d	<d	2.8	21.0
45	20 C, 3 L	7.9	4.41e3	74.6	<d	<d	<d	3.5	23.7

[1] Values given are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, 3,5-dinitroanaline, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

[2] Locations are distances relative to the muzzle of the gun: R = to the right, L = to the left, C = directly in center front second; distances are from center line.

[3] Less than detection limits.

[4] Values are trace below mean detection limits (see Table 2).

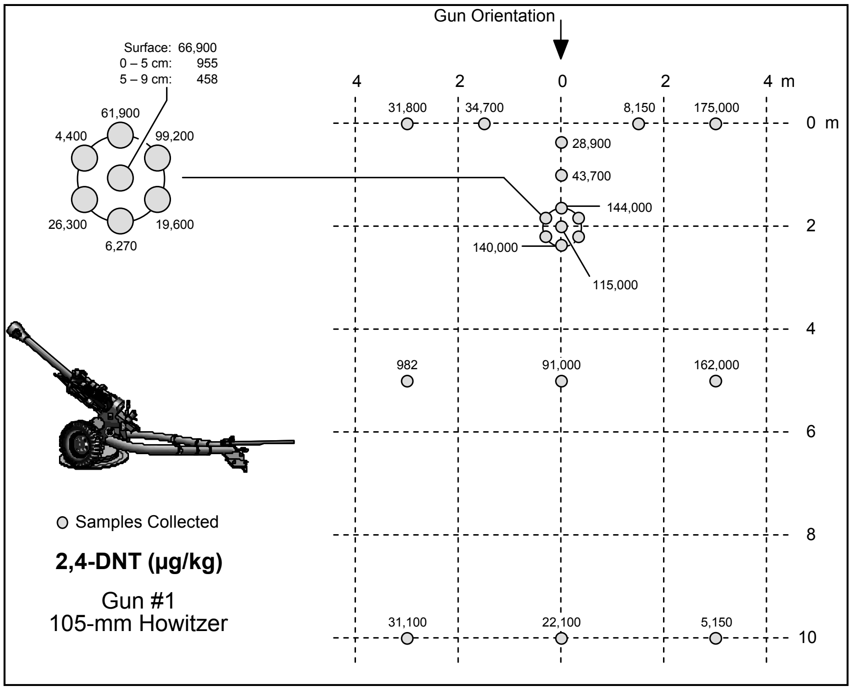

Figure 15. Distribution of 2,4DNT at Gun 1 firing point, Fort Lewis

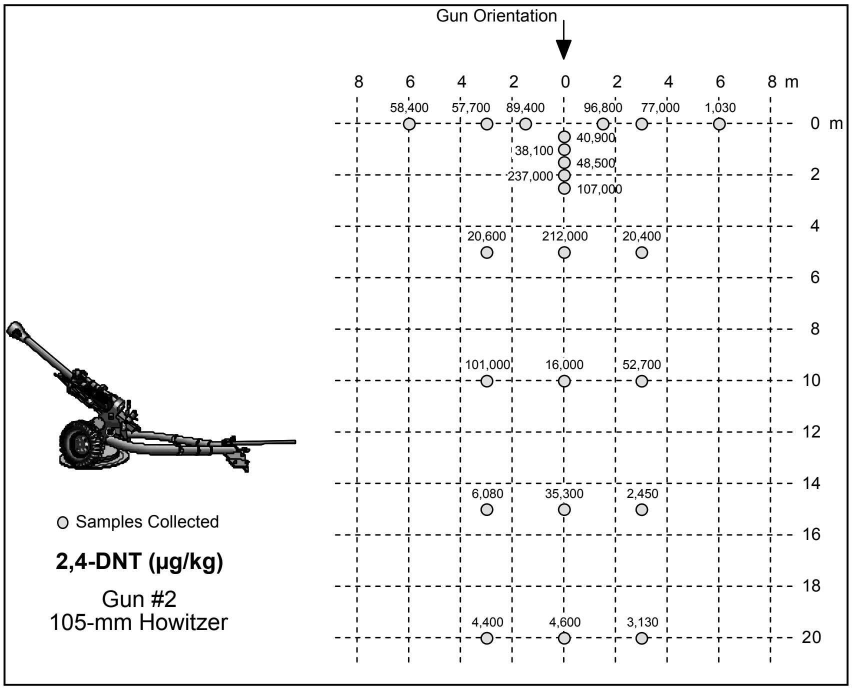

Figure 16. Distribution of 2,4DNT at Gun 2 firing point, Fort Lewis

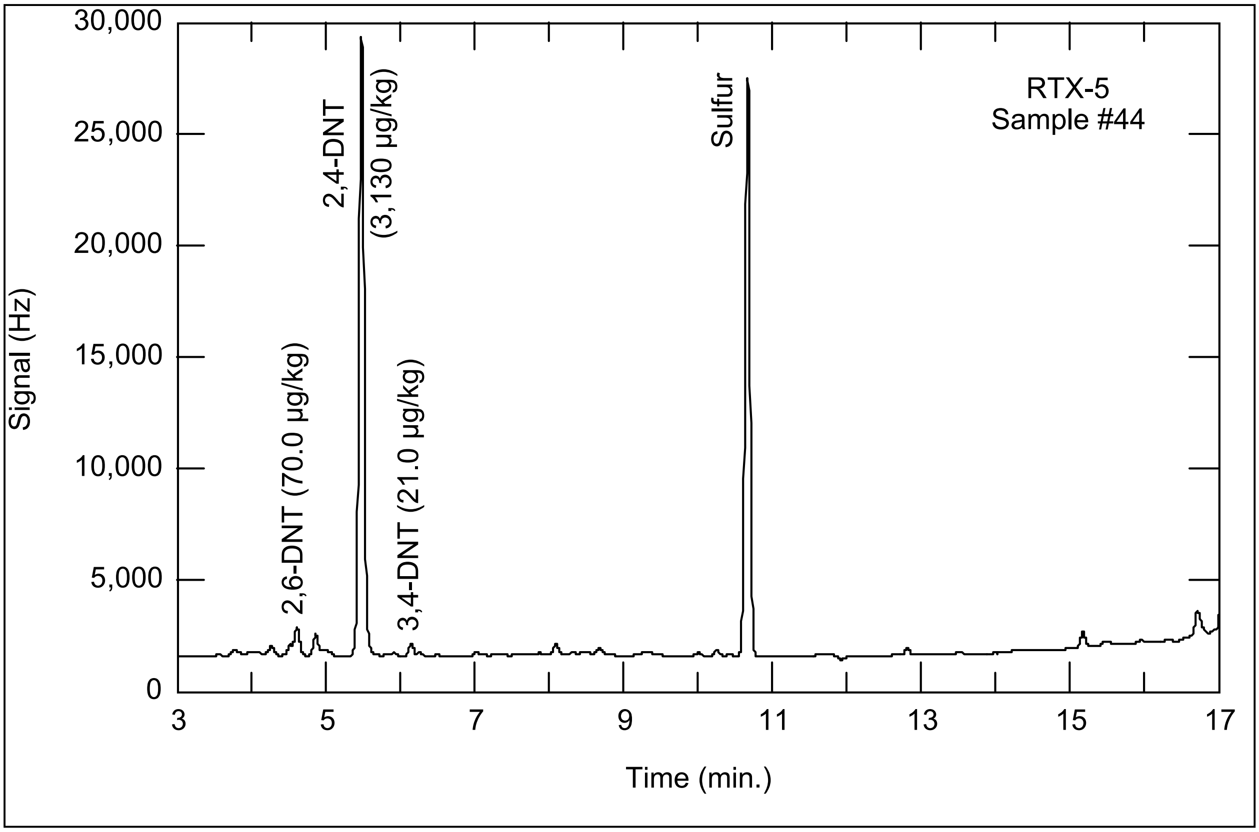

Figure 17. GC-ECD chromatogram of soil extract from surface soil sample collected at artillery firing point

spread over a relatively large surface area during firing activity, but the amount of residue deposited from a single round fired is probably quite small and perhaps not detectable even using the low-level GC-ECD method. One surface sample was also collected about 400 m to the east of the firing position, across the road from the firing point and away from the direction of fire. Analysis of this sample indicated that 2,4DNT was present at 33.5 µg kg^{-1}. The source of this 2,4DNT was apparently residues that were carried downwind from the firing activity.

Artillery range impact areas

Soil samples collected within the artillery range impact area were not collected randomly across the area, but were associated with specific detonation events as determined by visual observation and discussions with EOD technicians (Table 7). The first area was a crater apparently caused by the impact of a 105-mm artillery round within a week of the time sampled (Figure 18). The type of munition was determined on the basis of the metal debris found within the crater. Age was estimated by the visual presence of ash. Nine surface soil samples were collected at this location. Analyses indicated that no residues of

Table 7
Explosives Concentrations in Soils, µg kg^{-1}, from Artillery Impact Area, Fort Lewis[1]

Sample Number	Location[2]	RDX	TNT	4ADNT	2ADNT
Crater A, 105-mm Round ≤ 1 Week Old					
49	CR[3]	<3[4]	<1	<1.5	<d
50	CL[3]	<3	<1	<1.5	<d
51	WC	<3	<1	<1.5	<d
52	Wa	<3	<1	<1.5	<d
53	Wb	<3	<1	<1.5	<d
54	Wc	<3	<1	<1.5	<d
55	Wd	<3	<1	<1.5	<d
56	We	<3	<1	<1.5	<d
57	Wf	<3	<1	<1.5	<d
Crater B, 120-mm Mortar, ≤ 2 Weeks Old					
62	C Ash	<3	<1	<1.5	<d
63	CR[3]	<3	<1	6.1	2.9
64	CL[3]	<3	<1	6.4	2.5
65	WC	<3	<1	5.9	6.4
66	Wa	<3	<1	4.9	5.0
67	Wb	5.8	<1	12.0	7.3
68	Wc	4.1	<1	12.1	6.4
69	Wd	3.3	<1	7.1	3.9
70	We	<3	<1	8.5	3.0
71	Wf	<3	t[5]	8.6	5.9
72	Backgound 3 m from crater	<3	1.0	5.4	t
73	Backgound 3 m from crater	<3	42.5	5.3	t
74	Backgound 3 m from crater	<3	1.4	10.8	6.9
Crater C, 105-mm Round, ≤ 1 Week Old					
75	E[3]	<3	<1	<1.5	<d
76	E[3]	<3	<1	<1.5	<d
Crater D, 105-mm Round ≤ 1 Day Old					
77	CR[3]	93.4	8.7	3.9	t
78	CL[3]	81.5	<1	9.0	4.8
79	WC	27.2	<1	<1.5	<d
80	Wa	18.6	<1	3.0	2.5
81	Wb	16.0	1.2	9.3	6.4
82	Wc	42.5	21.0	27.8	21.5
83	Wd	52.0	13.6	14.3	8.7
84	We	20.0	1.7	7.7	5.1
85	Wf	57.1	4.6	9.2	7.5

(Continued)

[1] Values are for surface soils. The following undetected analytes were excluded from the table: HMX, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 1,3-dinitrobenzene,1,3,5-trinitrobenzene, 3,5-dinitroaniline, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

[2] Location is relative to craters A through F (cross headings). CR = right of center, CL = left of center, C = center, and E = edge of crater. W = wheel pattern, C = center of wheel, a – f = clockwise around wheel circumference.

[3] Composite sample.

[4] Less than detection limit (see Table 2).

[5] Trace detected below mean detection limit (See Table 2).

Table 7 (Concluded)

Sample Number	Location[2]	RDX	TNT	4ADNT	2ADNT
Crater E, 155-mm Round, Several Years Old					
88	CR[3]	<3	<1	<1.5	<2.5
89	CL[3]	<3	<1	<1.5	<2.5
90	WC	<3	<1	<1.5	<2.5
91	Wa	4.9	3.7	5.4	2.7
92	Wb	t	6.0	20.1	10.5
93	Wc	5.0	<1	13.2	9.0
94	Wd	3.9	<1	11.8	2.6
95	We	t	2.2	20.6	15.2
96	Wf	t	1.3	5.6	4.5
Background, No Crater within 3 m					
97	WC	23.7	2.9	13.1	8.8
98	Wa	17.3	4.0	18.5	5.8
99	Wb	<3	<1	<1.5	<2.5
100	Wc	19.5	t	13.7	8.8
101	Wd	25.4	110	10.3	4.5
102	We	8.9	<1	<1.5	<2.5
103	Wf	24.9	6.4	25.5	17.0
Craters I – VI from 105-mm Rounds ≤ 1 Year					
113	I[3]	4.8	1750	140	145
114	II[3]	<3	70.5	39.3	31.3
115	III[3]	5.5	147	26.4	21.5
116	IV[3]	<3	144	44.4	25.9
117	V[3]	<3	166	39.8	19.8
118	VI[3]	<3	59.2	13.5	5.4
Crater F, 60-mm Mortar ≤ 1 Year					
119	C[3]	<3	362	38.1	18.0
120	C[3]	<3	222	30.0	7.9
Background, Miscellaneous[6]					
58	1.5 m	<3	<1	<1.5	<2.5
59	2.0 m	<3	<1	<1.5	<2.5
60	1 m[7]	<3	<1	<1.5	<2.5
61	1 m[8]	<3	<1	<1.5	<2.5
86	1.5 m	15.0	<1	14.5	14.6
87	0.5 m	7.0	<1	12.1	6.6
105	Burned area[9]	20.3	<1	24.6	33.3
106	Burned area[9]	9.2	<1	14.1	11.3

[6] Locations in this group are distance from nearest crater.
[7] Nearest crater assumed to be formed by an 81-mm mortar at least one year before sampling.
[8] Nearest crater assumed to be formed by a 155-mm round at least one year before sampling.
[9] Burn assumed to be from illumination round.

Figure 18. Sampling crater from a 105-mm howitzer

explosives-related compounds were present above a detection limit of about 1 µg kg^{-1} (Table 7, samples 49-57).

The second area was a crater formed by the detonation of a 120-mm mortar, probably within 2 weeks of the date of sampling. At this location, 10 samples were collected in and around the crater, and 3 were collected about 3 m from the crater (Table 7, samples 62-74). Analyses indicated some very low levels of explosives-related residues in several of the samples associated with the crater and in the samples collected at the 3-m distant. The highest concentration was 42.5 µg kg^{-1} for TNT in one of the 3-m samples. Otherwise, only 4ADNT and 2ADNT were detected in a majority of samples, with the highest concentrations being 12.1 and 7.3 µg kg^{-1}, respectively.

The third area was another 105-mm crater (Table 7, samples 75 and 76). No explosives-related analytes were detectable above 1 µg kg^{-1} in the two composite samples collected within the crater. The fourth area was another 105-mm crater formed by 105-mm artillery fired by the National Guard the day before sampling. Nine samples were collected near this crater, two composite samples from within the crater and a seven-sample wheel centered on the crater. The center of the wheel sample was taken from the bottom of the crater, and the six other samples were collected around the rim of the crater (Table 7, samples 77-85). Explosives-related analytes detected in these samples included RDX, TNT, 2,4DNT, 4ADNT, and 2ADNT. A chromatogram for one of the composite samples taken from inside the crater is shown in Figure 19. RDX was found in each sample at concentrations ranging from 16.0 to 93.4 µg kg^{-1}. TNT was found in six of the

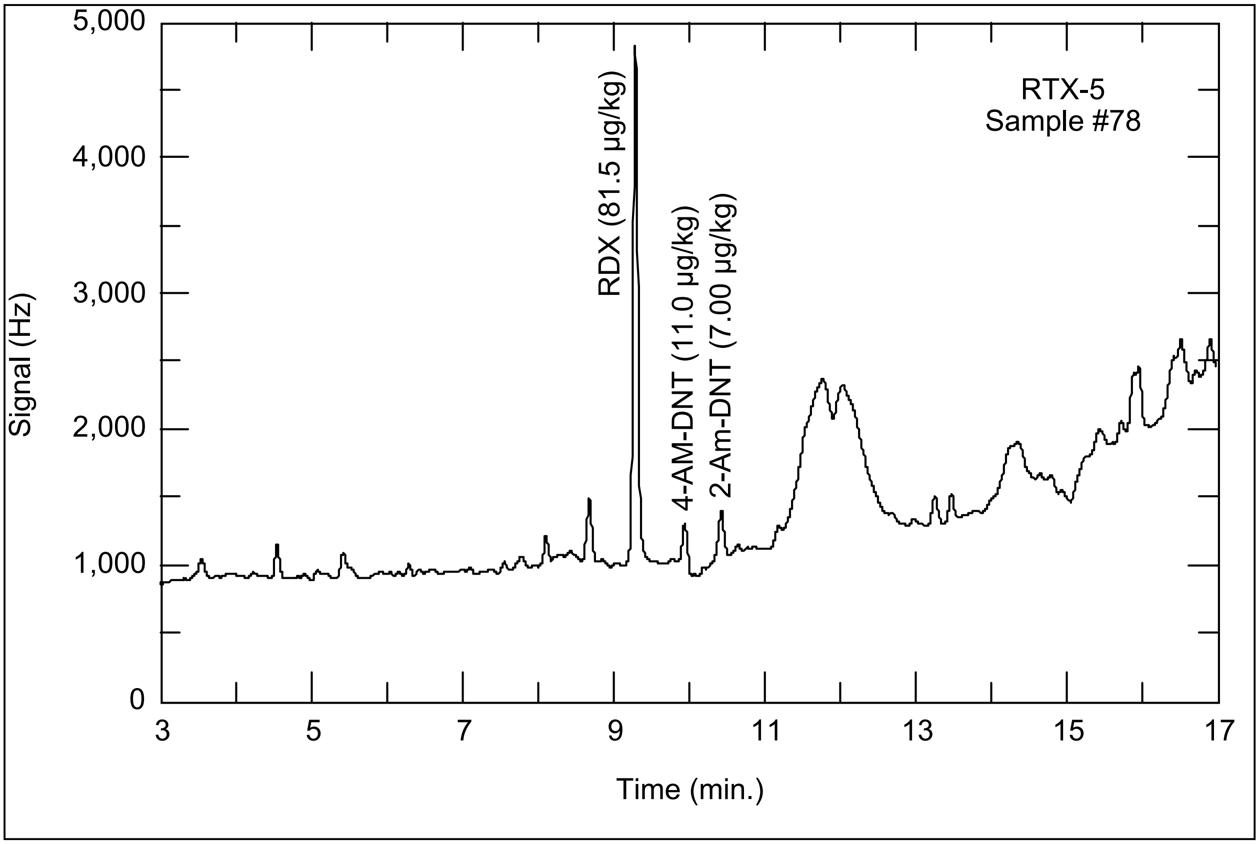

Figure 19. GC-ECD chromatogram of soil extract from surface soil sample collected at crater formed by the detonation of a 105-mm howitzer round

nine samples at concentrations ranging from 1.2 to 21.0 µg kg^{-1}. Each of the two transformation products of TNT, 4ADNT and 2ADNT, was found in eight of the nine samples at concentrations ranging from 5.4 to 20.6 µg kg^{-1}and 2.6 to 15.2 µg kg^{-1}, respectively. The 2,4DNT was detected in only two samples at concentrations of 7.3 and 9.9 µg kg^{-1}.

The discovery of RDX and TNT in a number of these samples was not surprising since the 105-mm rounds contain Composition B as the main charge. The fact that 4ADNT and 2ADNT were found at concentrations generally as high as that of TNT was unexpected, since the detonation forming this crater probably occurred only the previous day. The rapid formation of these transformation products from TNT, however, is consistent with the half-lives observed for TNT in a recent report by Miyares and Jenkins (2000) and some earlier work by Maskarinec et al. (1991) and Grant, Jenkins, and Golden (1993).

The fifth area was a 155-mm crater several years old judging by the vegetation cover. Nine samples were collected in and around this crater, two composites from within the crater and a seven-sample wheel centered on the crater as described previously (Table 7, samples 88-96). No explosives-related analytes were observed for the three samples collected within the crater, but RDX, 4ADNT, and 2ADNT were detected in all six of the samples collected around the rim of the crater. Concentrations of RDX ranged from trace to 5.0 µg kg^{-1}, 4ADNT from 5.4 to 20.6 µg kg^{-1}, and 2ADNT from 2.6 to 15.2 µg kg^{-1}. TNT was also detected in four of the six samples with concentrations ranging from 1.3 to 6.0 µg kg^{-1}. 2,4DNT was observed in two samples at 6.9 and 15.3 µg kg^{-1}. While detectable, the concentrations in all of these residues were very low, and would not have been detectable using SW-846 Method 8330. The main charge for 155-mm rounds generally contains TNT, not Composition B. Therefore, the RDX found in these samples may have originated from a source other than the 155-mm detonation.

The sixth area was a series of background samples collected in a wheel pattern within the range, but not close to any visual crater (Table 7, samples 97 to 103). Low levels of RDX, 4ADNT, 2ADNT, and TNT were observed in these samples, but concentrations were always below 30 µg kg^{-1}. These results indicate that low concentrations of explosives residues are distributed in some places over fairly large areas even when no craters are observable, but identification of a specific source is not possible.

A series of six craters were sampled that could be identified as recent 105-mm craters, probably formed from detonations within a week of sample collection (Table 7, samples 113-118). Composite samples from the inside walls of all six of these craters were similar in that TNT, 4ADNT, and 2ADNT were the residues at highest concentrations. TNT concentrations ranged from 59.2 to 1750 µg kg^{-1} in these samples; concentrations of 4ADNT and 2ADNT ranged from 13.5 to 140 µg kg^{-1} and 5.4 to 145 µg kg^{-1}, respectively. RDX was observed in only two of these samples, and the concentrations were low, 4.8 and 5.5 µg kg^{-1}. Since the 105-mm rounds contained Composition B as the main charge, either RDX has preferentially leached out of these craters, or the residues were deposited from a TNT-containing round instead and were not associated with the 105-mm rounds that made the craters. The preferential leaching of RDX from these craters would be somewhat surprising, since RDX dissolves more slowly than TNT from solid Composition B.[1] On the other hand, once the RDX is dissolved, soils have much less tendency to adsorb RDX than TNT.

TNT, 4ADNT, and 2ADNT were detected in two composite samples collected in a 1-year-old crater probably formed by detonation of a 60-mm mortar (Table 7, samples 119 and 120). Lack of RDX in this crater was surprising since the main charge in 60-mm mortar rounds is 0.43 kg of Composition B.

The next series of samples were collected at various points throughout the range (Table 7, samples 58-61, 86 and 87, and 105 and 106). Samples 58 and 59 were taken a short distance from an unidentified crater and contained no measurable residue. Likewise, samples 60 and 61 were taken near two very old craters and no residues were detectable. Samples 86 and 87 were collected next to more recent craters, and low concentrations of RDX, 4ADNT, and 2ADNT were found in each. Samples 105 and 106 were taken from an area that had recently burned due to an illumination round, and again concentrations of RDX, 4ADNT and 2ADNT were detectable.

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[1] P. H. Miyares and T. F. Jenkins, 1999, unpublished data.

The final samples collected from the artillery impact area were associated with a 155-mm round that had undergone a low-order detonation (Figure 20). This round was broken open and partially filled with the unexploded main charge. Analysis of the soil just below this round revealed a 2,4,6TNT concentration of 15,100,000 μg kg^{-1}, or 1.5 percent (Table 8). This was four orders of magnitude higher than any samples associated with craters formed from high-order detonations. This sample also contained high concentrations of 4ADNT and 2ADNT, 110,000 and 102,000 μg kg^{-1}, respectively; moderately high concentrations of 2,4DNT and 1,3,5TNT; and detectable concentrations of other isomers of DNT and 1,3DNB. The main charge remaining in the broken round was also sampled and analyzed. It contained 99.96 percent TNT with a small percentage of the manufacturing impurity, 2,4DNT (0.04 percent). High concentrations of TNT, its associated impurities, and transformation products were found in surrounding surface soils. Figure 21 shows a chromatogram for the extract of a soil sample collected 15 cm west of the round. Samples of soil collected at depths of 5 and 10 cm below this round also had very high 2,4,6TNT concentrations, 710,000 and 46,300 μg kg^{-1}, respectively. The 5-cm sample had even higher concentrations of 4ADNT and 2ADNT than the surface soil. Concentrations of 2,4,6TNT, 4ADNT, and 2ADNT were still moderately high in the soils collected at a distance of 15 cm on three sides of this low-order round.

Figure 20. A 155-mm round that had broken open due to a low-order detonation

Table 8
Explosives Concentrations in Proximity to a Single Low-order Detonation of a 155-mm Round on the Artillery Range at Fort Lewis ($\mu g\ kg^{-1}$ except where noted)[1]

Sample Number	Location[2]	TNT	2,4DNT	2,6DNT	4ADNT	2ADNT	1,3-DNB	1,3,5TNB	2,5DNT
104	Residue[3]	99.96%	0.04 %	<d[4]	<d	<d	<d	<d	<d
107	Surface	1.51e7	4.01e4	<d	1.1e5	1.02e5	1.21e3	1.47e4	<d
111	5 cm[5]	7.1e5	1.e4	264	1.46e5	1.53e5	281	<d	368
112	10 cm[5]	4.63e4	1.96e4	41.2	2.e4	2.97e4	37.4	141	25.9
108	15 cm[5]W[6]	2.5e3	9.4	<d	194	188	<d	62.5	<d
109	15 cm[5]E[6]	886	52.7	6.1	3.e3	3.38e3	<d	66.0	<d
110	15 cm[5]S[6]	1.5e4	221	7.7	7.23e3	7.69e3	10.4	382	<d

[1] Values are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene. The following analytes were excluded from the table, but were detected in sample 111 (concentrations are given in parentheses): 2,4,5-trinitrotoluene (69.0), and 2,3,4-trinitrotoluene (17.9). The following analytes were excluded from the table, but were detected in sample 112: 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 3,5-dinitroaniline, 3,5-dinitrotoluene, 3-nitroaniline.
[2] Locations are relative to the low-order round.
[3] High-explosive residue remaining in the low-order shell.
[4] Less than detection limits.
[5] Depth beneath the round.
[6] Direction from the round: W = west, E = east, S = south.

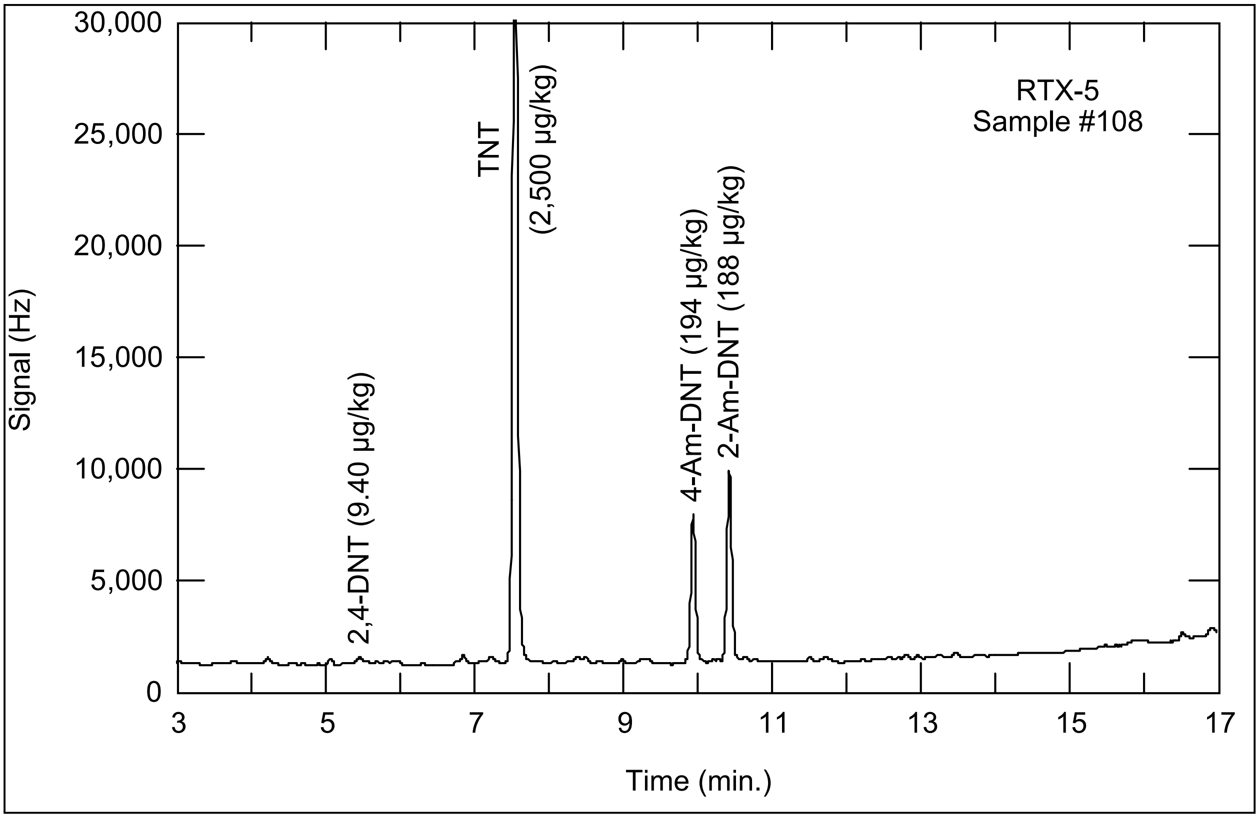

Figure 21. Chromatogram of soil sample collected 15 cm from position of a low-order 155-mm howitzer round

These results indicate that a low-order detonation is a significant source of high concentrations of contaminants, clearly many orders of magnitude greater concentrations than from rounds that detonate as engineered. A low-order 81-mm mortar round was also observed at the Fort Lewis impact area (Figure 22).

Figure 22. An 81-mm mortar round that had undergone a low-order detonation

Water analyses

Explosives. Only RDX was above analytical detection limits in monitoring wells and seeps at Fort Lewis (Table 9). The agreement of data among the three laboratories was excellent, even though two different methods were used and the concentrations were near the detection limit of the HPLC method. RDX was detected in eight of the eleven water samples. Concentrations were below 1 $\mu g\ kg^{-1}$ in all cases. The human health advisory level for RDX in drinking water is 2 $\mu g\ kg^{-1}$ (USEPA 1988b).

Geochemical parameters. Groundwater geochemistry is typical of the geographic area (Table 10). Groundwater is generally soft (sum of calcium and magnesium less than 50 mg L^{-1}). One sample, MW07, slightly exceeds the drinking water standard for total iron (0.3 mg L^{-1}). None of the samples exceed the drinking water standard for manganese (0.05 mg L^{-1}). Nitrate/nitrite values are well within the range for natural waters (0.1 to 10 mg L^{-1} (Driscoll 1987)). Total organic carbon, sulfate, and chloride values are relatively low, not atypical for this environment.

Table 9 **RDX Concentrations, μg kg^{-1}, in Groundwater and Surface Water Seepages Around the Perimeter of the Artillery Range at Fort Lewis[1]**			
Sample Number	**CRREL[2]**	**EL[3]**	**Anteon Corporation[3]**
MW1	0.28	0.38	0.3
MW2	0.19	0.27	0.2
MW3	0.18	na[4]	0.2
MW4	0.51	0.59	0.5
MW7	<0.1[5]	na	<0.2
A1ASP01	0.31	na	0.4
A1ASP02	0.15	na	0.2
A1ASP03	0.26	na	0.3
A1ASP04	0.73	na	0.8
A1ASP05	<0.1	na	<0.2

[1] Samples were collected in August 2000. RDX was the only analyte detected.
[2] Analyzed by Method 8095, GC-ECD (USEPA 1999).
[3] Analyzed by Method 8330, RP-HPLC-UV (USEPA 1994).
[4] Sample not analyzed by this laboratory.
[5] Less than detection limits.

Table 10 **Geochemical Parameters, mg L^{-1}, in Groundwater at Fort Lewis**								
Well	**Calcium**	**Iron**	**Manganese**	**Magnesium**	**Nitrate/ Nitrite**	**TOC[1]**	**Sulfate**	**Chloride**
MW01[2]	8.60	0.069	0.007	2.96	0.37	<3.0[3]	13J[4]	2.0J
MW02	9.47	<0.02	<0.001	3.63	0.23	<3.0	6.4J	2.1J
MW03	7.87	0.048	0.002	3.05	0.26	<3.0	<20	1.7J
MW04	7.70	<0.02	<0.001	2.67	0.35	<3.0	<20	2.0J
MW07	11.5	0.319	0.014	4.86	1.6	<3.0	<20	1.6J
A1ASP03[5]	7.10	0.029	0.004	2.45	0.055J	<3.0	<20	1.6J
A1ASP05	7.66	<0.02	<0.001	2.31	0.44	<3.0	<20	2.2J

[1] Total organic carbon.
[2] Monitoring well number.
[3] Less than detection limit.
[4] J values are below the statistically reliable detection limit.
[5] Seepage area number.

Historical firing records

Firing records for the six most heavily used rounds indicated that the 105-mm artillery round was the item most heavily fired, followed by the 81-mm mortar and the 155-mm artillery round (Table 11). Range loading of explosives residues from each type of round can be estimated by making several assumptions and using known low-order detonation rates (Table 12). For example, in the year 2000 firing records indicate that 7,458 rounds were fired into the Fort Lewis impact area by 105-mm howitzers (Table 11). On average, about 0.07 percent of those fired undergo a low-order detonation (Table 12). Thus, five of the 105-mm rounds can be estimated to have undergone a low-order detonation. If all of these contained Composition B as the main charge, then each round would contain about 1,252 g of RDX (Table 13). If half of the main charge remained undetonated for each low-order detonation, then 626 g of RDX would be deposited on the Fort Lewis range from low-order detonations of 105-mm rounds in 2000.

Table 11
Firing Record of the Most Commonly Fired Munitions for 1997- 2000 at Fort Lewis[1]

Round	DODIC[2]	1997	1998	1999	2000[3]	Total
81-mm	C256	1,997	2,112	2,789	2,075	8,973
105-mm	C445	10,585	3,166	9,505	7,458	30,714
120-mm	C623	474	-[4]	-	359	833
120-mm	C788	-	75	288	-	363
107-mm	C697	219	128	262	216	825
155-mm	D544	207	7,564	261	841	8,873

[1] Records encompass the available electronic database from January 1997 through July 2000 and include the most commonly fired items as indicated by Mr. Del Larson, Range Operations Officer.
[2] Department of Defense Identification Code.
[3] Data through July 2000 only.
[4] No record of firing for this item in this year.

Table 12
Mean Dud and Low-order Detonation Rates for Munitions Items Commonly Used at Fort Lewis[1]

Round	DODIC[2]	Items Tested	Duds, %	Low Orders, %
81-mm	C256	9,122	2.16	0.22
105-mm	C445	10,003	4.39	0.07
120-mm	C623, C788	-[2]	-	-
107-mm (4.2-inch)[3]	C697	1,518	2.24	0.02
155-mm	D544	6,216	2.75	0.02

[1] Rates based on test data acquired by U.S. Army Defense Ammunition Center, McAlester, OK (Dauphin and Doyle 2000).
[2] No data.
[3] Department of Defense Identification Code.

Table 13
High-explosive Load Carried by Munitions Items Commonly Fired at Fort Lewis[1]

Round	DODIC[2]	Main Charge, g		Supplemental Charge		Pellet Booster		Pellet Auxiliary Booster		Main Charge Total, g
		RDX	TNT	HE[3]	Wt (g)	HE	Wt (g)	HE	Wt (g)	
M67	G881	110.6	71.9	-[4]	-	-	-	-	-	184.3
81-mm	C256[5]	571.5	371.5	-	-	Tetryl	22.1	Tetryl	63.0	943
105-mm	C445	-	2086	TNT	136	-	-	-	-	2086
105-mm	C445[5]	1252	814	TNT	132	-	-	-	-	2086
120-mm	C623[5]	1790	1170	?[6]	?	?	?	?	?	2990
120-mm	C788	-	2100	-	-	-	-	?	?	2100
107-mm	C697	1252	814	TNT	132	-	-	-	-	2086
155-mm	D544[5]	4191	2725	TNT	136	-	-	-	-	6916
155-mm	D544	-	6622	TNT	136	-	-	-	-	6622

[1] Source of data is the Munitions Items Disposition Action System (MIDAS) and personal communication from Mr. Mark Serben, Office of the Product Manager for Mortar Systems, TACOM, Picatinny Arsenal, NJ, March 19, 2000.
[2] Department of Defense Identification Code.
[3] High explosive.
[4] Not present.
[5] Main charge is Composition B, which is typically composed of 60 percent RDX and 39 percent TNT.
[6] Unable to determine presence or quantity.

For the total number of 105-mm rounds fired in 2000, potential loading from high-order detonations can also be estimated by taking into account dud rates (Table 12). About 7,126 rounds are estimated to have undergone high-order detonations. An experimentally derived estimate of the amount of explosives residue that is produced from the high-order detonation of a 105-mm round is not yet available; however, an estimate for 60-mm mortars that also contain Composition B is 258 g of RDX, or about 20.6 percent of the RDX present in the 105-mm round. Experiments conducted by firing 60-mm rounds onto a snow-covered range indicate that about 0.00007 percent of the RDX originally present in the round remained undetonated and was deposited on the range (Jenkins et al. 2000). If this same percentage can be applied to high-order detonations of 105-mm rounds, then each detonation would deposit about 0.88 mg of RDX. Multiplying this by the 7,126 high-order detonations results in an estimate of about 6.2 g of RDX deposited from high-order detonations of 105-mm rounds at Fort Lewis in 2000.

These estimates are preliminary. Source terms for rounds other than 60-mm mortars are currently under development. However, even a small number of low-order detonations appear to contribute a very large percentage of the total explosives residues deposited from live firing. If the 0.00007 percent is correct, then one low-order detonation in which half of the explosive remains can contribute as much residue as about 700,000 high-order detonations. Based on these estimates, efforts should be made to locate and remove the debris from low-order detonations as soon as possible. This action alone may substantially reduce the amounts of explosives residues contaminating surface soils at impact ranges.

Summary and Conclusions

Three training areas were sampled at Fort Lewis, WA: an impact area within the hand grenade range, a 105-mm howitzer firing point, and a portion of the impact area within the heavy artillery and mortar ranges. A set of eleven water samples from monitoring wells and seeps adjacent to the artillery impact area were also analyzed. Soil samples were also collected at a hand grenade range at Fort Richardson, AK.

RDX was detected in all 96 soil samples, both surface and shallow subsurface, at the two hand grenade ranges. Concentrations in surface soils ranged up to 51,200 μg kg^{-1} at Fort Lewis, and 518 μg kg^{-1} at Fort Richardson. TNT and HMX concentrations were also detectable in most soils from these two grenade ranges. Whether these residues are a result of the large number of high-order detonations of hand grenades or the much lower number of low-order detonations is uncertain. Overall, concentrations of explosives-related contaminants were an order of magnitude higher at the Fort Lewis than at the Fort Richardson hand grenade range. This may be due to higher use at Fort Lewis. While RDX concentrations were moderate, removal of the contaminant to prevent potential groundwater contamination would not be difficult because these ranges are relatively small.

At the Fort Lewis artillery range where surface and near-surface soil samples were collected at a 105-mm howitzer firing point, 24DNT, a component of the single-based propellant, was found at concentrations as high as 237,000 μg kg^{-1}. Whether 2,4DNT is leaching deeper into the soil profile is uncertain, because only two shallow subsurface samples were analyzed.

In the artillery range impact area at Fort Lewis, concentrations of explosives residues associated with craters formed by high-order detonations were very low, often below a detection limit of 1 μg kg^{-1} (1 part per billion). RDX, the analyte of most concern for groundwater contamination, was always less than 100 μg kg^{-1} (ppb) in these soil samples. Concentrations of TNT were extremely high (1.5 percent) in the surface soil under a 155-mm round that had undergone a low-order detonation, and remained substantial in soils collected beneath this round at 5- and 10-cm depths. Clearly the residues of explosives resulting from low-order detonations are many orders of magnitude higher than those that result from high-order detonations. Therefore, efforts should be made to locate and eliminate the debris resulting from low-order detonations.

Results of analysis of water samples obtained from five monitoring wells and five seeps that border the artillery range at Fort Lewis indicated a low level (<1 ppb) of RDX contamination. The source of this contamination is uncertain. Results from Fort Lewis and Fort Richardson suggest that very low concentrations of explosives residues are widespread at testing and training ranges. The use of an analytical method that has lower detection limits than the current standard method for explosives residues, SW-846 Method 8330 (USEPA 1994), detection limit of 250 ug kg^{-1}, allowed delineation of contamination at training ranges. The GC-ECD method developed recently by Walsh and Ranney (1999) has detection limits near 1 μg kg^{-1} for many explosive residues and is particularly appropriate for use in range characterization studies.

The distribution of explosive residues at all the ranges investigated was spatially very heterogeneous. Concentrations of explosives-related compounds in soils collected less than a meter apart differed by over two orders of magnitude at hand grenade ranges, and by as much as an order of magnitude at artillery firing points. The spatial heterogeneity at artillery impact areas was large as well, although difficult to define numerically since many of the concentrations were below detection limits. Areas that were visibly free of craters, however, often exhibited explosives concentrations as high as or higher than soils collected from the rim of a fresh crater. Thus sampling methods, such as compositing in order to provide representative samples for a given area, may be extremely important for optimizing impact range characterization.

From preliminary estimates of residues produced from high-order detonations and the frequency of low-order detonations, low-order detonations seem to contribute a significant portion of the residues deposited on surface soils in artillery impact areas. Development of better estimates of the residues produced from detonations of various military munitions is crucial. Development of these estimates is proposed under the addition to this project.

3 Transport Parameters for Firing Range Residues

Introduction

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

The dissolution rate of explosives residues from free product on the soil surface or from cracked or partially fragmented munitions is one of the main processes affecting fate and transport of explosives on firing ranges. Concentration gradients observed in the soil profile are consistent with kinetic limitations on solubilization and with different rates of dissolution for TNT, RDX and HMX (Jenkins et al. 1997). However, the data are limited. Thiboutot et al. (1998) have also shown that the rates of dissolution of TNT and HMX from the formulation octol differ substantially. Accurate dissolution kinetics for explosives and for explosives formulations are key to describing the fate and transport of explosives residues from firing ranges into groundwater.

Once the residues are in solution, the main factor affecting fate and transport of explosives residues is advection; contributing factors are adsorption, transformation, and irreversible soil binding (Brannon and Myers 1997). The fate and transport process descriptors required for estimating the movement of explosives residues through soil and into groundwater are the adsorption coefficient and the transformation rate coefficient. The adsorption coefficient is a mathematical expression that describes the distribution of a chemical compound between soil and water at equilibrium. The transformation rate coefficient is a kinetic parameter that describes the removal of a contaminant from solution when equilibrium is unattainable due to confounding processes. When transformation and/or irreversible sorption are pronounced, equilibrium is not attainable and the transformation rate coefficient is appropriate for describing fate and transport. One example of this is the partitioning of TNT under certain conditions that promote reduction of nitro to amino groups with subsequent changes in partitioning and with chemical reactions between the reduction products and soil components. Transformation rate coefficients generally follow first-order kinetics (Brannon and Myers 1997).

Data defining fate and transport process descriptors for explosives residues have been directed toward TNT, its transformation products, RDX, and to a lesser extent, HMX. A summary of existing environmental transport parameters for compounds encountered on ranges provides a basis for identifying important data gaps. Filling these data gaps is the focus of the current study. (This report will be supplemented with a future, more comprehensive report of data gaps that will be periodically updated as data are generated by the authors and others.) The dissolution data will be published in greater depth in Lynch.[1]

Objectives

The objectives of this study were to identify data gaps in existing fate and transport process descriptors, to provide process descriptors for selected explosives residues for which data are lacking, and to conduct an initial evaluation of dissolution kinetics for TNT, RDX, and HMX. Fate and transport process parameters were determined for the following TNT-related compounds as a first priority, since no data were found for these compounds, and they have been detected in soils on ranges and in groundwater: 2,4DNT, 2,6DNT, 1,3,5TNB, 1,3DNB.

Determination of Explosives Processes Data Gaps

Fate and transport process descriptors for the primary explosives, their manufacturing impurities, and transformation products of TNT are available (Table 14). The presence or absence of existing information on adsorption coefficients and transformation rate coefficients was noted. Explosives detected in soils or groundwater from sites such as arsenals, depots, and ammunition plants are included (Murrmann and Nakano 1971; Leggett, Jenkins, and Murrmann 1977; Walsh 1990; Walsh and Jenkins 1992; Pennington et al. 1995b; Pennington et al. 1999). Analytical standards for transformation products of RDX and HMX have only recently become available; therefore, little data concerning their occurrence are available. Fate and transport process information is almost totally lacking for nitrobenzene, tetryl, nitroglycerin, and PETN. Information for 2,4DNT, 2,6DNT, 1,3,5TNB, 1,3DNB, 3,5DNA, and picric acid is limited. Although not included in Table 14, process descriptors are needed for the transformation products of RDX and HMX.

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[1] Personal Communications, 2001, LTC J. C. Lynch, U.S. Army.

Table 14
Summary of Existing References and Identification of Data Needs in Process Descriptors for Explosives Contamination

Contaminant	Existing Information		Further Study Needed	
	Adsorption Coefficients	Transformation Rate Coefficients	Yes	No
TNT	1, 2, 7, 9, 10, 11,12, 14, 17, 19, 21, 22, 23	3, 4, 5, 9, 10, 11, 15, 17, 21 22		x
RDX	1, 2, 9, 10, 11, 17, 18, 20, 22, 23	3, 5, 9, 10, 11, 16, 22		x
HMX	5, 9, 10, 11, 17	5, 9, 10, 11		x
2ADNT	6, 7, 8	3, 5, 6		x
4ADNT	6, 7, 8	3, 5, 6		x
2,4DANT	6, 7, 8, 9	3, 5, 6		x
2,6DANT	6, 7, 8, 9	3, 5, 6		x
2,4DNT	8, 9, 11	9, 1	x	
2,6DNT	8, 9	9, 11	x	
1,3,5TNB	8, 9, 11	9, 11	x	
1,3DNB	8, 9, 11	9, 11	x	
Nitrobenzene	8		x	
3,5-DNA	11		x	
Tetryl	9	9	x	
Picric Acid	11	11	x	
Nitroglycerine			x	
PETN			x	

Note: Key to references:

1 Ainsworth et al. 1993.
2 Brannon et al. 1992.
3 Brannon and Myers 1997.
4 Brannon, Price, and Hayes 1998.
5 Brannon et al. 1999.
6 Brannon et al. in preparation.
7 Cattaneo et al. 2000.
8 Haderlein, Weissmahr, and Schwarzenbach 1996.
9 McGrath 1995.
10 Myers et al. 1998.
11 Pennington et al. 1999.
12 Pennington et al. 1995a.
13 Pennington et al. 1995b.
14 Pennington and Patrick 1990.
15 Price, Brannon, and Hayes 1997.
16 Price, Brannon, and Yost 1998.
17 Price et al. 2000.
18 Sheremata et al. 2001.
19 Sheremata and Hawari 2000.
20 Singh et al. 1998.
21 Townsend, Myers, and Adrian 1995.
22 Townsend and Myers 1996.
23 Xue, Iskandar, and Selim 1995.

Materials and Methods

Partitioning kinetics

Two aquifer soils from the Louisiana Army Ammunition Plant, Minden, LA, LAAP-C and LAAP-D, and a surface soil, Yokena clay, were used to measure partitioning kinetics. The tests were conducted under nitrogen in a glove box.

Sufficient soil (62.5 g) and distilled, deionized, deoxygenated water (250 ml) were added to 500-ml polycarbonate centrifuge tubes to make a soil-to-water ratio of 1:4. Tests containing the aquifer soils were spiked with a stock solution of 2,6DNT to a final concentration of 10 ppm. Tests with the surface soil were loaded and sampled like the aquifer soils, but were spiked with a 10-ppm mixture of TNT, 2,4DNT, 1,3,5TNB, 1,3DNB, and 2,6DNT. Samples were placed on a reciprocating shaker at 280 excursions per minute. At predetermined sampling times (0.5, 1, 6, 24, 48, 72, 96, and 168 hr), a 10-ml aliquot was removed and centrifuged at 8,288 relative centrifugal force (RCF) for 30 min. The aqueous sample was removed and frozen until analyzed for all EPA SW-846 Method 8330 (USEPA 1994) analytes plus 2,6DANT, 2,4DANT,and 4,4'AZOXY. The aqueous samples from the surface soil were preserved with ethylenediaminetetraacetate (EDTA) to a final concentration of 5μM (Brannon, Price, and Hayes 1998). At the completion of the 168 hr the soil was also analyzed. The testing was carried out in duplicate.

Adsorption partitioning

Adsorption partitioning was conducted with the same soils and in a 1:4 ratio of soil to water. Concentrations of explosives were 10, 7.5, 5, 2.5, and 1 μg per ml of solution phase. The LAAP-C test was spiked with 2,6DNT; the LAAP-D test was spiked with 2,6DNT and 2,4DNT separately; and the Yokena clay was spiked with the mixture described in the previous paragraph. Duplicate samples were shaken for 24 hr, centrifuged at 8,288 RCF for 30 min, and the aqueous phase removed and analyzed for the same analytes as in the kinetics test. The aqueous samples from the Yokena clay were preserved with EDTA to a final concentration of 5 μM.

Dissolution kinetics

Dissolution kinetics were determined on three high explosives (TNT, RDX, and HMX) and three explosives formulations (octol, Composition B, and LX14 (Table 15)). Military explosives were available on site at EL. Formulations were obtained from U.S. Army Artillery Research Development and Engineering Command (ARDEC), Picatinny Arsenal, NJ. These studies were designed to estimate the rates of dissolution of the high explosives during rainfall events of various intensities.

Environmental variables. Initial range finding studies identified temperature, surface area, and energy input as significant to the dissolution process, and present under possible exposure scenarios. To determine the impact of each variable on dissolution rate, one variable was allowed to change (for example temperature at 10, 20, and 30 ^{o}C), while the other two variables were held constant (i.e., surface area and stirring rate). Each set of conditions was performed at least twice. Beakers covered with aluminum foil containing 500 ml of reverse osmosis water were allowed to equilibrate to temperature overnight. Stirring propellers from overhead mixers were lowered into the beakers, adjusted to the proper rpm setting, and dry explosives added to the beaker sequentially. At

Table 15
High Explosives Investigated in the Dissolution Kinetics Study

High Explosive	Composition			
	TNT	RDX	HMX	Stabilizer
TNT	x			
RDX		x		
HMX			x	
Composition B	x (39.5%)	x (59.5%)	(trace)	wax (1%)
Octol	x (30%)		x (70%)	
LX-14			x (95.5%)	estane (5.5%)

specified time intervals five separate samples were collected from the beaker for analysis. Water was temperature equilibrated by placement in a water bath that was insulated from room temperature with a layer of 20-mm hollow plastic balls. Bath water was circulated through a refrigeration unit to control temperature. Surface areas were based on study design parameters and the characteristics of the high explosives available. Energy inputs other than temperature also affect dissolution rates. Rainfall energy is one source of such energy input. To replicate this fluctuation in energy input, three differing stirring rates, 90, 150 and 210 rpm, were used.

Surface area. Surface areas of the pure explosives were calculated using two different methods. For TNT a surface area to mass ratio was determined by breaking TNT into sets of grains (varied from 5 to 12 grains per set), measuring length and width of individual grains under a microscope with a calibrated optical reticle, and then weighing the sets. A good relationship between mass and estimated surface area could be drawn when grains were longer than about 2.5 mm; therefore, tests were performed with grains longer than 2.4 mm. The TNT surface area to mass ratio was approximately 23.28 $cm^2 g^{-1}$ (0.04296 g cm^{-2}). Because HMX and RDX crystal sizes were too small and varied to measure by this technique, an alternate approach was employed. The military specifications for each explosive are based on standard sieve analyses. This information, combined with explosive density, assuming the crystals were spherical, and assuming evenly distributed crystal size distributions, permits an estimation of surface area. HMX and RDX surface area to mass ratios were estimated to be 1.12 and 0.10 cm^2 mg^{-1}, respectively.

Analytical protocol. Five hundred microliters of each sample was pipetted into a clean 4-ml vial to which 500 µL of 0.45-µm filtered acetonitrile was added and the vial capped. The vial was then vortexed for 5 sec and allowed to stand for at least 25 min. Samples were pipetted into 0.3-mil glass inserts with a kim spring held in 4-ml glass vials and sealed with a Teflon/silica cap. Analysis was performed with a Waters HPLC with a 486 tunable absorbance detector and auto sampler running Millennium Software package and following Method 8330 (USEPA 1994).

Results and Discussion

Transport parameters

The aquifer soils were high in sand, ranging from 27 to 77 percent sand, and low in organic carbon (Table 16). Cation exchange capacity (CEC) was also relatively low, ranging from 6.6 to 15.5 Meq 100 g^{-1}. This is in marked contrast to the surface soil, which was high in clay, organic carbon, and CEC. Transformation rate coefficients were higher in the surface soil than in the aquifer soils for all tested compounds by at least an order of magnitude (Table 17). These results indicate that 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB were much less stable in the surface than in the aquifer soils. Adsorption coefficients were generally higher in the surface than in the aquifer soils (Table 18). Failure to achieve steady-state concentrations in the surface soil precluded determination of an adsorption coefficient for 1,3,5TNB. Results suggest that 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB will be degraded and strongly adsorbed in surface soils, but relatively mobile in aquifer soils.

Table 16
Soil Characteristics

Soil	Sand, %	Silt, %	Clay, %	CEC, Meq 100 g^{-1}	Total Organic Carbon, %
Sharkey Clay	13.8	37.5	48.7	38.9	2.4
LAAP-C	77	11	12	6.6	0.08
LAAP-D	27	41	32	15.5	0.2

Table 17
Transformation Rate Constants K, hr^{-1}, for 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB in Soils

Soil	Compound	K, hr^{-1}	R^2
LAAP-C (Aquifer Soil)	2,4DNT[1]	0.0021	0.75
LAAP-D (Aquifer Soil)	2,4DNT[1]	0.0005	0.23
Yokena Clay	2,4DNT	Transformation rate too rapid to measure	
LAAP-C (Aquifer Soil)	2,6DNT	0.0023	0.80
LAAP-D (Aquifer Soil)	2,6DNT	0.0035	0.99
Yokena Clay	2,6DNT	0.0235	0.85
LAAP-C (Aquifer Soil)	1,3,5TNB[1]	0.0027	0.74
LAAP-D (Aquifer Soil)	1,3,5TNB[1]	0.0005	0.38
Yokena Clay	1,3,5TNB	0.1800	0.995
LAAP-C (Aquifer Soil)	1,3DNB[1]	0.0013	0.53
LAAP-D (Aquifer Soil)	1,3DNB[1]	0.0019	0.61
Yokena Clay	1,3DNB	0.0476	0.97

[1] Data from Pennington et al. (1999).

Table 18
Adsorption Coefficients for 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB in Soils

Soil	Compound	K_d, L kg^{-1}	R^2
LAAP-C (Aquifer Soil)	2,4DNT[1]	0.67	0.85
LAAP-D (Aquifer Soil)	2,4DNT	1.67	0.75
Yokena Clay	2,4DNT	12.5	0.95
LAAP-C (Aquifer Soil)	2,6DNT	0.96	0.96
LAAP-D (Aquifer Soil)	2,6DNT	1.83	0.88
Yokena Clay	2,6DNT	5.96	0.99
LAAP-C (Aquifer Soil)	1,3,5TNB[1]	0.49	0.99
LAAP-D (Aquifer Soil)	1,3,5TNB[1]	0.27	0.88
Yokena Clay	1,3,5TNB	Steady-state concentrations not attained	
LAAP-C (Aquifer Soil)	1,3DNB[1]	0.32	0.59
LAAP-D (Aquifer Soil)	1,3DNB[1]	No significant adsorption	
Yokena Clay	1,3DNB	17.7	0.95

[1] Data from Pennington et al. (1999).

Dissolution kinetics

Dissolution rates for different explosive surface areas showed good agreement as illustrated for TNT dissolution at 10 °C (Figure 23). TNT, RDX, and HMX at other temperatures behaved similarly. These data indicate that the procedures were reproducible and accurately estimated the surface area of different amounts of explosives.

Increased temperature resulted in increased dissolution rates for all explosives (Figures 24 and 25). Both TNT and RDX dissolution rate increased by a factor of approximately four as water temperature increased from 10 to 30 °C. Therefore, temperature is a critical factor affecting the dissolution rates of explosives, and must be considered when evaluating the transport of explosives on firing ranges. Increasing stir rate also increased the dissolution rate of explosives (Figure 26). These results imply that the rate at which water flows past exposed explosives will affect the dissolution rate, because a constant dissolution rate as a function of stir rate could not be achieved.

Dissolution rates for TNT, RDX, and HMX decreased in the order TNT>HMX>RDX at 10 °C and 150 rpm (Figure 27). This suggests that TNT will be dissolved faster than RDX and HMX. However, this does not mean that higher concentrations of TNT than RDX or HMX will be observed in groundwater. TNT is less stable in soil than is RDX or HMX (Price, Brannon, and Hayes 1997; Price, Brannon, and Yost 1998; Price et al. 2001; Miyares and Jenkins 2000; Grant, Jenkins and Golden 1993).

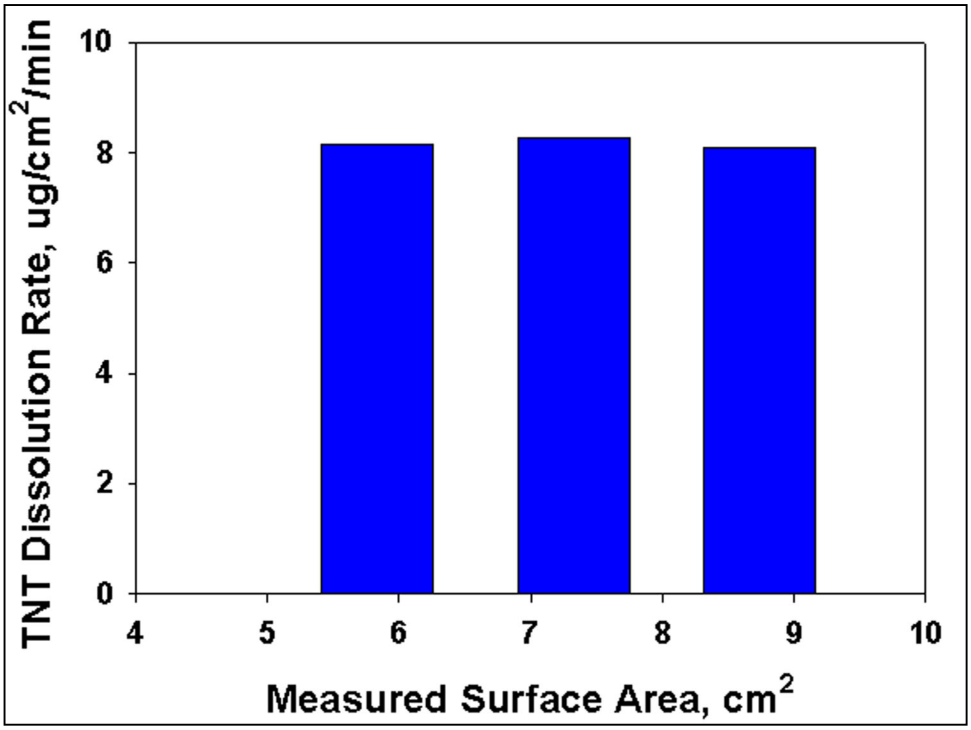

Figure 23. TNT dissolution rate as a function of estimated surface areas

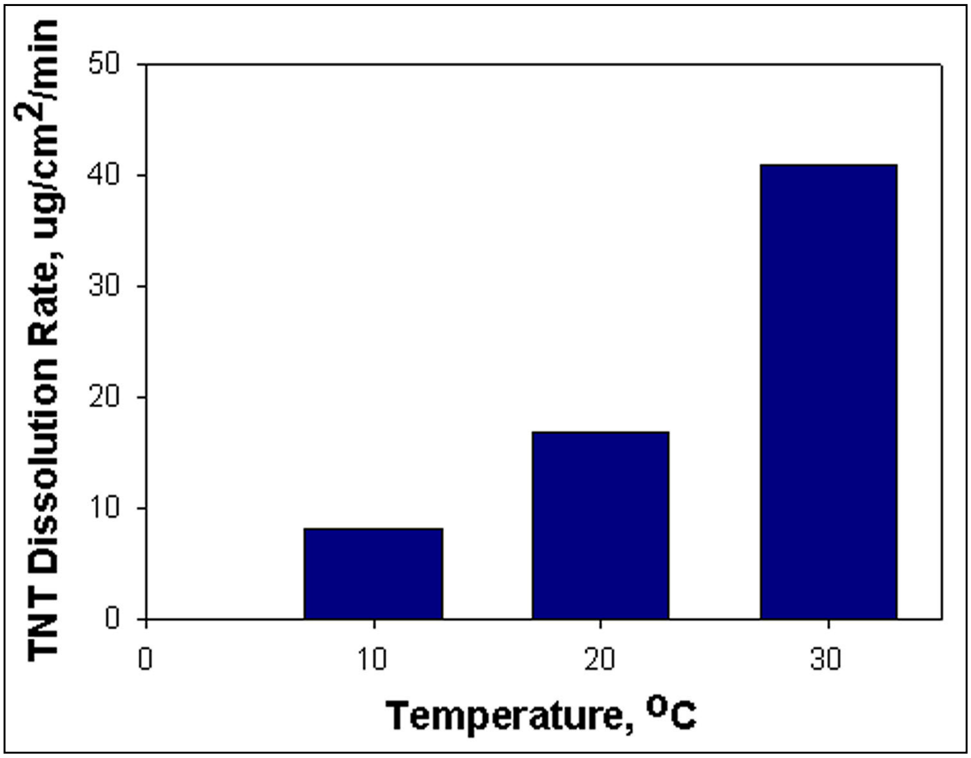

Figure 24. TNT dissolution rate as a function of temperature

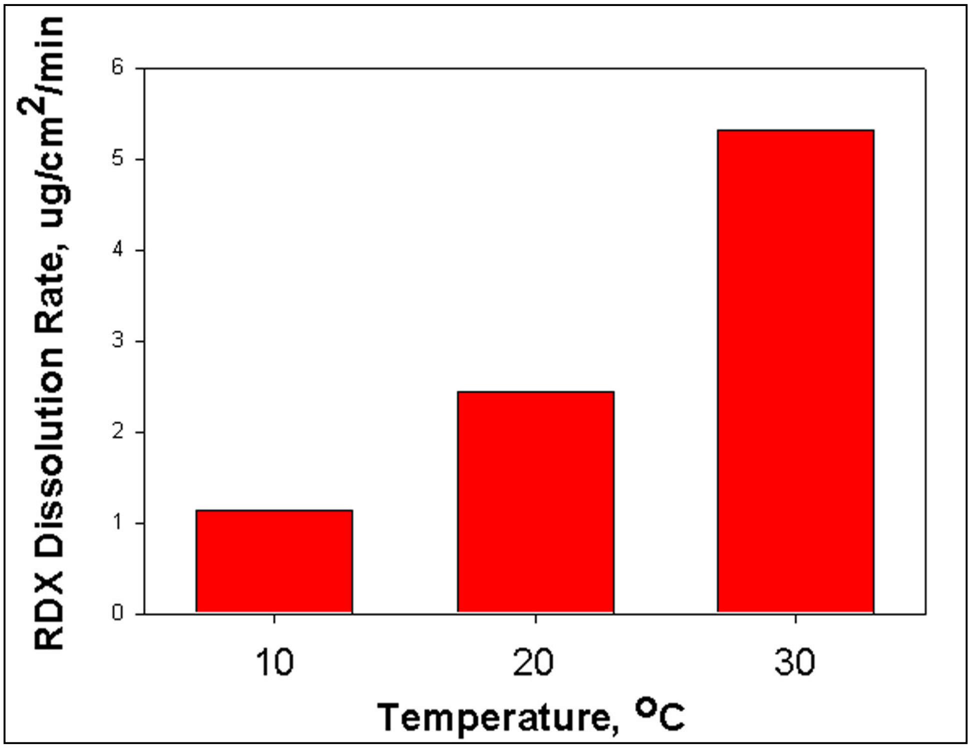

Figure 25. RDX dissolution rate as a function of temperature

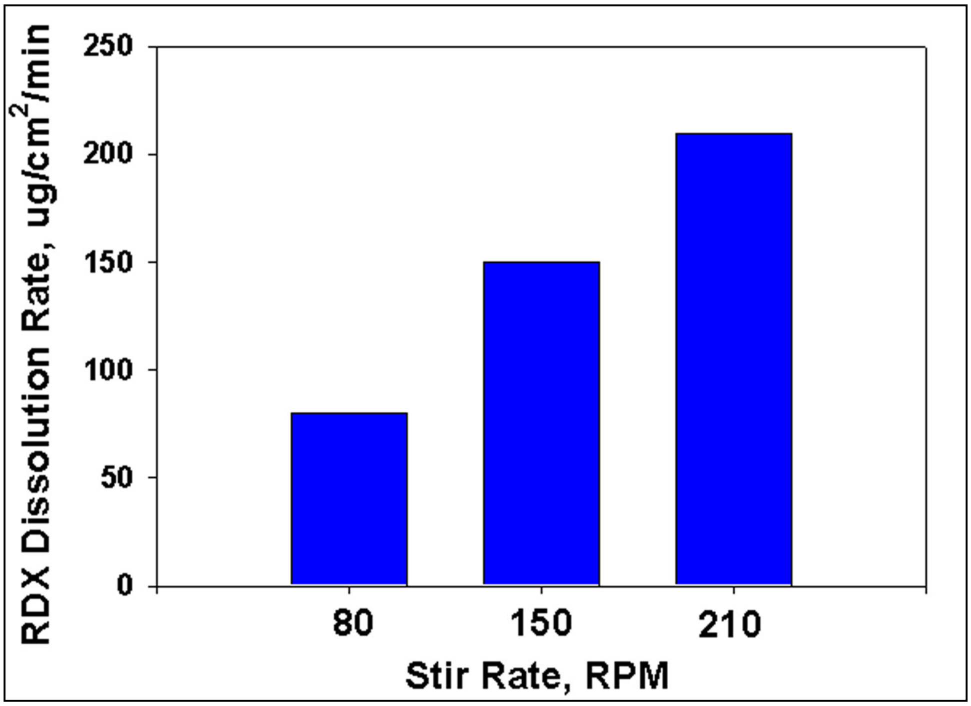

Figure 26. RDX dissolution rate as a function of stirring rate

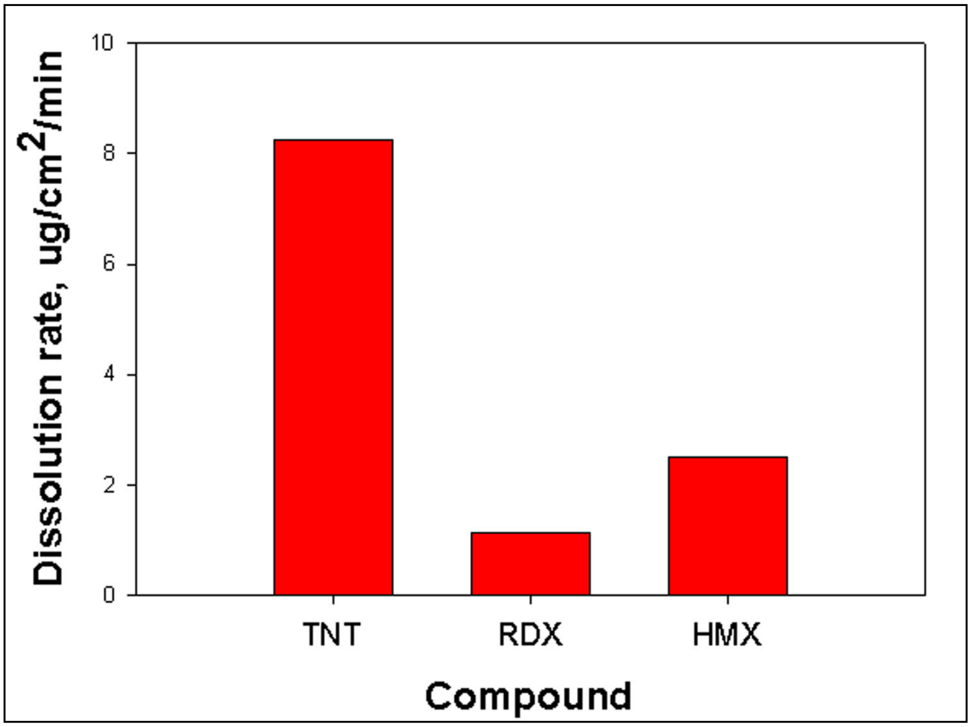

Figure 27. Dissolution rates of TNT, RDX, and HMX at 10 °C and 150 rpm stirring rate

Conclusions

Examination of existing environmental transport parameter data showed that process information was almost totally lacking on nitrobenzene, tetryl, nitroglycerin, and PETN. Process information on 2,4DNT, 2,6DNT, 1,3,5DNT, 1,3DNB, 3,5DNA, and picric acid were incomplete. Process information for 2,4DNT, 2,6DNT, 1,3,5DNT, and 1,3DNB were obtained during this and the Installation Restoration Research Program studies. Results for transformation rate and adsorption coefficients indicate that 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB disappear faster and adsorb more in a surface than in an aquifer soil.

Dissolution kinetics showed that the surface area estimation procedures were reproducible and accurately estimated the surface area of different amounts of explosives. Increased temperature resulted in increased dissolution rates for TNT, RDX, and HMX. Increasing stir rate also increased the dissolution rate of explosives. Dissolution rates for TNT, RDX, and HMX decreased in the order TNT>HMX>RDX at 10 °C and 150 rpm. This indicates that TNT will be mobilized faster than RDX and HMX. However, this does not mean that higher concentrations of TNT than RDX or HMX will be observed in groundwater. That will depend on the relative stability of the compounds once they are exposed to soils. TNT is less stable in soil than is RDX or HMX.

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14. ABSTRACT

The current state of knowledge concerning the nature and extent of residual explosives contamination on military testing and firing ranges is inadequate to ensure management of these facilities as sustainable resources. The objective of this project is to develop techniques for assessing the potential for environmental impacts from energetic materials on testing and training ranges; methods for defining the physical and chemical properties, concentration, and distribution of energetics and residuals of energetics in soils; and the potential for transport of these materials to groundwater. The approach includes characterization of postblast residues from various heavy artillery munitions and from hand grenades by sampling surface soils in craters from both high- and low-order detonations. Residues from specific munitions will also be determined by sampling soot deposited on snow by the blast. Where possible, groundwater and surface water associated with the ranges will also be sampled. In addition to range characterization, the study will also generate soil transport parameters for explosives and explosives breakdown products for which such data are lacking. Transport parameters of interest include dissolution kinetics, soil/water partitioning coefficients, and transformation/degradation rates.

(Continued)

15. SUBJECT TERMS

Detonation residues	Explosives	RDX	Training ranges
Dinitrotoluene	HMX	Test ranges	Transformation rates
	Partition coefficients	TNT	

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During the first year of the project, surface soils were collected from a heavy artillery impact range and at gun position firing points at Fort Lewis, WA, and at hand grenade ranges at Fort Lewis, Camp Bonneville, WA, and Fort Rickardson, AK. Groundwater from monitoring wells and surface seepages around the perimeter of the heavy artillery impact range at Fort Lewis were also sampled for residual explosives. Historical firing records for Fort Lewis were combined with soil concentration data to estimate the mass of explosives potentially generated over time at the heavy artillery impact range. Results indicate very low residual concentrations of explosives in high-order detonation craters from heavy artillery. The hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) concentrations were always less than 100 ppb in these surface soils. However, concentrations in soils associated with low-order detonations were extremely high, ranging up to 1.5 percent RDX. These results suggest that range management for removal of low-order detonations may be advisable to reduce the source of potential contamination. At the firing points 2,4-dinitrotoluene (2,4DNT), the residue of a single-based propellant, was detected. Explosives concentrations on hand grenade ranges were relatively high. At Fort Lewis, RDX concentrations ranged up to 51 ppm and at Fort Richardson up to 0.5 ppm. These preliminary results suggest that management of residual contamination on hand grenade ranges may be necessary to protect the environment.

An examination of existing data indicated a lack of process information for nitrobenzene, tetryl, nitroglycerin, and pentaerythritol tetranitrate (PETN). Process descriptors for 2,4DNT, 2,6-dinitrotoluene (2,6DNT), 1,3,5-trinitrobenzene (1,3,5TNB), 1,3-dinitrobenzene (1,3DNB), 3,5-dinitroaniline (3,5DNA), and picric acid were incomplete. Transformation/degradation rates were determined for 2,4DNT, 2,6DNT, 1,3,5TNB, and 1,3DNB. Dissolution rates were determined for neat 2,4,6-trinitrotoluene (TNT), RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) at 10 ºC and 150 rpm. Decreasing order of dissolution was TNT > HMX > RDX. However, these results are not necessarily predictive of groundwater concentrations, since these explosives will be affected by transport parameters and compound-specific retardation effects, as well as dissolution kinetics.

Results to date suggest that management of ranges to control released residuals of high explosives may be necessary to ensure environmental protection of local receptors including groundwater. The research will contribute techniques for range characterization and for development of a source term for explosives residuals resulting from various range activities. These data will be useful for ensuring environmental compliance and the continued use of test and training ranges as sustainable resources.