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Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2

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Abbreviations

AcN	Acetonitrile
ADNTs	Aminodinitrotoluenes
2ADNT	2-amino-4,6-dinitrotoluene
4ADNT	4-amino-2,6-dinitrotoluene
2A4NT	2-amino-4-nitrotoluene
4A2NT	4-amino-2-nitrotoluene
CG	Camp Guernsey, Wyoming
CRREL	Cold Regions Research and Engineering Laboratory
3,5DNA	3,5-dinitroaniline
1,3DNB	1,3-dinitrobenzene
2,4DNT	2,4-dinitrotoluene
DREV	Defence Research Establishment Valcartier (Canada)
EL	Environmental Laboratory
EOD	Explosive ordnance disposal
ERDC	Engineer Research and Development Center
GC-ECD	Gas chromatography-electron capture detection
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
LAW	Light Antitank Weapon
MMR	Massachusetts Military Reservation
3-NA	3-nitroaniline
NG	Nitroglycerin
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RP-HPLC-UV	Reversed-phase high performance liquid chromatography ultraviolet detection
SARM	Standard Analytical Reference Materials
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
UXO	Unexploded ordnance
YTC	Yakima Training Center, Washington

Preface

This report was prepared by the U. S. Army Engineer Research and Development Center (ERDC) in partnership with the Defence Research Establishment Valcartier (DREV), Canada, the University of Florida and AMEC Earth and Science, Inc. (AMEC). 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 and Engineering Division (EPED), Environmental Laboratory (EL), ERDC, Vicksburg, MS. Co-principal investigators were Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch (ESB), Cold Regions Research and Engineering Laboratory, ERDC, Hanover, NH; Dr. James M. Brannon, Geochemist, EPED, ERDC, EL; Drs. Guy Ampleman and Sonia Thiboutot, Defence Research Establishment Valcartier, Québec, Canada; LTC Jason Lynch, University of Florida, Gainesville, FL, and Mr. Jay Clausen, AMEC, Westford, MA.

Range soil characterization research reported in Chapter 2 was conducted by Dr. Jenkins, Ms. Marianne E. Walsh, Research Chemical Engineer, Mr. Alan D. Hewitt, Research Physical Scientist, Environmental Sciences Branch; Mr. Jeffrey A. Stark, Physical Sciences Technician, Civil Engineering Research Branch; and Ms. Nancy Perron, Physical Sciences Technician, Snow and Ice Branch, ERDC, CRREL; Dr. Pennington and Dr. June E. Mirecki, Geochemist, ERDC, EL; Mr. Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Lebanon, NH; and Ms. Charlotte A. Hayes, Staff Scientist, DynTel, Vicksburg, MS. Characterization of Canadian ranges reported in Chapter 3 was conducted by Drs. Ampleman and Thiboutot, and Mr. Jeff Lewis, DREV. Research on soil partitioning and explosives dissolution reported in Chapter 4 was conducted by Dr. James M. Brannon, ERDC, EL; LTC Jason Lynch and Dr. Joseph J. Delfino, University of Florida, Gainesville, FL, and Ms. Hayes, DynTel.

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

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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, extent, and fate of contamination is inadequate to ensure sound management of ranges as sustainable resources. The potential for environmental impacts, including contamination of drinking water supplies, mandates that DoD demonstrate responsible management of these facilities in order to continue testing and training activities.

Regulatory precedent

In January, 2000, the U. S. Environmental Protection Agency (EPA) 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, 42U.S.C.§ 300i(a) (USEPA 2000). The purpose of the Order was to require the respondents to "undertake Rapid Response Actions and Feasibility Studies, Design and Remedial Actions to abate the threat to public health presented by 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 a 21,000-acre installation located on Cape Cod, MA. The Training Ranges and Central Impact Area is approximately 14,000 acres located on the Camp Edwards portion of the installation. The Central Impact Area, approximately 2,000 acres, has artillery and mortar targets and is

surrounded by firing ranges, artillery and mortar positions, and training areas (AMEC 2001). The Cape Cod Aquifer, a sole source aquifer for western Cape Cod, lies directly beneath the Training Ranges and Central Impact Area. Based on the findings of lead, explosives, explosives-related compounds, pesticides and other organic contaminants in soils, and RDX, TNT, HMX and some organics in groundwater, the USEPA ordered the respondents to conduct feasibility studies at several MMR areas including the Central Impact Area (USEPA 2000). The order also required rapid response actions for contaminated soils at several gun positions, target positions, and for contaminated sediments at a wetland site.

MMR Update

The following is a brief summary of the last five years of work conducted at the Massachusetts Military Reservation. The goal of the Impact Area Groundwater Study Program (IAGWSP) is to assess and clean up the impacts of certain types of historic training activities conducted at the Camp Edwards' Impact Area and training ranges. These areas lie directly over the Sagamore Lens, the most productive part of the Cape Cod Aquifer. The National Guard Bureau is required by EPA to conduct the project and is overseen by both the EPA and the Massachusetts Department of Environmental Protection.

Administrative Order No. 4 (AO4) was issued on January 4, 2001 under the Resource Conservation and Recovery Act (RCRA) to the National Guard Bureau. This order requires that munitions found subsurface or in burial pits be properly stored and disposed of in a Contained Detonation Chamber (CDC), or by other means which prevent the release of explosives, metals and other contaminants into the environment. As of June 2001, 1703 items had been destroyed using the CDC with additional items awaiting disposal.

More than 170 monitoring wells have been installed and over 300 soil samples collected throughout the 15,000-acre training ranges and Impact Area as part of the program. As a result of the investigation, several sites/areas of Camp Edwards are being more closely examined to assess the nature and extent of contamination from past military activities. The following major sites are under investigation:

- Demolition Area 1
- Southeast Corner of the Ranges
- Central Impact Area
- Gun and Mortar Firing Positions

- Chemical Spill-19

For each major site, a feasibility study must be prepared to evaluate potential alternatives for conducting groundwater and soil cleanup. A feasibility study evaluates technologies and alternatives to be used for the containment, treatment and/or removal of contamination from a site. In addition, the IAGWSP is conducting an investigation and a feasibility study to address potential environmental impacts from unexploded ordnance throughout Camp Edwards.

Demolition Area 1. Soil and groundwater investigations have been conducted at Demolition Area 1 to identify the nature and extent of contamination at the site. Investigations began in June of 1997 and continue. For groundwater, the contaminants of concern (COCs) are the explosive compounds – RDX, TNT, HMX, 2ADNT, 4ADNT, 2,4DNT, and perchlorate.

RDX and perchlorate have migrated the farthest in the groundwater. Plumes of these compounds as currently defined extend about 5,500 feet west of Demo Area 1 and are about 400 feet wide and 100 feet deep in the aquifer. The maximum measured groundwater contamination found is 370 parts per billion (ppb) for RDX and 300 ppb for perchlorate. The lifetime health advisory for RDX in drinking water is 2 ppb (USEPA 1988b). No federal or state drinking water standard has been set for perchlorate, but the EPA has calculated that a safe exposure level in drinking water for perchlorate is in the range of 4 – 18 ppb. A detailed evaluation of six remedial technologies for these constituents is currently under discussion with the regulatory agencies.

The 12 contaminants of concern for soil are under review by the regulatory agencies. They are primarily explosives and propellants, but also include several other contaminants such as metals, semi-volatile organic compounds (SVOCs), and dioxin. Once approved by the agencies, the selected COCs will form the basis for evaluating the cleanup alternatives for the soil contamination.

Southeast corner of the ranges. Explosives have been detected in groundwater and soil southeast of the Impact Area and north of Snake Pond. This area lies at the top of the groundwater mound of the Sagamore Lens of Cape Cod's sole source aquifer. Groundwater flows out radially from this area. This area contains three former defense contractor test ranges (the "J" Ranges) and one Massachusetts Army National Guard range (the "L" Range). The U.S. Army - from the 1930s to the 1950s - extensively used this entire area for training. Existing documentation on defense contractor activities at the J Ranges

suggests that bulk explosives were disposed of to the ground surface as well as below ground into holding tanks. Open burn/open detonation disposal of munitions also occurred in numerous locations throughout the J Ranges. In addition, buried caches totaling approximately 1700 mortar rounds have been exhumed from locations since 1998. Also various test firings and research and development activities by numerous contractors occurred in this area. The L Range was utilized for training with high explosives during the 1940s and from the 1970s to the 1980s.

Central Impact Area. Detections of explosives at various depths and locations in the aquifer track back to, or originate from, the Central Impact Area where mortar and artillery rounds were fired for many years. To date, an area of groundwater containing primarily RDX and HMX, has been delineated as extending as far as 11,000 feet northwest from its probable source. The groundwater contamination underlies an area of approximately 621 acres with approximately 880 million to 1.3 billion gallons of water having been affected above the 2 ppb health advisory for RDX. The main source for the explosives in groundwater appears to be an area along Turpentine Road and Tank Alley, which coincides with the location of the targets for the Central Impact Area. The source likely covers about 440 acres of land within the Central Impact Area.

Gun and mortar firing positions. Camp Edwards contains approximately 36 current and former locations from which artillery and mortar rounds were fired. EPA requested that NGB conduct detailed evaluations of these positions based on detections in soil of elevated levels of the propellant and explosive compound 2,4DNT in addition to several metals, SVOCs and pesticides. The IAGWSP is evaluating contamination at these positions and will begin developing remedial alternatives for cleanup in the near future.

Chemical Spill-19 (CS-19). The CS-19 site is a small area in the west-central region of the Impact Area. The area was used for the burial and burning of ordnance. The highest concentration of RDX detected in groundwater at this location was 20 ppb in the central area of CS-19. Elevated levels of explosives, metals and SVOCs have also been found in soils at this location. Groundwater contamination in this area, which is currently known to extend 2,500 feet west and is underlain by contamination originating further up gradient in the Central Impact Area, is currently being addressed by the Air Force under the Installation Restoration Program (IRP) through a Remedial Investigation/Feasibility Study.

Administrative Order No. 3 identified several rapid response actions required to protect the groundwater at Camp Edwards. The first round of rapid response actions has been completed. The areas included contaminated soils at the:

- KD range firing points and target areas
- Gun position 7
- Armored Personnel Carrier
- J-3 Wetland
- Study Area 2 of the Impact Area

These areas are located within the training ranges and Impact Area and have been investigated as part of the ongoing IAGWSP. The results of these investigations have identified explosives, metals, propellants, and pesticides in soil and sediment. Several of the areas had concentrations of contaminants detected above Massachusetts Contingency Plan (MCP) Reportable Concentration Soil-1 (RCS-1) levels. The RCS-1 levels are concentrations that, when exceeded, require notification of MADEP and may require further investigation and remediation of contamination.

A soil-sampling program was conducted to determine the extent of soil contamination within five rapid response areas that exceeded the proposed soil cleanup goals. Results of the sampling program identified approximately 810 cubic yards of contaminated soil that exceeded the Rapid Response Action (RRA) soil cleanup goals.

The RRA addressed the following requirements:

- Elimination of current and potential sources of contaminants to the aquifer from soils and sediment in the areas
- Development and implementation of a monitoring plan to assess compliance with the cleanup goals for source control measures
- Excavation, treatment and/or disposal of contaminated sediments, soils, debris and other materials generated during the RRA
- Restoration of areas disturbed by the removal actions, particularly vegetation and habitat

A second round of Rapid Response Actions to address contamination at Mortar Target 9 and the former H Range is currently underway.

An extensive Munitions Survey Project (MSP) has been underway since July of 1998 in addition to the investigation and remediation of soil and groundwater contamination at Camp Edwards. The MSP was designed to locate buried munitions at locations on Camp Edwards. Phase I of the project was intended to investigate selected sites by conducting geophysical surveys to detect subsurface metallic objects (anomalies or targets). Phase II of the MSP will involve investigations of other sites at Camp Edwards. To verify the geophysical surveys, a limited number of subsurface validations have been performed during Phase I of the MSP. Before field investigations for the MSP began, several sites, locations, and functional areas were selected for investigations. Those areas included selected gun and mortar positions, Demolition Area 1, Central Impact Area, the High Use Target Area, a slit trench, selected water bodies, and portions of the J Ranges.

The MSP was designed to acquire data that could be used to support the groundwater study. In particular, it was intended to fill significant gaps in data relevant to the issue of ordnance, buried munitions, and burial pits at Camp Edwards. The intention of the MSP was to provide to stakeholders information about the current condition of the ranges and locations at Camp Edwards. The original set of tasks drafted in mid-1999 has been refined and modified as new information about buried ordnance at Camp Edwards has been discovered and analyzed.

The survey focuses on locating large burial pits or disposal sites because such sites were assumed to be potential sources of explosive chemicals detected in groundwater. Preliminary findings suggest that smaller burial sites or even individual unexploded ordnance can be located using geophysical techniques. All of the information gathered as part of the MSP will be utilized to support the UXO Feasibility Study required by the EPA Administrative Order No. 3.

Characterization investigations prior to project CP1155 initiation

Antitank ranges. Extensive range characterization research has been conducted by the Canadian Force Base (CFB) Valcartier, Quebec (Thiboutot et al. 1997, 1998, 2000, Ampleman et al. 2000, Dubé et al. 1999). Characterization of a light antitank weapon (LAW) rocket ranges at Fort Ord, CA, and at CFB Valcartier have also been studies 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 due to 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

μg kg^{-1} in surface soils at Valcartier, and as high as 587,000 μg kg^{-1} in surface soils at Fort Ord. However, TNT concentrations were only about one one-hundredth 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 (CFAD), 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 μg 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 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 (CHPPM) conducted a study at the artillery impact area at Camp Shelby, MS (U. S. Army Center for Health Protection and Preventative Medicine, in press). 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 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 Duxburg 1998; Kaplan 1993; Hawari et al. 2000; McCormick, Cornell and Kaplan 1985; Spanggord et al. 1983) and chemical reactions with soil components (Kaplan and Kaplan 1982, Caton, Williams, and Griest 1994, Pennington et al. 1995a, 1997, 1998, Thorne and Leggett 1997, Thorn 1997, Haderlein, Weissmahr, and Schwarzenbach 1996).

These studies have been focused on the principal high explosives contamination typically resulting from manufacturing and from loading, assembling and packaging (LAP) of explosives into casings. The primary difference between fate and transport of explosives residues on ranges and contamination associated with LAP facilities is the integrity of the delivery system, the transport of explosives from the munitions, and the environment (aquatic, terrestrial, wetland, etc.) in which the delivery system comes to rest. Instead of solubilized explosives concentrated in lagoons and washout areas as has been observed at LAP 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 on-going and leveraged studies

Range characterization

U. S. Army Alaska Public Works. The ERDC-CRREL 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.

Army Environmental Center. The Army Environmental Center is conducting a SERDP-sponsored project, CP 1226 "UXO Corrosion – Potential Contamination Source" to identify the type, character, and rate of perforations in casings of UXO underlying soil at U.S. military installations. The goal of the corrosion project is to examine approximately 200 pieces of ordnance during the study. Soils collected in proximity to UXO will be analyzed at ERDC. Data will be leveraged with data amassed in CP 1155. The Army Environmental Center is also conducting a "Range Sustainment Program" to proactively ensure access to ranges and to protect drinking water sources on active ranges. Project CP 1155 has been coordinated with this project and will share site access with this project whenever possible to benefit both efforts. Coordination with the AEC firing points emissions study, which will define airborne emissions from firings of various munitions, has also been achieved.

Confined Burn Facilities Projects. Efforts have been made over the last several years to find alternative to incineration, or open burning and open detonation of unnecessary munitions and explosives. Unlike SERDP Project CP1155, which focuses on post blast residues of munitions under active firing, these studies are focused primarily on air quality when disposing of unneeded munitions by burning or detonating. The Tooele Army Depot, Tooele, UT, has used various incineration technologies including a furnace capable of burning 140-180 kg of energetics material per hour, and the so-called "bang box" configurations for confined burning to capture air emissions for further treatment. A 1000 cubic meter "bang box" that can test 227 g of explosives or 2.27 kg of propellants has also been used at the Dugway Proving Ground, UT. The box, formally known as the Propellant, Explosive, and Pyrotechnic Thermal Treatment Evaluation and Test Facility, is instrumented to measure emissions. The Naval Sea System (NAVSEA) Surface Warfare Center Division, Indian Head, MD, also has a Confined Burn Facility (CBF) where they are conducting a project sponsored by ESTCP, "Confined Burn Facility Open Burning Ground Replacement Technology," the goal of which is to develop an environmentally acceptable, economical, and proven alternative to open burning of munitions.

Fate and transport studies

Army Environmental Quality Technology Program. Two studies are currently under execution at the ERDC-EL concerning fate and transport processes for explosives. The studies are funded

under the Installation Restoration Research Program (IRRP) 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 the 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 assessment 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 insure a comprehensive and unified database. Approximately 10 percent of the funds for defining fate and transport parameters will be contributed by the SERDP project.

UXO in marine environments. The Naval Facilities Engineering Service Center, Port Huene, CA, and the Space and Naval Warfare Systems Center, San Diego, CA, are conducting a study in conjunction with the ERDC Environmental Laboratory to determine toxicological and geochemical interactions of ordnance and explosives in marine environments. Geochemical studies will determine dissolution, adsorption, and transformation rates of explosives in marine environments. Process descriptors determined in freshwater will be compared with those determined in salt water to determine what descriptors are affected by salinity. Process descriptors for any explosives unique to marine activities will also be determined. The toxicology studies will focus on toxicity, bioaccumulation, trophic transfer, and tissue concentrations of explosives in marine environments, and the toxic effects of mixtures of explosives on marine organisms.

Scope of project CP1155

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 off-site 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 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 DoD with techniques to assess the potential for groundwater contamination from residues of high explosives (TNT, 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:

(1) Provide a unified database system that will include (a) 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 (b) 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.
(2) 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.
(3) Provide new data for the relevant environmental processes controlling the fate and transport of residues of high explosives on ranges.

Summary of previous year (FY00) results

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, 2,4DNT, 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%) 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 main charge debris resulting from low-order detonations.

Results of analysis of water samples obtained from 5 monitoring wells and 5 seeps that border the artillery range at Fort Lewis indicated a low level of RDX contamination (<1 ppb). 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, SW846 Method 8330 (USEPA 1994), detection limit of 250 μg 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 $\mu g\ kg^{-1}$ for many explosives residues and is particularly appropriate for use in range characterizations studies.

The distribution of explosives 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.

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 IRRP 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 surface than in aquifer soils.

Dissolution kinetics showed that the surface area estimation procedures were reproducible and accurately estimated the surface area of different amounts of explosives. Increased temperature and stir rate resulted in increased dissolution rates for TNT, RDX, and HMX. 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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2 Characterization of Explosives Contamination at Military Firing Ranges: Yakima Training Center, Washington Camp Guernsey, Wyoming

Introduction

Background

In the first year of this project, training ranges at Ft. Lewis, WA, were sampled to assess the potential for contamination of groundwater with explosives-related contaminants on military training ranges (Jenkins et al. 2001, Pennington et al. 2001). This included surface soil samples collected at three functional areas within the Ft. Lewis range complex; a hand grenade range impact area, a firing point for 105-mm howitzers, and a portion of the artillery and mortar impact area. Groundwater was sampled from monitoring wells and seepage areas around the periphery of the artillery range. Historical firing records from an electronic database were reviewed to determine the kinds of munitions items that had been fired on the heavy artillery range over time. Surface soil samples were also collected from a second hand grenade range at Ft. Richardson, Alaska. All of these samples were analyzed for the presence of explosives residues using a new GC-ECD method (SW846 Method 8095, USEPA 1999, Draft) that provides detection limits about two orders of magnitude lower than SW846 Method 8330 (USEPA 1994), the method commonly used for the analysis of explosives in soil and water.

RDX was detected in all of the soil samples, both surface and shallow subsurface, at both 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 were also detectable in most soils from these two grenade ranges. Recent results from detonations of hand grenades on a snow-covered range suggest that these residues were not due to high order detonation of grenades that functioned as engineered, but to the relatively few

low-order detonations of grenades that did not detonate when thrown and were subsequently detonated by EOD personnel. Overall, concentrations of explosives-related contaminants were an order of magnitude higher at the Fort Lewis grenade range than at the Fort Richardson grenade range, probably due to higher usage of the Fort Lewis range. While RDX concentrations were moderate, removal of the contaminant to prevent potential groundwater contamination should not be difficult because the size of ranges, particularly compared with the artillery range impact areas, are quite small.

At the Ft. Lewis artillery range, surface and near surface soil samples were collected at a 105-mm howitzer firing point and in the main impact area. At the firing point, samples were collected in front of two howitzers that had each fired about 600 rounds from the same position. Samples were collected at distances out to 10m and 20m for the two guns. Overall, 2,4-DNT, a component of single-based propellant was found at concentrations as high as 237,000 µg/kg in surface soil.

At the Fort Lewis artillery range impact area, soil samples were collected in and around craters formed by detonation of various artillery and mortar rounds. Concentrations of explosives residues associated with these high order detonations were very low, often below a detection limit of 1 µg/kg (1 part-per-billion). RDX, the analyte of most concern for groundwater contamination, was always less than 100 µg/kg in these soil samples.

Soil samples were also collected under and adjacent to a l55-mm round that had undergone a low-order detonation. In this case, the concentration of TNT was extremely high in the surface soil under the round (1.5%) and was still substantial in soils collected at 5- and 10-cm depths. Residues of explosives resulting from low-order detonations are many orders of magnitude higher than residues that result from high-order detonations.

Results of analysis of the water samples obtained from 5 monitoring wells and 5 seeps that border the artillery range at Fort Lewis indicated a low level (<1 µg/L) of RDX contamination (Jenkins et al 2001, Pennington et al. 2001). The source of this contamination was not determined. Results of soil analyses from Fort Lewis and Fort Greeley indicate that very low concentrations of explosives residues are more widely spread at testing and training ranges than observed previously (Jenkins et al 2001, Pennington et al. 2001, Walsh et al. 2001). The use of an analytical method that has lower detection limits than the current standard method for explosives residues, SW846 Method 8330 (USEPA 1994), detection limit of 250 µg/kg, 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 for many explosives residues and is particularly appropriate for use in range characterization studies. Method 8330

has been adequate for characterization of explosives contamination at Army ammunition plants and depots, where concentrations were much higher, but these limits may be inadequate to delineate contamination at many areas within training ranges.

The distribution of explosives residues at all the ranges investigated was spatially very heterogeneous. Concentrations of explosives-related compounds in soils collected less than a meter apart at hand grenade ranges differed by over two orders of magnitude. At artillery firing points, concentrations of propellant residues differed by as much as an order of magnitude over the same distance. At artillery impact areas, the spatial heterogeneity was large as well, although it is difficult to define numerically since many of the concentrations were below detection limits. Concentrations of explosives residues for soils collected in areas that were visibly free of craters, however, often had explosives concentrations as high or higher than soils collected from the rim of a fresh crater. Thus site characterization using discrete samples will not provide representative samples even over fairly small areas, and a sampling strategy employing multi-increment (or composite) samples will be necessary to provide quality data for making important range management and /or remediation decisions.

Objectives

The overall objective of the range characterization portion of this project was to assess the potential for contamination of groundwater with explosives-related contaminants on military training ranges. Objectives for the FY 2001 study were to sample two additional installations with various types of range activities. This was to include both firing points and impact areas for artillery and mortars, and an antitank firing range. A specific objective was to test the use of composite sampling as a means of collecting representative samples in areas with various contamination sources. An addition objective was to determine whether surface intact and ruptured UXO items were localized contamination sources at the various types of ranges. These sampling studies at firing points and impact ranges will also be used to determine if the conclusions obtained at the Fort Lewis artillery ranges can be generalized to other sites.

Yakima Training Center, WA

Location

Yakima Training Center occupies most of the land between the Columbia River and Interstate Highways 90 and 82, in central Washington state (Figure 1). The 510-square-mile facility includes one of the two largest unaltered shrub-steppe habitats in Washington state (the other is the Hanford Reservation). Shrub-steppe in Washington is characterized by generally dry areas of sagebrush and bunchgrass. Military

training has taken place at the center since 1942. The climate is arid with an annual rainfall of 7.9 inches, measured in the city of Yakima.

Approach

Surface soils were sampled at several different types of ranges at YTC in May 2001. These locations include the following: a firing point and an impact area at an antitank range, firing points and impact areas for 155-mm howitzers, a firing point for the 120-mm main tank gun, and the detonation point for a Claymore mine. Surface water samples were collected at several points where surface streams were found either in or on the boundary of the Central Impact Area. Several potable water wells were also sampled.

Antitank range

Initial sampling was conducted at Range 7, which is used for practice with light anti armor weapons (LAW), AT-4 antitank rockets, and 40-mm grenades, including those filled with high explosives (HE). Soil sampling at this site included surface composite samples and discrete samples from the surface to depths as deep as 15 cm. Surface samples were collected from 0–1 cm.

The area around one of the most heavily impacted targets, an armored personnel carrier (APC), was selected for intensive sampling (Figure 2). Duplicate surface composite samples were collected around the perimeter of this target within distance intervals from the edge of the APC of 0-2m, 2-5m, 5-10m and 10-15m (Figure 3). Discrete surface and shallow subsurface samples (to 5 cm) were also collected at several points within this area. Discrete and shallow subsurface samples were also collected next to an intact 40-mm (HE-filled) grenade, and a cracked HE-filled LAW rocket (Figure 4). Duplicate surface composite soil samples were collected in an area 5–10 m in front of the firing point for LAW and AT-4 rockets at Range 7.

Multi-Purpose Range Complex, 120-mm tank firing point

The next range sampled was referred to as the Multi-Purpose Range Complex (MPRC). This range is set up as a battle run for tanks. The main tank gun (120-mm) was fired at several fixed positions against an array of moving targets (Figure 5). One of the fixed firing points at this range was sampled as shown in Figure 6. Surface composite, surface discrete, and several shallow subsurface discrete samples (1–2 cm) were collected for this firing point, up to 75 m from the muzzle position. Apparently, both single- and double-based propellants are used with this weapon.

155-mm howitzer firing points

Several firing point positions recently used for practice firing of 155-mm howitzers were visually inspected. The gun positions used at these firing points were located by finding the disturbed soils resulting from the rear spades that are used to absorb the gun recoil. Several of these gun positions were clearly identifiable by the deep indentations in the soil. Based on the dimensions of the howitzers, the position of the muzzle and the direction of fire were estimated. From the soil conditions and information from range control, these firing activities were determined to have occurred within the past several months.

Surface composite samples were collected in several zones at distances of 5, 10, 20 and 50 meters for one gun position as shown in Figure 7. Discrete surface and shallow subsurface samples (as deep as 5 cm) were also collected as shown. Duplicate surface soil composites were collected in an identical pattern at a second gun position. No discrete samples were collected at this position.

Apparently, both single- and triple-based propellant are used for 155-mm howitzers. The major component of single-based propellant is nitrocellulose, while 2,4DNT is used as a plasticizer. The major components of triple-based propellants are nitrocellulose, nitroglycerine (NG), and nitroguanidine.

A set of composite and discrete samples were also collected at the recently used firing point of a M 198 (155-mm) direct fire gun. Four composite and 12 discrete surface samples were collected as shown at distances as great as 32 m from the firing pad (Figure 8).

Mortar firing point

A portion of the range used for practice firing of various types of mortars was sampled. As with the artillery firing points, the exact positions of individual mortars were unknown. Visual reconnaissance was used to locate and identify an individual position, which appeared to be a firing position for an 81-mm mortar. Figure 9 shows the exact layout for surface composite and discrete samples collected at this site. Samples were collected as far as 20 m from the firing point at this location. The double-based propellant for 81-mm mortars is composed of 57.75% nitrocellulose, 40.0% NG, 1.5% potassium nitrate and 0.75% ethyl centralite (diethyldiphenyl urea

HEP 105-mm round

Two discrete samples were collected under a HEP (high explosive plastic) 105-mm round that

was found between OP-1 (observation point 1) and OP-2. The first sample was collected directly under the round (0–1 cm) and the second was collected at the 1–2 cm depth. It appeared that the round had been blown in place using C4, but was not totally destroyed.

Central impact area

Several sets of samples were collected in areas that had recently been targeted with 155-mm howitzer fire in the Central Impact Area. The first area was within an old bomb crater and around a recent 155-mm crater that was 9 meters from a tank target (Figure 10). Four discrete samples were collected around the crater rim at the cardinal directions. Duplicate surface composites were collected around the perimeter of the crater, 1-m from the edge of the rim.

A second set of samples was collected around the rim of a single 155-mm crater. Four discrete surface samples were collected as discussed above. Four composite samples were also collected at distances as far as 8 m from the center of the crater (Figure 11).

Several discrete samples were collected near a 155-mm white phosphorus (WP) dud and near a new 155-mm HE (intact) round. A discrete surface soil sample and two depth samples (as deep as 5 cm) were collected in the area of a 155-mm low order illumination round. A corroded 105-mm dud was also observed in this area as well. Surface discrete samples were collected next to the nose and tail of this round.

A discrete sample was collected in the center and four discrete samples were collected around the rim of a 155-mm crater. Two discrete surface samples were collected next to an illumination round located next to the 155-mm crater (Figure 12). Five discrete samples were collected around a second crater in an identical manner. One composite sample was collected in a 1-m perimeter around this second crater (Figure 13).

Four discrete surface samples and a single composite sample were collected near a ruptured 81-mm illumination mortar round in a crater. One surface sample was collected under the round.

Claymore mine detonation area

The final area sampled at YTC was on the edge of the central impact area where a Claymore mine had been detonated within the previous week. Four composite and 12 discrete surface samples were at distances as great as 30 m from the point of detonation (Figure 14).

Water sampling

Three potable water wells and three surface water locations were sampled. The potable water wells included one inside the pump house near Yakima Research Station, one at the intersection of Training Areas 2A and 3B, and one at the intersection of Training Areas 8B and 11B. These were sampled by tapping the spigots. Surface water was sampled at Selah Creek in Range 10, in Lmumma Creek just off the road at the northwestern edge of Range 19, and in Lmumma Creek on the Central Impact Area near the lowest point on the range in a stand of willows and reeds. Surface water was sampled by placing the sample container into the stream. 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 under Materials and Methods). 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.

Camp Guernsey, WY

Location and setting

Camp Guernsey has been a component of the Wyoming National Guard since 1939. It is located in Southeastern Wyoming on the North Platte River about 90 miles north of Cheyenne. It encompasses about 34,000 acres of which 31,360 acres are available for training. The climate in the summer is generally dry with warm days and cool nights. The total annual precipitation is 9 inches with 70% of that falling during the growing season. The terrain consists of rolling hills covered with blue gramma, buffalo grass and sagebrush. The soil is predominantly sandy loam. The elevation ranges from 4300 to 5280 feet.

Soil sampling at Camp Guernsey was concentrated at the artillery impact area and was conducted the week of September 17, 2001 (Figure 15), and at an artillery firing point where 155-mm howitzers were fired on October 1, 2001. Surface water samples were also collected on September 24, 2001.

Approach

Just before our sampling activities the artillery range had been used for training by various units with 155-mm howitzers using HE, WP and illumination rounds. Several unexploded 155-mm rounds of various types were found and identified by EOD personnel from the Wyoming National Guard.

Artillery impact area

There are a number of individual targets in the artillery impact area at Camp Guernsey. These targets are vehicles of various types (trucks, armored personnel carriers, etc.) and were used primarily for target practice using 155-mm howitzers and various types of mortars. One truck target was selected at random which appeared to have been used to about the same degree as others within the area based on debris and target damage (Figure 16).

Duplicate surface composite samples were collected in an elliptical pattern at distances averaging 1, 5, 10 and 15±1 m from the truck target. Each composite sample was made up of 30 individual increments collected within the top 1.0 cm of soil. Discrete surface and shallow subsurface soil samples were also collected at 1, 5, 10 and 15 m from the target. The depths of individual samples were in most cases 0-1 cm, 1-5 cm, 5-10 cm, and 10-15 cm.

A set of core samples was collected at depths from the surface to 16 cm adjacent to a broken 155-mm round.

Low order rounds and a low order 500-lb bomb

Perimeter composite samples were collected as described above at distances of 3, 5, and 10 meters from an unexploded 155-mm HE round (UXO 1). Duplicate discrete samples were also collected at these same distances from the round; duplicates were collected a meter apart.

Discrete and composite samples were collected in an identical manner around a second unexploded 155-mm round (UXO 2) and around an unexploded 81-mm mortar round and a 155-mm round lying together (UXO 3).

Soil samples were collected around a low-order 500-lb bomb (Mark 82) estimated by personnel from the Wyoming National Guard to have been on site for at least 2 years (Figure 17). The explosive

that remained in the bomb (estimated at 50 lb) had turned red in the sun suggesting that the main charge was TNT. Reddish colored surface soil was observed in several locations at distances as far as 4.7 meters from the bomb. Discrete surface and subsurface soil samples were collected in areas where the reddish colored soils were observed. Composite soil samples were also collected around the perimeter of this low-order detonation at 3, 5, and 10 meters from the bomb.

Blow-in-place of UXO items and low order 500-lb bomb

After the soil samples were collected around these items, a team of personnel from the Wyoming National Guard and Special Forces 3rd BN 10th SFG (A) detonated UXO 1, 2, and 3 and the low order 500-lb bomb on the afternoon of 19 September. For UXO 1 and 2, two 1.25-lb blocks of C4 were used. For UXO 3, four C4 blocks were used, and for the 500-lb bomb, three C4 blocks were used.

The following morning duplicate composite and discrete soil samples were collected in and around the craters formed from these detonations. For UXO 1, surface composites were collected around the perimeter of the crater at distances of 3, 5, and 10 meters. Discrete surface samples were collected in the center and around the perimeter of the crater at 70 cm (four samples in the cardinal directions). Duplicate surface discrete samples were also collected at 3, 5, and 10 m southwest of the center of the crater as described above.

At the craters formed from the detonation of UXOs 2 and 3, duplicate surface composites were collected at 3, 5 and 10 meters. Discrete surface samples were collected around the crater, either 50 cm or 1.5 m from the center and duplicate discrete samples were collected at 3, 5, and 10 meters as described above.

For the crater formed from the detonation of the bomb, duplicate surface composite samples were collected at distances of 3, 5, and 10 meters from the crater. Surface discrete samples were collected at the center of the crater and around the rim in the four cardinal directions. Duplicate discrete samples were also collected at 3, 5, and 10 m south of the crater. A set of 7 discrete samples was collected using a wheel pattern (4 ft diameter) centered at 3.5 m southeast of the crater (Figure 18) (Jenkins et al. 1997a).

Artillery firing points

Since no firing activity took place during the week we sampled at Camp Guernsey, Col. Joe Michaels, Facility Manager at Camp Guernsey, volunteered to collect soil samples before and after firing of 155-mm howitzers using our sampling design (Figure 19). This activity was conducted two weeks after the primary sampling event.

To collect firing point samples, two gun positions were set and centerlines established from the muzzle in the direction of fire. A set of duplicate composite surface soil samples were collected for each gun position, prior to firing, perpendicular to the center line at distances 0, 5, 10, 20, and 50 meter from the muzzle. The 0-m samples were collected at a distance of three meters on both sides of the centerline. The 5- and 10-m samples were collected five meters on both sides of the centerline, and the 20- and 50-m samples were collected 10 m on both sides of the centerline. At least 30 increments were collected per sample.

After the three 155-mm howitzer battery had fired 43 rounds, samples were collected in an identical manner in front of both guns. All rounds fired used green bag charge 3 (D540 M3), single-based propellant. Samples were shipped on ice to CRREL by overnight carrier.

Surface water sampling

Surface water samples were collected at the same sites included on the facility routine monitoring plan. These included the following springs: Deer Corn and Ryan Springs in the North Training Area, Sawmill Springs in Sawmill Canyon just northwest of the Artillery Range Impact Area, and Pet Springs just south of the Artillery Range Impact Area (Figure 15).

Materials and Methods

Soil sample collection and shipment

All surface composite soil samples at YTC and CG were collected using stainless steel hand shovels, which were carefully wiped with clean towels, washed with acetone, and air dried between samples. Each sample was composed of at least 30 individual increments collected randomly within the area sampled. Individual increments were collected from 0–1 cm from the surface. As individual increments were collected, they were placed into polyethylene plastic bags, which were sealed with twist ties once all increments for a given composite were collected. Each bag was placed in a zip-lock bag and

shipped to the laboratory in ice filled coolers (FedEx overnight). Upon arrival at CRREL the samples were frozen at –30°C until extracted and analyzed.

Surface discrete samples were collected in an identical manner as individual increments for the composites. Depth samples were collected using a 3/4-inch stainless steel soil corer. Sampling devices were cleaned as described above between samples. Discrete samples were placed into glass jars, enclosed within a zip lock bag, shipped to CRREL, and frozen as described above.

Soil extraction

Soil samples were allowed to warm to room temperature, and air-dried. Dried soils were either homogenized within the laboratory, or ground using a Lab Tech ESTA Vibratory Ring Mill (grinding was conducted by Chuck Ramsey) prior to subsampling. Whether soils were ground or not, subsampling was conducted by spreading the soil into a thin layer in an aluminum pie pan, mixing thoroughly, and randomly collecting at least 10 individual portions using a stainless steel spatula to create a 10-g subsample. Each subsample was placed into a 40-ml glass vial and a 20-ml aliquot of acetonitrile (AcN) was added. The vials were then individually placed on a vortex mixer for 30 seconds to suspend the soil particles, and the vials were placed in an ultrasonic bath for 18 hours. The temperature of the bath was maintained at less than 25°C with cooling water. The vials were then removed from the bath and allowed to stand undisturbed for at least 30 minutes. For samples to be analyzed by gas chromatography (GC), the extracts were filtered through a 25-mm Millex-FH (0.45 µm) disposable filter, discarding the first milliliter and collecting the remainder in a clean autosampler vial. For samples to be analyzed by reversed-phase high performance liquid chromatography (RP-HPLC), a 1.0-ml portion of the filtered extract was mixed with 4.0 mL of reagent grade water. These processed extracts were refrigerated until analyzed. Most samples from YTC and CG were analyzed by GC. High concentration samples were analyzed by RP-HPLC. The decision on which type of analysis to conduct first was made based on our knowledge of the concentrations of analytes that would likely be present for a given type of sample. For instance, results from previous investigations indicated that concentrations of HMX in soil samples from antitank rocket ranges were often in the 10,000 to 100,000 µg/kg range (Jenkins et al. 1997b; Jenkins et al. 1998). This is well above the linear range of the GC-ECD detector, but easily analyzed by RP-HPLC-UV. For artillery ranges, however, results from the work at Ft. Lewis indicated that the concentrations of explosives in most samples are below 50 µg/kg (Jenkins et al. 2001; Pennington et al. 2001), too low for RP-HPLC-UV analysis, but detectable using GC-ECD.

GC-ECD analysis

The autosampler vials containing the acetonitrile soil extracts were placed into GC autosampler trays that were continuously refrigerated by circulating 0°C glycol/water through the trays. The samples were injected into an HP-6890 GC equipped with a micro cell Ni^{63} micro-electron capture detector (GC-μECD). Results were obtained according to the general procedure outlined in EPA SW846 Method 8095 (EPA 1999, Draft). Direct injection of 1 μL of soil extract was made into a purged packed inlet port (250°C) equipped with a deactivated Restek Uniliner. Primary analysis was conducted on a 6-m x 0.32-mm ID fused-silica column, with a 1.5-μm film thickness of 5%-(phenyl)-methylsiloxane (RTX-5 from Restek, Bellefonte, PA). The GC oven was temperature programmed as follows: 100°C for 2 min, 10°C/min ramp to 260°C, 2-min hold. The carrier gas was helium at 10 mL/min (linear velocity approximately 90 cm/sec). The ECD makeup gas was nitrogen flowing at 40 mL/min. If a peak was observed in the retention window for a specific signature compound, the extract was reanalyzed on a confirmation column, 6 m x 0.53 mm ID having a 0.1-μm film thickness of 50 % cyanopropylmethyl – 50 % phenylmethyl-polysiloxane (RTX-225 from Restek). Further details of the procedure may be found in SW-846 Method 8095 (USEPA 1999, Draft). If analyte concentrations were within the linear range of the ECD, concentrations reported were taken from the determination on the primary column, unless there appeared to be co-elution with another compound. In such cases, reported concentrations were taken from the determination of the confirmation column. Estimated detection limits for the GC-ECD analysis are given in Table 1.

RP-HPLC analysis

Extracts were also analyzed by RP-HPLC according to the general outline provide in SW846 Method 8330 (USEPA 1994). When samples were analyzed by both GC-ECD and RP-HPLC, concentrations above 500 μg/kg were taken from the HPLC analysis, which had a higher range of linearity. RP-HPLC analysis was conducted on either a SpectraSystem AS3000 set at 254 nm, or a modular system composed of a Spectra-Physics Model SP8800 ternary HPLC pump, a Spectra-Physics Spectra 100 variable wavelength 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 3396A digital integrator set to measure peak heights. Separations were conducted on a 15-cm × 3.9 mm NovaPak C-8 column (Waters, Milford, MA) eluted with 85/15 water/isopropanol (v/v) at 1.4 mL/min. Samples were introduced by overfilling a 100-μL sampling loop. Concentrations were estimated against a multianalyte standard using peak heights. Estimated detection limits for the RP-HPLC method are presented in Table 1.

Soil geochemistry

Selected composite soil samples were analyzed for pH (Mehlich 1984), total Kjeldahl nitrogen and total organic carbon (TOC) (American Public Health Association 1985), particle-size distribution (Day 1956 as modified by Patrick 1958, Gee and Bauder 1986), cation exchange capacity (CEC) (Rhoades 1982), and total iron (Olson and Ellis 1982).

Analyses of water

Laboratory analyses for geochemical parameters included total iron, calcium, magnesium and manganese (Method 6010, USEPA 1988a), 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, and 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.

Analysis of water samples for explosives was conducted by GC-ECD according to SW846 Method 8095 (USEPA 1999, draft). Samples were extracted using solid phase extraction and eluted with acetonitrile. Extracts were analyzed by GC-ECD as described above. Analytes and method detection limits are provided in Table 1.

Results and Discussion

Yakima Training Center, WA

Antitank Range

Analytical results from discrete and composite soil samples collected at the antitank firing range at Yakima Training Center are presented in Table 2. HMX was the analyte found at highest concentration in nearly every soil sample collected near the armored personnel carrier (APC) target. Mean HMX surface concentrations in the composite samples collected at distances from the APC decreased from about 47,000 µg/kg at 0-2 m, to 16,000 µg/kg at 2-5 m, to 6,300 µg/kg at 5-10 m, and to 3,600 µg/kg at 10-15 m. High concentrations of HMX in soils at antitank ranges have been observed at Canadian Force Base Valcartier (Jenkins et al. 1997b, Thiboutot et al. 1998), Ft. Ord (Jenkins et al. 1998), and at several other Canadian antitank ranges (Thiboutot et al. 1998). The presence of HMX as the major contaminant at antitank ranges is consistent with the use of LAW and AT-4 rockets on these ranges. High concentrations in surface soils are thought to arise due to the high incidence of rupture of these rockets without detonation, spreading the explosive fill onto the soil. The explosive fill for these rockets is octol, which is

70 % military grade HMX and 30 % military grade TNT. According to specification, RDX in military Grade A HMX cannot exceed 7 %; in Grade B HMX, RDX cannot exceed 2 % (U.S. Army 1984).

The concentration of HMX in shallow subsurface soils is also presented in Table 2. At a distance of 1 m from the APC, for example, HMX concentrations at depths of 0-1 cm, 1-3 cm, 3-7 cm and 7-10 cm were 53,500, 18,200, 26,700, and 1,180 µg/kg, respectively. Except for samples collected very close to the APC (0.5 m), concentrations generally decline substantially in going from the surface to depth. HMX concentrations in soil collected next to a broken LAW rocket were much higher, ranging from 10,400,000 µg/kg in surface soil, 1,020,000 µg/kg in soil at 2-6 cm depth, and 49,300 µg/kg at a 6-10 cm depth.

Mean RDX concentrations in the surface composite samples decline regularly from 1,930 µg/kg at a distance of 0-2 m from the target to 88 µg/kg at a distance of 10-15 m. RDX concentrations also decline with depth. For example, the concentration of RDX in a core sample collected 1 m from the target decline from 7,070 µg/kg in the surface soil to only 315 µg/kg at a depth of 7-10 cm (Table 2). Similarly, RDX declines from 45,700 µg/kg at the surface, to 4,760 µg/kg at the 2-6 cm depth, and to 1,530 µg/kg at the 6-10 cm depth for samples collected next to a broken LAW rocket. While RDX concentrations are generally much lower than HMX, RDX may be of greater concern since RDX has a higher reported toxicity than HMX and is the contaminant of most concern in the ground water at MMR (USEPA 1988b, 2000).

In the mean composite samples RDX concentrations range from 1.9 to 6.6 % of the HMX present. These values are within the range expected if the RDX originated as an impurity in military grade HMX. However, results from the discrete samples indicate that the percentage of RDX relative to HMX ranges as high as 121% for surface samples collected about 50 cm from the target. In addition, the percent of RDX relative to HMX generally increases at depth, probably due to the higher solubility of RDX relative to HMX (about 60 mg/L for RDX and about 5 mg/L for HMX) (Burrows et al. 1989). Thus there must be another source of RDX contamination at this range. This source of RDX may be either 40-mm grenades, which are also fired at this range, or C4, which is used to dispose of duds that are encountered by EOD personnel. Many 40-mm practice rounds were found on the site as well as one live, intact 40-mm HE filled grenade (Figure 20).

Despite the high concentration of TNT in octol (30%), concentrations of TNT, and the major TNT transformation products (4-ADNT and 2-ADNT), were much lower than either HMX or RDX in the antitank ranges soils. The exception was for a soil sample collected next to a ruptured LAW rocket where

TNT was present at very high concentration (358,000 µg/kg) and the HMX/TNT ratio was only slightly lower than that in octol. Generally the concentrations of TNT, 4ADNT, and 2ADNT were below RP-HPLC detection limits of about 100 µg/kg. These antitank range soils were not analyzed by GC-ECD due to the very high HMX and RDX concentrations, which could contaminate the injector and electron capture detector, and result in excessive instrument down time. The much lower TNT concentration in these soils, relative to HMX, is consistent with results from the Arnhem antitank range at CFB Valcartier (Jenkins et al. 1997b) and the antitank range at Ft. Ord (Jenkins et al. 1998). This is likely due to environmental transformation of TNT to its mono amino derivatives (4ADNT and 2ADNT) and subsequent humification of these compounds (Thorne and Leggett 1997). Under the aerobic conditions generally present in surface soils in the arid environment at Yakima, HMX and RDX will not be subject to these types of degradative processes. In addition, HMX and RDX have lower water solubilities than TNT, dissolve much slower into water than TNT, and hence a greater percentage remains at the surface where they were deposited (Lynch et al. 2001).

Relatively low concentrations of 2,4DNT (generally less than 100 µg/kg) were detectable in composite samples near the tank target. Concentrations were higher than those found for TNT in many of these samples. Initially its source was attributed to single based propellant where it is used as a plasticizer. However, the concentrations of 2,4DNT in surface composites near the firing point were either below or just above the detection limit (about 1 µg/kg). Therefore, it does not appear that propellant can be the source of 2,4DNT in this case.

Nitroglycerine (NG) was also found in all of the composite and in several discrete samples collected near the target area of the antitank range. In the composite samples, however, the NG was distributed differently than the HMX. For example, there is no apparent concentration decrease as sample distances from the target increases. Unlike 2,4DNT the source of the NG is probably the propellant used for the antitank rockets which is triple based and contains about 20% NG. In previous studies of antitank ranges, data were not reported for NG (Jenkins et al. 1997b, Thiboutot et al. 1998). However, when GC-ECD chromatograms for samples from the Arnhem range at CFB Valcartier were re-examined, peaks for NG were observed. Therefore, NG is likely to be present at other antitank ranges as well.

Two composite surface soil samples were also collected 5-10 m in front of the LAW and Rocket firing points (Table 2). This location was at least 100 m from the impact area; hence, any compounds detected should be associated with firing activities rather than detonations. NG was the only target analyte detected in these samples above analytical detection limits. The mean concentration of NG in this

region was 2,740 µg/kg. The source of NG at the firing points must be the propellants used in these munitions.

Multi-Purpose Range Complex (MPRC), 120-mm tank firing point

Analytical results for soil samples collected in front of the tank firing position on the MPRC are presented in Table 3. Two components of gun propellants, NG and 2,4DNT, were found 10 meters in front of the firing position at concentrations as high as 17,000 µg/kg and 33,000 µg/kg, respectively. This confirms that both single-and double-based propellants are used at this range. Detectable concentrations of both analytes were still detectable 75 m from the firing point, the farthest distance sampled. These analytes were detected over the width sampled, which was 30 meters (15 meters to either side of our center line drawn from the firing point to the nearest target). Based on these results two types of propellant were used at this firing point, single-based propellant in which 2,4DNT is used as a plasticizer, and triple-based propellant which is composed of NG, nitrocellulose and nitroguanidine. The area in which these residues were deposited appears to be quite large, at least 2,600 m^2.

2,6DNT was also detected in most of the samples collected at this firing point. 2,6DNT is an impurity in military grade 2,4DNT. The ratio of 2,4- to 2,6DNT in the five discrete samples where the 2,6DNT was present above 100 µg/kg was 68±14 µg/kg. Recent results from biodegradation studies by Spain (Personal communication[*]) indicate that 2,6DNT does not degrade to any extent when 2,4DNT is present and the ratio of 2,4- to 2,6DNT decreases as biodegradation takes place. The ratio of 68 indicated that this material had undergone very little degradation since being deposited from firing activities.

Concentrations of NG in the surface soils (0-2.5 cm) 20-m from the firing position ranged from 442 to 6,610 µg/kg for NG while samples collected at the 2.5- to 5-cm depth ranged from 62 to 1,400 µg/kg. Likewise for 2,4DNT, concentrations in the top 2.5 cm ranged from 660 to 9,360 µg/kg, while at the 2.5-5-cm depth they ranged from 149 to 5,300 µg/kg. Thus, some downward transport of these compounds has occurred even at this arid site. Deeper samples were not collected due to concerns about the possible presence of UXO.

[*] Dr. James Spain, US Air Force Research Laboratory, Tyndall Air Force Base, Florida, personal communication, 2001.

The mean 2,4- to 2,6DNT ratio in the five subsurface soil samples was 76±16. This ratio indicated that very little biodegradation of the 2,4DNT had occurred in the subsoil at the time these samples were collected.

The only other energetics-related compounds detected at the MPRC were in a few samples, generally near the firing point, where low concentrations of TNT and RDX were detected. The samples where TNT was detected generally had 2,4DNT concentrations in excess of 3,000 µg/kg indicating that the TNT was probably an impurity in the military grade 2,4DNT. The source of the low levels of RDX in a few of these soil samples is unknown.

155-mm howitzer firing points

Results from the analysis of discrete and composite soil samples from two 155-mm howitzer firing points are shown in Table 4. No target analytes were detected in composite samples collected at Gun Position 1. In the composites from Gun Position 2, 2,4DNT was found in 5 of the 13 samples. This included both duplicates at distances of 5 and 10 m from the muzzle, and one of the two duplicates collected at 20 m from the muzzle. Concentrations in these samples ranged from 11 to 94 µg/kg. No NG or other explosives-related analytes were detected in any of these composites.

In the discrete samples from Gun Position 1, 2,4DNT was detected in 6 of the 23 surface samples. The highest concentration was 2,670 µg/kg for a sample right under the muzzle. Concentrations of 2,4DNT in the remaining 6 samples ranged from 5 to 185 µg/kg with these positive samples located randomly over the area sampled and as far from the muzzle position as 50 m. 2,4DNT was not detected in the five shallow subsurface samples.

NG was not detected in any of the discrete or composite samples. RDX was detected in two discrete samples, but the concentrations were only 5 and 9 µg/kg, respectively.

Overall, the concentrations of explosives and propellant residues at the 155-mm firing point were very low, even when detectable using GC-ECD Method 8095. This result agrees with that found at Camp Shelby, MS (CHPPM 2000), where almost all results were below the detection limit of the analytical method used (RP-HPLC Method 8330). The fact that 2,4DNT was detected at the Yakima firing points and NG was not indicates that the propellant used at these firing points was probably single-based, where 2,4DNT is the plasticizer with nitrocellulose as the main component.

The final firing point position sampled at YTC was a position used for direct fire of 155-mm howitzers. This position was within a hundred meters of the central impact area and had recently been used for firing activity. Four composite samples were collected at distances ranging from 7 to 32 m from the firing pad. Analysis of these samples indicated the presence of NG and 2,4DNT, but the deposition pattern appears to indicate independent deposition of the two propellant-related analytes (Table 5). For NG, the concentrations decline at increasing distance from the firing pad; for 2,4DNT, the concentrations are only detectable at distances of 22 and 32 m from the pad. Thus it appears that triple-based propellant was used for the direct fire of the 155-mm howitzers and that some other firing activity also took place at this location, depositing 2,4DNT.

Results from analysis of the 12 discrete samples collected at this area are consistent with the results from the composite samples. Again NG and 2,4DNT were detected in many of these samples with the highest 2,4DNT concentrations for samples collected at 22 and 32 m from the firing pad. The concentration gradient for NG, as a function of distance from the pad, was not identifiable in the discrete samples. The highest concentrations for NG in the discrete samples were found at 12 and 22 m from the pad.

Mortar firing point

The results from analysis of surface soil samples from the 81-mm mortar firing position are presented in Table 6. Four composite samples were collected 5, 10, 15, and 20 m from the position of the base plate, as indicated by physical soil disturbance. NG was detected in three of the four samples at distances as far as 10 m from the base plate position at concentrations ranging from 2 to 246 µg/kg. No other target analytes were detected. These results were consistent with the composition of the double-based propellant used with 81-mm mortars.

A set of 13 discrete samples was also collected within the same area. NG was detected in 7 of the 13 at distances as far as 20 m from the base plate location, but concentrations were always less than 45 µg/kg. NG was detected in some samples at a given distance, but not in others from the same distance. The lack of a discernable pattern to this deposition indicates that the deposition was spatially random. As with the composite samples, no other target analytes were detected in any of these discrete samples.

If samples from this location had been analyzed by RP-HPLC, NG would not have been detected, even if a modification to Method 8330 had been employed in which a lower wavelength was used on the UV detector.

Central impact area

Several target analytes were detected in one or more of the eight samples collected in and near four detonation craters at the artillery range impact area. However, concentrations were always less than 25 µg/kg (Table 7). RDX was detected in four of these samples with a maximum concentration of 17 µg/kg. NG was detected in two samples, and 2ADNT and 4ADNT were detected in one.

Results for the discrete samples collected around the same four craters, plus a fifth one, confirm that target analyte concentrations are very low. RDX was detected in 1 of the 22 crater samples, but the concentration was only 8 µg/kg. No other target analytes were detected in these samples.

Samples were also collected in the impact area around various types of objects that we observed during range reconnaissance. Surface soil was sampled under the nose of relatively recent in tact 155-mm howitzer round that we observed on the surface. Analysis indicated that RDX was present at 719 µg/kg. In addition, 2ADNT and 4ADNT, transformation products of TNT, were found at 49 and 58 µg/kg, respectively. The presence of the environmental transformation products of TNT demonstrated that while TNT was not detected, it had been present at some point in the past.

Soil samples were collected under the front and back of a corroded 155-mm dud that was tentatively identified by EOD personnel as a WP round. Concentrations of RDX were 6,720 and 53,500 µg/kg for soils collected under the front and back of the round, respectively. RDX is used in the burster for this round. Water had apparently entered the round and leached RDX into the soil beneath. HMX, a manufacturing impurity of RDX, was present in the soil as well.

Using the more sensitive GC-ECD method, no target analytes were detected in the set of surface and shallow subsurface soils beneath a 155-mm illumination round.

Several target analytes were detected in two surface soil samples collected next to a very corroded 105-mm HE dud that was sitting on the surface. These included RDX, 2,4DNT, 2,6T, 2ADNT, 4ADNT and PETN. The highest concentration was for 2,4DNT at 144 µg/kg in one of the samples. 2,4DNT is not a component of the explosive in 105-mm howitzer rounds and was probably deposited from a different source, such as propellant. The RDX concentrations in these two samples were 7 and 8 µg/kg. The concentrations of 2ADNT and 4ADNT were 9 and 5 µg/kg in one of the two samples. TNT was not detected, but the presence of the monoamino transformation products indicated that it had been

present at one time. The low concentrations of RDX and the TNT transformation products could have originated from Composition B in the 105-mm dud. However, the very low concentrations indicated that the round is not yet a significant source of explosives residues to the site.

Except for a very small concentration of NG (4 µg/kg) in one of the two samples, no target analytes were detected next to an Air Force illumination round. A low concentration of NG (12 µg/kg) was detected in the surface soil next to a 105-mm HEP (high explosive plastic) round, but not in the subsurface. No other target analytes were detected in these samples.

Claymore mine

The results for the four surface composite samples collected in front of the detonation point for a Claymore mine are presented in Table 8. The only target analytes detected in these samples were NG and 2,4DNT. Concentrations of NG in the 5-, 10-, and 15-m samples, were 1,270, 66, and 96 µg/kg while the concentration at 20 m was less than the detection limit. For 2,4DNT, the concentration found at 10 m was 4 µg/kg, while at 15 m it was 3 µg/kg.

Nearly identical results were found from analysis of the 12 discrete samples collected in this same area. Mean NG concentrations declined from 851 µg/kg at 5 m, to 151 µg/kg at 10 m, to 132 µg/kg at 15 m, and to 72 µg/kg at 20 m. 2,4DNT was detected in 7 of the 12 samples with concentrations randomly varying from 4 to 18 µg/kg. The only other target analyte detected in these samples was RDX (2 µg/kg), in one of the three samples collected at the 5-meter distance.

The Claymore mine that was detonated was placed along the fence line separating the impact area of the range from the maneuver and firing point area. Since Claymore mines do not contain NG or 2,4DNT, their presence in these samples was not due to the detonation of the Claymore. Rather, these compounds were undoubtedly deposited from propellants from artillery and mortars fired over the fence line into the impact area. The small amount of RDX found in one sample may have originated from the Claymore mine, but the inability to detect RDX in the other samples makes even that uncertain.

Soil geochemistry

Soils at the Yakima Training Center are loam to sandy loam with a slightly acid pH (Table 9). TOC and CEC are moderate, averaging less than 2 % and 10 meq 100 g^{-1}, respectively. Soils are generally typical of the region.

Potable and surface water

Ground and surface water was generally soft (sum of Ca and Mg <50 mg L^{-1}, Table 10). Total iron was less than the EPA drinking water standard of 0.3 mg L^{-1}, except in surface water from Lmumma Creek on the impact area where it was only slightly higher (0.62 mg L^{-1}). All other parameters were low and typical of the environment. No explosives or degradation products of explosives were detected.

Camp Guernsey, WY

Artillery impact area

A set of multi-increment composite soil samples was collected as shown in Figure 21. The results for the surface composites around the truck target selected on the artillery range at Camp Guernsey indicated that the concentrations of explosives residues were quite low (Table 11). The highest concentrations were for HMX in the samples nearest the target (1-m samples) with a mean concentration for duplicates of 151 µg/kg. RDX, 2ADNT and 4ADNT were detected in most of these samples at concentrations at or below 54 µg/kg. TNT was also detected in several of these samples, but the concentrations were below 20 µg/kg.

Concentrations in the discrete samples collected as this site were also very low, always below 30 µg/kg except for a sample in the depth interval 5-10 cm collected 5 m from the target. In this samples, the concentrations of TNT, 2ADNT, 4ADNT, and TNB were 22,700, 1080, 1080, and 200 µg/kg, respectively. Concentrations for the other depth intervals for this sample, including those above and below this sample were below 15 µg/kg in all cases. The reason why one subsurface sample had a much greater concentration than any other is unclear.

Overall, concentrations of explosives-related analytes in these samples were very low. In fact, if Method 8330 were used exclusively for these samples, almost all values would have been below analytical detection limits. These results agree with those from Yakima, and those obtained by CHPPM 2000) for Camp Shelby, and indicate that explosives residues in most areas of artillery impact areas are quite small, even near targets.

Characterization of area near low order 500-lb bomb prior to detonation

During exploration of the artillery impact area at Camp Guernsey we noticed a large munitions item that had apparently undergone a low order detonation (Figure 22). The item was subsequently

identified by EOD personnel as an Air Force 500-lb bomb (Mark 82). The bomb contained a large amount of residual explosive, perhaps as much as half of the original explosive charge. The explosive had been exposed to the light and had turned red in the sun indicating that at least a portion of the explosive fill was TNT. Analysis of the explosive revealed that it was TNT with a few tenths of a percent of TNB, a major photochemical degradation product of TNT. Because no Air Force bombing had occurred in the last several years (according to EOD team), this ruptured bomb had been on site for at least two years.

When the area near the bomb was explored, several areas of reddish stained soil were observed, as far as 4.7 m from the bomb. Subsequent analysis of these soils indicated that this reddish stain was due to the deposition of TNT, either when the bomb partially detonated, or when rainfall eroded and spread the explosive fill downslope.

Analysis of the surface soil sample collected next to the ruptured bomb indicated a TNT concentration of 9,440,000 µg/kg or 0.944% (Table 12). The TNT concentrations at the 1-3 cm, and 4-7 cm depths at this location were 240,000, and 42,000 µg/kg, respectively. Surface soil samples at 1, 2, and 4.7 m down slope were 467,000, 4,660, and 8,050, 000 µg/kg, respectively. Clearly the ruptured bomb has caused substantial localized contamination with TNT. The major biotic, abiotic and photochemical transformation products of TNT (2ADNT, 4ADNT, and TNB) were also found in these samples.

The mean concentrations of TNT in the duplicate surface composite samples collected at 3, 5, and 10 meters from the bomb were 13,000, 260, and 306 µg/kg, respectively. 2ADNT, 4ADNT and TNB were also detected in these samples. The mean ratio of TNT/2ADNT for these composite samples was about 6. This indicated that a substantial portion of the TNT that was deposited had been subject to environmental transformation.

Characterization of area near low order 500-lb bomb after in was blown in place

After the area around the 500-lb bomb was sampled, the EOD team destroyed this bomb using a blow-in-place technique. Analysis of duplicate surface composites indicated that the TNT concentrations after the detonation were 74,600, 10,200, and 943 µg/kg at 3, 5, and 10 m from the crater (Table 12). These values increased from 13,000, 260, and 306 µg/kg, respectively, prior to detonation. The mean ratio of TNT to its microbial degradation product, 2ADNT, increased in these samples from about 6 prior to detonation to about 33 after detonation, confirming that much of the TNT found after detonation was deposited by the blow-in-place detonation of the low-order bomb.

Concentrations of TNT in the discrete samples collected near the crater varied from 66,700 µg/kg in the center of the crater to 3,980 µg/kg on the west rim of the crater. The mean ratio of TNT to 2ADNT for these samples averaged about 6 indicating that much of the TNT found in the crater area had been deposited prior to the blow-in-place detonation.

The concentrations of TNT in samples that were collected in the sampling wheel pattern, centered a distance of 3.5 m from the crater, varied from 28,000 to 206,000 µg/kg. The mean TNT concentration for these seven samples was 72,300 ± 62,300 µg/kg. The mean ratio for TNT/2ADNT for the five samples was 27, an indication that the bulk of the TNT found at a distance of 3.5 m from the crater was freshly deposited, rather than being present prior to detonation.

Overall, these results indicate that the blow-in-place detonation of this ruptured 500-lb bomb resulted in TNT contamination at distances at least as far as 10 m from the location of the detonation. Higher concentrations of TNT were found in surface soil at a distance of 3.5 m from the crater than within or on the edge of the crater. This may be indicative of the so-called "halo" effect, where deposition beyond a certain radius is higher than within that radius.

Soil samples collected before and after demolition of 155-mm duds

A series of samples were collected in the impact area at Camp Guernsey at distances ranging from 3 to 10 m from several 155-mm surface duds and one 81-mm dud. The area sampled was not heavily cratered, and these samples could serve as typical background level samples for this impact range. After these soil samples were collected, the rounds were detonated by EOD personnel with C4 and a second set of composite surface samples were collected in an identical manner. Results of these analyses are presented in Table 13.

Several analytes were detected in the samples collected around UXO #1, a 155-mm howitzer dud. The analytes detected at highest concentration were 2ADNT, 4ADNT and TNT, which were present in all six of the samples collected. Concentrations ranged from 67 to 268 µg/kg for the individual ADNTs with a mean of about 170 µg/kg, and from 7 to 210 µg/kg for TNT with a mean of 55 µg/kg. Concentrations just above analytical detection limits were observed for RDX, 2,4DNT and 2,6DNT in a few of these samples. The concentrations of none of these analytes were correlated in any way with their position relative to the 155-mm dud, and hence the source of these residues is unknown.

An identical set of surface composites were collected around UXO 2, also a 155-mm dud. 2ADNT and 4ADNT were again detected in all six samples, but the concentrations ranged from 4 to 12 µg/kg. No TNT was detected in these samples, but RDX was detected just above detection limits in five of the samples and HMX was detected in one sample at 193 µg/kg.

A third set of six surface composites were collected in an area containing a 155-mm dud and an 81-mm dud, in an identical pattern as for UXO 1 and 2. HMX, RDX, TNT, 2ADNT and 4ADNT were detectable in all six samples at concentrations ranging from 4 to 551 µg/kg. Mean concentrations for HMX, RDX, TNT and the individual ADNTs were 248, 115, 129, and 136 µg/kg, respectively. Again, the source of these residues was not obvious.

Results for samples collected the following day after all these rounds were destroyed by detonating them in place using C4 are presented in Table 11. For the area around UXO 1, there was a dramatic increase in the concentrations of RDX, TNT, and HMX. For example, the mean concentration of RDX increased from 10 µg/kg prior to the detonation to 65,600 µg/kg after the detonation. Likewise, the mean concentration of TNT and HMX increased from 55 mg/kg and less than detectable, respectively, to 25,300 and 7,900 µg/kg. The relative concentrations of RDX, TNT and HMX in soil, after the blow-in-place operation, were about the correct proportion for deposition of Composition B. While the concentration of RDX, TNT, and HMX were much higher than prior to detonation, the concentrations of 2ADNT and 4ADNT did not increase, indicating that these compounds are not formed during detonation.

Analytical results for UXO 2 were quite different. Concentrations of RDX, TNT and HMX were generally below detection limits prior to the blow-in-place operation and only TNT appears to have increased to about 100 µg/kg due to the deposition from the detonation. For UXO 3, mean concentrations of RDX, TNT, and HMX before the item was blown in place were 115, 129, and 248 µg/kg, respectively, and 1150, 6,100, and 789 µg/kg after the blow-in-place operation.

Therefore it appears that the degree of deposition of explosives residues due to blow-in-place operations is quite variable, sometimes resulting in only minor contamination of the area, and other times resulting in substantial local contamination.

Artillery firing point, Camp Guernsey

Analytical results for soils collected at the firing point of 155-mm howitzers indicated that no propellant residues above the analytical detection limits for GC-ECD Method 8095 were found in any of

these samples, either before or after firing. Since the propellant used for this firing activity was single based, we had expected to see detectable levels of 2,4DNT. Thus it appears that very little propellant residues were deposited from this firing activity.

Surface water springs

Groundwater geochemistry is typical of the geographic area (Table 14). Groundwater is generally slightly hard (sum of calcium and magnesium greater than 50, but less than 100 mg L^{-1}). One sample, Ryan Springs, slightly exceeded the drinking water standard for total iron (0.3 mg L^{-1}) and for manganese (0.05 mg L^{-1}). Nitrate/nitrite values were well within the range for natural waters (0.1 to 10 mg L^{-1}, Driscoll 1987). Although two samples contained chloride levels greater than typical for groundwater (about 6 mg L^{-1}, Tardy 1971), levels were not sufficient to cause concern. Sulfate levels were generally normal (less than 100 mg L^{-1}, Davis and DeWiest 1966). No explosives or explosives degradation products were detected in Camp Guernsey springs.

Historical firing records

Firing records at Yakima Training Center for the most heavily used high explosives rounds over a 33-month period indicated that the 155-, 81-, 120-, and 105-mm were fired most extensively (Table 15). These rounds were also commonly fired at Ft. Lewis (Pennington et al. 2001) and at Camp Guernsey (Table 16). An average of more than 3,000 155-mm howitzer rounds are fired each year at Yakima. Some of these contain RDX and TNT, while others contain TNT only. If Composition B is used, 60 % of the main charge is RDX and 39 % is TNT (Table 17). That means that 4,191 g of RDX is present in each round. If 0.02 % of the 3,000 rounds fires low order (Table 18), less than one low order detonation occurs each year. Since 9,082 rounds were fired over the 33-month period, only 2 low order detonations are anticipated during that time. Although unrealistic to expect the maximum quantity of RDX to remain, if this occurred the RDX quantity would be 8,382g. On the other hand, nearly 250, or 2.75 %, are likely to be duds requiring post deposition detonation by EOD personnel. If as much as one percent of the main charge fails to be expended by the detonation in place, 10,478 g of RDX and 6,812 g of TNT are potentially deposited on the surface soil. These values indicate the importance of achieving complete detonation when conducting range clearance for duds. Further, these data suggest that low order detonations, while not necessarily posing an explosion hazard, should be managed rather than left behind because they have the potential for posing an environmental hazard.

Conclusions

Various types of military testing and training ranges are quite different with respect to their potential for contaminating underlying ground water resources with residues of explosives (CHPPM2000, Jenkins et al. 1997a, 1997b, 1998, 2001, Pennington et al. 2001, Thiboutot et al. 1998, Walsh et al. 2001). For example, at antitank rocket ranges, surface soils near targets have been found to be contaminated with HMX residues at concentrations in the tens to thousands of parts-per-million. In contrast, soils near targets at artillery ranges have concentrations of RDX and TNT in the low parts-per-billion range. In both cases, though, soil concentrations of explosives-related residues can be in the percent level next to ruptured ordnance. For artillery ranges it appears that the non-point source of explosives residues for ground water contamination is quite low, with a number of much higher point sources randomly located across the site

Adequate characterization of artillery ranges is impossible using small numbers of discrete samples. Discrete samples are not representative of even small geographical areas. Much better representation of the area can be obtained using multi-increment composite samples. Results to date suggest that combining 30 individual increments to make up the composite sample results in adequate reproducibility in many cases. The ability to reproduce samples with an acceptable level of uncertainty provides confidence that the sample is representative of the area in question.

The results of this study indicate that the practice of detonating dud rounds using C4 sometimes leads to substantial contamination with explosives residues. The degree of contamination is quite variable, and the size of the contaminated areas is currently poorly defined. The use of C4 can result in incomplete detonation, and C4 is composed of 91% RDX, a potentially significant groundwater contaminant. Ground water contamination with RDX has resulted in the suspension of live fire training at the Massachusetts Military Reservation (USEPA 2000), and has been found at low levels in ground water at Ft. Lewis (Jenkins et al. 2001, Pennington et al. 2001). Increased consideration should be given to improving the efficiency of detonation for blow-in-place operations, and the use of more environmentally benign demolition charges.

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Table 1
Explosives Detection Limits for Soil and Water

Analyte	Soil, ug kg^{-1}		Water, ug L^{-1}
	RP-HPLC	GC-ECD	GC-ECD
HMX	26	26	0.004
RDX	34	3	0.004
TNB	16	3	0.007
TNT	16	1	0.01
2,6DNT	19	0.8	0.003
2,4DNT	28	0.8	0.009
2ADNT	38	2.5	0.003
4ADNT	32	1.6	0.003
TNB	20	22	0.007
NG	20	2	0.2
DNA	Co-elutes with NB	2	
DNB	100	0.7	0.004
Tetryl	600	20	0.009
PETN		<16	0.2

Table 2
Explosives Concentrations in Soils from Yakima Anti-Tank Firing Range[1], µg kg^{-1}

Sample Number	Munitions/Target	Sample Location[2]	Sample Depth, cm	HMX	RDX	TNT	NG	2,4DNT	2ADNT	4ADNT
Discrete Samples										
Y1	40-mm grenade	near intact	0-0.5	6380	8210	<16	102	<28	<38	<32
Y2	40-mm grenade	near intact	0.5-2.5	1440	563	<16	7850	150	<38	<32
Y3	Artillery Target	50 cm NE	Surface	75000	90400	<16	<20	<28	<38	<32
Y4	Artillery Target	50 cm NE	0.5-1.0	17900	13100	<16	<20	<28	<38	<32
Y5	Artillery Target	50 cm NE	1.0-4.0	19900	4290	<16	<20	<28	<38	<32
Y6	Artillery Target	50 cm NE	4.0-7.0	19400	3540	<16	<20	<28	<38	<32
Y7	Artillery Target	50 cm NE	7.0-10.0	20500	4040	<16	<20	1510	<38	<32
Y8	Artillery Target	1 m N	Surface	53500	7070	<16	<20	<28	<38	<32
Y9	Artillery Target	1 m N	1.0-3.0	18200	6060	<16	<20	<28	<38	<32
Y10	Artillery Target	1 m N	3.0-7.0	26700	6800	<16	<20	<28	<38	<32
Y11	Artillery Target	1 m N	7.0-10.0	1180	315	<16	<20	<28	<38	<32
Y12	Artillery Target	4 m N	Surface	19000	215	<16	200	<28	17.5	100
Y13	Artillery Target	4 m N	1.0-3.0	4240	125	<16	175	<28	47.5	25
Y14	Artillery Target	4 m N	3.0-7.0	4530	97.5	<16	<20	<28	<38	<32
Y15	Artillery Target	4 m N	7.0-10.0	1120	80.0	<16	<20	<28	<38	<32
Y16	Artillery Target	8 m N	Surface	1900	775	55.0	13000	480	20.0	72.5
Y17	Artillery Target	8 m N	1.0-3.0	338	293	<16	<20	<28	<38	<32
Y18	Artillery Target	8 m N	3.0-7.0	298	62.5	<16	<20	800	<38	<32
Y19	Artillery Target	8 m N	7.0-10.0		27.5	<16	<20	<28	<38	<32
Y20	Artillery Target	12 m N	0-2.0	2940	<34	37.5	4120	208	72.5	75
Y21	Artillery Target	12 m N	7.0-10.0	153	195	<16	10600	163	<38	<32
Y22	Artillery Target	12 m N	7.0-10.0	43	87.5	<16	<20	<28	<38	<32
Y23	Ruptured Law Rocket	Next to	0-0.5	10400000	45700	358000	<20	1770	17700	24700
Y24	Ruptured Law Rocket	Next to	2.0-6.0	1020000	4760	41700	1260	483	4380	5580
Y25	Ruptured Law Rocket	Next to	6.0-10.0	49300	1530	1720	895	183	1700	1820
Composite Samples										
YC1	Artillery Target	0.2 m	Surface	35600	3130	<16	<20	<28	<38	<32
YC2	Artillery Target	0-2 m	Surface	58000	736	61.4	270	52	333	459
YC3	Artillery Target	2-5 m	Surface	11700	259	73.1	1100	148	114	133
YC4	Artillery Target	2.5 m	Surface	20800	344	35	1300	88	118	152
YC5	Artillery Target	5-10 m	Surface	1760	115	14	92	<28	11	<32
YC6	Artillery Target	5-10 m	Surface	10800	196	47	467	17	93	78
YC7	Artillery Target	10-15 m	Surface	6510	83	117	7	8	32	27
YC8	Artillery Target	10-15 m	Surface	771	92	12	2750	98	<38	<32
YC9	Rocket Firing Position	Front 5-10 m	Surface	<26	<34	<16	1840	6	<38	<32
YC10	Rocket Firing Position	Front 5-10 m	Surface	<26	3	<0.8	3630	<28	<38	<32

[1] The following undetected analytes were excluded from the table: 2,6DNT, 1,3DNB, 1,3,5TNB, 3,5DNA, PETN. All shaded data were generated using RP-HPLC analysis. All other data were generated using GC-ECD.
[2] Upper case abbreviations indicate cardinal directions relative to munitions or target; numerals indicate distance from munitions or target.

Table 3
Explosives Concentrations in Soils near a Tank Firing Point at Yakima Multi-Purpose Range Complex[1], µg kg^{-1}

Sample Number	Sample Location[2]	Sample Depth, cm	RDX	TNT	NG	2,4DNT	2,6DNT
Discrete Samples: 120-mm Tank Gun							
Y95	10 m F, 10 m R	Surface[5]	<34	4	1540	8620	138
Y96	10 m F, 5 m R	Surface	142	34	17000	30500	376
Y97	10 m F, C	Surface	25	27	5370	30400	552
Y98	10 m F, 10 m L	Surface	113	29	6560	33000	392
Y99	10 m F, 5 m L	Surface	3	4	1600	3280	16
Y100	20 m F, 10 m R	Surface	2	<16	6610	2530	16
Y124	20 m F, 10 m R	2.5-5	<3	<1	972	149	2
Y101	20 m F, 5 m R	Surface	<34	<16	4050	6160	32
Y125	20 m F, 5 m R	2.5-5	<34	1	1400	5300	60
Y102	20 m F, C	Surface	<3	<1	442	660	<0.8
Y126	20 m F, C	2.5-5	<34	<16	448	904	14
Y103	20 m F, 5 m L	Surface	<34	2	646	4180	63
Y127	20 m F, 5 m L	2.5-5	<34	<16	342	668	7
Y104	20 m F, 10 m L	Surface	4	6	2070	9360	162
Y128	20 m F, 10 m L	2.5-5	<3	<1	62	344	6
Y105	30 m F, 5 m R	Surface	<34	<16	862	1340	20
Y106	30 m F, 10 m R	Surface	<3	<1	356	280	4
Y107	30 m F, C	Surface	2	<1	880	216	<0.8
Y108	30 m F, 5 m L	Surface	2	<1	668	698	7
Y109	30 m F, 10 m L	Surface	<3	<1	270	157	1
Y110	50 m F, 15 m, R	Surface	<3	<1	547	114	1
Y111	50 m F, 10 m R	Surface	1	<16	1110	2150	7
Y112	50 m F, 5 m R	Surface	<3	<1	280	356	2
Y113	50 m F, C	Surface	<3	<1	308	54	<0.8
Y114	50 m F, 5 m L	Surface	1	<16	568	1340	3
Y115	50 m F, 10 m L	Surface	<3	<1	56	40	<0.8
Y116	50 m F, 15 m L	Surface	<3	<1	320	56	<0.8
Y117	75 m F, 15 m R	Surface	<34	<16	2650	801	8
Y118	75 m F, 10 m R	Surface	6	<16	2250	258	<0.8
Y119	75 m F, 5 m R	Surface	<3	<1	1090	130	2
Y120	75 m F, C	Surface	<3	<1	860	442	5
Y121	75 m F, 5 m L	Surface	<3	<1	114	3	<0.8
Y122	75 m F, 10 m L	Surface	<3	<1	152	8	<0.8
Y123	75 m F, 15 m L	Surface	<3	<1	16	<0.8	<0.8
Composite Samples: 120-mm Tank Gun							
YC28	10 m F	Surface	<100	<100	6030	26500	392
YC33	10 m F	Surface	<100	<100	3090	22200	418
YC29	20 m F	Surface	<100	<100	1890	5550	32
YC30	20 m F	Surface	<100	<100	705	10900	230
YC36	30 m F	Surface	<34	1	604	480	2
YC37	30 m F	Surface	<100	<100	669	3860	<19
YC31	50 m F	Surface	<34	<16	306	14	<19
YC32	50 m F	Surface	<100	<100	348	1350	<19
YC34	75 m F	Surface	<34	<16	496	56	<19
YC35	75 m F	Surface	<34	<16	513	319	<19

[1] The following undetected analytes were excluded from the table: TNB, PETN, 4ADNT, 2ADNT, HMX, DNA, DNB, Tetryl. All shaded data were generated using RP-HPLC analysis. All other data were generated using GC-ECD.
[2] Sample location is relative to munitions or target; F = Front, R = Right, C = Center, L = Left.

Table 4
Explosives Concentrations in Soils at Two 155-mm Howitzer Firing Points, Yakima Training Center[1], µg kg^{-1}

Sample Number	Sample Location[2]	Sample Depth, cm	HMX	RDX	2,4DNT
Discrete Samples: Howitzer Firing Point # 1					
Y26	5 m W	Surface	<26	<3	24
Y27	At muzzle	Surface	7	9	<0.8
Y28	5 m E	Surface	<26	<3	<0.8
Y29	5 m W	Surface	<26	<3	<0.8
Y30	C, 5 m out	Surface	<26	<3	<0.8
Y31	5 m E, 5 m out	Surface	<26	<3	24
Y32	10 m W, 10 m out	0.0-2.5	<26	<3	<0.8
Y33	10 m W, 10 m out	2.5-5.5	<26	<3	<0.8
Y34	5 m W, 10 m out	0.0-2.5	<26	<3	<0.8
Y35	5 m W, 10 m out	2.5-5.5	<26	<3	<0.8
Y36	C, 10 m out	0.0-2.5	<26	<3	<0.8
Y37	C, 10 m out	2.5-5.5	<26	<3	<0.8
Y38	5 m E, 10 m out	0.0-2.5	<26	<3	<0.8
Y39	5 m E, 10 m out	2.5-5.5	<26	<3	<0.8
Y40	10 m E, 10 m out	0.0-2.5	<26	5	5
Y41	10 m E, 10 m out	2.5-5.5	<26	<3	<0.8
Y42	10 m W, 20 m out	Surface	<26	<3	<0.8
Y43	5 m W, 20 m out	Surface	<26	<3	5
Y44	C, 20 m out	Surface	<26	<3	185
Y45	5 m E, 20 m out	Surface	<26	<3	<0.8
Y46	10 m E, 20 m out	Surface	<26	<3	<0.8
Y47	15 m W, 50 m out	Surface	<26	<3	<0.8
Y48	10 m W, 50 m out	Surface	<26	<3	<0.8
Y49	5 m W, 50 m out	Surface	<26	<3	6
Y50	C, 50 m out	Surface	<26	<3	<0.8
Y51	5 m E, 50 m out	Surface	<26	<3	<0.8
Y52	10 m E, 50 m out	Surface	<26	<3	<0.8
Y53	15 m E, 50 m out	Surface	<26	<3	<0.8
Composite Samples: Howitzer Firing Point # 1					
YC11	5 m	Surface	<26	<3	<0.8
YC12	10 m	Surface	<26	<3	<0.8
YC13	20 m	Surface	<26	<3	<0.8
YC14	50 m	Surface	<26	<3	<0.8
Composite Samples: Howitzer Firing Point # 2					
YC16	5 m	Surface	<26	<3	19
YC17	5	Surface	<26	<3	11
YC18	10 m	Surface	<26	<3	65
YC19	10 m	Surface	<26	<3	16
YC20	20 m	Surface	<26	<3	94
YC21	20 m	Surface	<26	<3	<0.8
YC22	50 m	Surface	<26	<3	<0.8
YC23	50 m	Surface	<26	<3	<0.8

[1] The following undetected analytes were excluded from the table: TNT, NG, 2,6DNT, 2ADNT, 4ADNT, TNB, PETN, DNA, DNB, Tetryl. All data were generated using GC-ECD analysis.
[2] Sample location is relative to the Howitzer muzzle; W = West, E = East, C = Center.

Table 5
Explosives Concentrations in Soils at Direct Fire 155-mm Firing Point near Central Impact Area, Yakima Training Center[1], µg kg^{-1}

Sample Number	Sample Location[2]	Sample Depth, cm	NG	2,4DNT	2,6DNT
Discrete Samples					
Y153	7 m, 5 m R of C	Surface	1220	52	<0.8
Y154	7 m C	Surface	45	3	<0.8
Y155	7 m, 5 m L of C	Surface	75	<0.8	<0.8
Y156	12 m, 5 m R of C	Surface	1250	<0.8	<0.8
Y157	12 m, C	Surface	2610	<0.8	<0.8
Y158	12 m, 5 m L of C	Surface	20100	<0.8	<0.8
Y159	22 m, 5 m R of C	Surface	5900	<0.8	<0.8
Y160	22 m, C	Surface	9430	11	<0.8
Y161	22 m, 5 m L of C	Surface	11800	8250	190
Y162	32 m-5 m R of C	Surface	1160	10	<0.8
Y163	32 m, C	Surface	9660	240	<0.8
Y164	32 m, 5 m L of C	Surface	12300	12	<0.8
Composite Samples					
YC60	7 m	Surface	25700	<28	<19
YC61	12 m	Surface	2952	<28	<19
YC62	22 m	Surface	6012	3225	50
YC63	32 m	Surface	1852	266	<19

[1] The following undetected analytes were excluded from the table: HMX, RDX, TNT, 2ADNT, 4ADNT, TNB, PETN, DNA, DNB, Tetryl. All shaded data were generated using RP-HPLC analysis. All other data were generated using GC-ECD.
[2] The sample location is relative to the firing pad. The first number is out from the firing pad and the next number is the cardinal direction from the firing pad; R = Right, L = Left, C = Center.

Table 6
Explosives Concentrations in Surface Soil at an 81-mm Mortar Firing Point, Yakima Training Center[1], µg kg^{-1}

Sample Number	Sample Location[2]	NG
Discrete Samples		
Y58	1 m F	<22
Y59	3 m L, 5 m out	45
Y60	C	<22
Y61	3m R, 5 m out	32
Y62	5 m L, 10 m out	40
Y63	C, 10 m out	26
Y64	5 m R, 10 m out	<22
Y65	5 m L, 15 m out	<22
Y66	C, 15 m out	11
Y67	5 m R, 15 m out	40
Y68	5 m L, 20 m out	<22
Y69	C, 20 m out	23
Y70	5 m R, 20 m out	8
Composite Samples		
YC24	5 m	13
YC25	10 m	246
YC26	15 m	2
YC27	20 m	<22

[1] The following undetected analytes were excluded from the table: HMX, RDX, TNT, 2,4DNT, 2,6DNT, 2ADNT, 4ADNT, TNB, PETN, DNA, DNB, Tetryl. All data were generated using GC-ECD analysis.
[2] Sample location is in reference to the base plate of 81-mm mortar firing point; F = Front, L = Left, C = Center, R = Right.

Table 7
Explosives Concentrations in Soils collected at Yakima Central Impact Area Range 26[1], µg kg^{-1}

Sample No.	Munitions/ Target	Sample Location[2]	Sample Depth, cm	HMX	RDX	NG	2,4DNT	2,6DNT	2ADNT	4ADNT	PETN
Discrete Samples											
Y71	81mm IR[3] Ru[4]		Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y72	155-mm #1	E	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y73	155-mm #1	N	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y74	155-mm #1	W	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y75	155-mm #1	S	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y76	155-mm #2	E	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y77	155-mm #2	S	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y78	155-mm #2	N	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y79	155-mm #2	W	Surface	26	8	<22	<0.8	<0.8	<2.5	<1.6	<16
Y80	155-mm #3	N	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y81	155-mm #3	W	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y82	155-mm #3	S	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y83	155-mm #3	E	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y92	155-mm #4	C	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y93	155-mm #4	W	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y94	155-mm #4	N	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y129	155-mm #4	W	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y130	155-mm #4	S	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y133	155-mm #5	C	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y134	155-mm #5	N	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y135	155-mm #5	E	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y136	155-mm #5	S	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y137	155-mm #5	W	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y84	New 155-mm, dud	Under Nose	Surface	26	719		7	3	49	58	<16
Y85	155-mm, WP	FR	Surface	1770	6720	3	22	0.8	0.8	2.5	<16
Y86	155-mm, WP	BR	Surface	5240	53500	3	22	0.8	0.8	2.5	<16
Y87	155-mm, IR Broken HE charge in sample	F	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y88	155-mm, IR Broken HE charge in sample	F	1.0	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y89	155-mm, IR Broken HE charge in sample	F	5.0	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y90	105-mm, HE filled, Rusty	Nose	Surface	<26	8	<22	144	3	9	5	115
Y91	105-mm, HE filled, Rusty	Tail	Surface	<26	7	<22	<0.8	<0.8	<2.5	<1.6	<16
Y131	AFI[5] Broken	Casing	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
Y132	AFI Broken	Casing	Surface	<26	<3	4	<0.8	<0.8	<2.5	<1.6	<16
Y56	105-mm	Under HEP	Surface	<26	<3	12	<0.8	<0.8	<2.5	<1.6	<16
Y57	105-mm	Under	2.5	<26	<3	12	<0.8	<0.8	<2.5	<1.6	<16

		HEP									
Sample No.	**Munitions/ Target**	**Sample Location,[6] m**	**Sample Depth, cm**	**HMX**	**RDX**	**NG**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**PETN**
Composite Samples											
YC38	155-mm #1	0-1.0	Surface	<26	17	22	<0.8	<0.8	3	4	<16
YC39	155-mm #2	1.0	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
YC40	155-mm #2	1.0	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
YC41	155-mm #3	1.0	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16
YC42	155-mm #3	2.0-3.0	Surface	<26	14	<22	<0.8	<0.8	<2.5	<1.6	<16
YC43	155-mm #3	5.0-6.0	Surface	<26	15	<22	<0.8	<0.8	<2.5	<1.6	<16
YC44	155-mm #3	7.0-8.0	Surface	<26	15	15	<0.8	<0.8	<2.5	<1.6	<16
YC50	155-mm #5	1.0	Surface	<26	<3	<22	<0.8	<0.8	<2.5	<1.6	<16

[1] The following undetected analytes were excluded from the table: TNT, TNB, DNA, DNB, Tetryl. All data were generated using GC- ECD analysis.
[2] Sample location is relative to crater of particular munitions; E = East, N = North, W =West, S = South, C = Center, FR = Front of Round, BR = Back of Round
[3] Illumination round.
[4] Ruptured.
[5] Air Force illumination round
[6] Sample location is in reference to crater.

Table 8
Explosives Concentration in Soil from a Claymore Mine Detonation Area, Yakima Training Center[1], µg kg^{-1}

Sample Number	Sample Location[2]	Sample Depth, cm	RDX	NG	2,4DNT
Discrete Samples					
Y139	5 m from, 3 m RC	Surface	2	1050	<0.8
Y140	5 m from, C	Surface	<3	1340	18
Y141	5 m from, 3 m LC	Surface	<3	163	<0.8
Y142	10 m from, 3 m RC	Surface	<3	175	7
Y143	10 m from, C	Surface	<3	128	<0.8
Y144	10 m from, 3 m LC	Surface	<3	153	5
Y145	15 m from, 3 m RC	Surface	<3	49	<0.8
Y146	15 m from, C	Surface	<3	199	14
Y147	15 m from, 3 m LC	Surface	<3	147	17
Y148	20 m from, 3 m RC	Surface	<3	67	4
Y149	20 m from, 3 m RC	Surface	<3	16	<0.8
Y150	20 m from, 3 m LC	Surface	<3	137	9
Composite Samples					
YC64	5 m from	Surface	<3	1270	<0.8
YC65	10 m from	Surface	<3	51	4
YC66	15 m from	Surface	<3	96	3
YC67	20 m from	Surface	<3	<22	<0.8

[1] The following undetected analytes were excluded from the table: HMX, TNT, 2,6DNT, 2ADNT, 4ADNT, TNB, PETN, DNA, DNB, Tetryl. All data were generated using GC-ECD.
[2] Sample location is relative to detonation point; RC = Right of Center, C = Center, LC = Left of Center.

Table 9
Soil Geochemistry, Yakima Training Center

Site	TOC[1] %	CEC[2] meq/100g	Total Iron %	pH	Particle Size			TKN[3] mg kg^{-1}
					Clay %	Sand %	Silt %	
YC 34,35	1.91	15.7	1.89	6.6	18.3	51.6	30.1	805
YC 11,13,14	1.46	16.7	2.05	6.6	16.4	44.4	39.2	1000
YC 41,42,43,44	2.0	19.6	2.14	6.2	20.1	48.5	31.4	1115
YC 24,25,226,27	1.72	17.2	2.12	6.2	23.0	56.5	20.5	1318
YC 9,10	2.31	16.3	2.7	6.7	20.2	50.9	28.9	1644

[1]Total organic carbon
[2]Cation exchange capacity
[3]Total Kjeldahl nitrogen

Table 10
Geochemistry of Water Samples, Yakima Training Center, mg L^{-1}

Sample Location	Ca	Fe	Mg	Mn	NO_2/NO_3	SO_4	Cl
YRS Well	23.3	<0.120	14.2	<0.004	0.13	14 J	7.8
Lmumma Creek	40.9	0.070 J	19.4	0.0082	<0.10	30	21
Range 55	18.8	0.150	9.30	0.0043	0.91	15 J	6.4
Selah Creek	21.4	0.250	10.8	0.0308	<0.10	12 J	7.1
Range 19	32.8	<0.120	17.2	0.0083	0.33	23	16
Lmumma Creek Impact Area	27.1	0.620	14.6	0.0828	0.24	15 J	10

Table 11
Explosives Concentrations in Soils at the Artillery Impact Area at Camp Guernsey[1], µg kg^{-1}

Sample No.	Sample Location[2]	Sample Depth, cm	HMX	RDX	TNT	2ADNT	4ADNT	TNB
Discrete Samples								
G1	1 m	Surface-1.0	<26	<3	<1	11	10	<3
G2	1 m	1.0-5.0	<26	<3	<1	<2.5	<1.6	<3
G3	1 m	5.0-10.0	3	<3	<1	<2.5	<1.6	<3
G4	5 m	Surface-1.0	<26	<3	<1	7	10	<3
G5	5 m	1.0-2.0	4	4	<1	5	9	<3
G6	5 m	2.0-5.0	<26	<3	<1	11	14	<3
G7	5 m	5.0-10.0	<26	<34	22700	1080	1080	200
G8	5 m	10.0-17.0	2	<3	<1	4	5	<3
G41	1 m, D	Surface	4	13	<1	8	12	<3
G42	1 m, D	Surface	<26	<3	<1	<2.5	<1.6	<3
G43	5 m, D	Surface	<26	8	<1	6	10	<3
G44	5 m, D	Surface	<26	<3	<1	11	18	<3
G45	10 m, D	0.0-1.0	<26	<3	<1	6	10	<3
G46	10 m, D	1.0-5.0	<26	<3	<1	5	9	<3
G47	10 m, D	5.0-10.0	<26	<3	<1	6	10	<3
G48	10 m, D	10.0-15.0	<26	<3	<1	<2.5	<1.6	<3
G49	15 m, D	0.0-1.0	<26	<3	<1	11	15	<3
G50	15 m, D	1.0-5.0	<26	<3	<1	15	17	<3
G51	15 m, D	5.0-10.0	29	<3	<1	10	19	<3
G52	15 m, D	10.0-15.0	25	12	<1	3	6	<3
Composite Samples								
GC1	1 m	Surface	116	<34	<16	<38	<32	<16
GC2	1 m	Surface	186	<34	<16	<38	<32	<16
GC3	5 m	Surface	<26	3	6	11	19	<3
GC4	5 m	Surface	<26	4	<1	8	11	<3
GC5	10 m	Surface	<26	3	13	40	54	<3
GC6	10 m	Surface	<26	<3	13	14	23	<3
GC7	15 m	Surface	<26	<3	<1	6	11	<3
GC8	15 m	Surface	<26	3	<1	7	13	<3

[1] The following undetected analytes were excluded from the table: 2,6DNT, 2,4DNT, TNB, PETN, DNA, DNB, Tetryl. All shaded data were generated using RP-HPLC analysis. All other data were generated using GC-ECD.
[2] Sample location is relative to truck target; D = Down slope.

Table 12
Explosives Concentrations in Soils Near a Ruptured 500-lb Bomb, Camp Guernsey[1], µg kg^{-1}

Sample Number	Sample Location[2]	Sample Depth, cm	HMX	RDX	TNT	2,4DNT	2,6DNT	2ADNT	4ADNT	TNB	DNA
Discrete Samples: Low Order 500-lb Bomb Prior to Detonation with C4											
G63	4.7 m	Surface	<10000	<10000	8050000	<10000	<10000	<10000	<10000	48000	<10000
G64	2 m D	Surface	204	38	4660	98	138	2980	4532	274	206
G65	1 m D	Surface	<2000	<2000	467000	<2000	<2000	9200	8000	3600	<2000
G66	ES	Surface	<10000	<10000	9440000	<10000	<10000	<10000	<10000	50000	<10000
G67	ES	1.0-3.0	4200	600	240000	<28	<19	<10000	<10000	3200	
G68	ES	4.0-7.0	1280	<1000	42000	1960	<1000	19400	15900	960	<10000
G19	Piece of explosive in 500 lb bomb		<0.1%	<0.1%	99+%	<0.1 %	<0.1 %	<0.1 %	<0.1 %	<0.2%	<0.1 %
Sample Number	**Sample Location[3]**	**Sample Depth, cm**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**	**DNA**
Discrete Samples after Bomb Detonated with C4											
G24	Center	Surface	<2000	<2001	66700	<2000	<2000	7400	2900	1100	<2000
G69	NR	Surface	178	<34	7400	<28	<19	10700	9190	202	
G70	ER	Surface	<26	<34	45500	<28	<19	4360	2160	<16	
G71	SR	Surface	<26	128	20500	246	98	5031	4040	340	142
G72	WR	Surface	<26	28	3980	<28	<19	1000	808	68	20
G90	3 m S	Surface	<2000	160	68000	<2000	<2000	2600	1360	560	<2000
G91	3 m S	Surface	<5000	<5000	150000	<5000	<5000	<5000	<5000	1200	<5000
G92	5 m S	Surface	<1000	<1000	29000	<1000	<1000	2160	1560	220	<1000
G93	5 m S	Surface	<1000	<1000	24100	<1000	<1000	1160	1860	200	<1000
G94	10 m S	Surface	<26	80	820	<28	<19	210	390	98	
G95	10 m S	Surface	<26	14	482	<28	<19	<100	<100	<16	
G96	WS, 3.5 m SW of C	Surface	<1000	120	28000	<1000	<1000	960	1160	160	<1000
G97	WS, 3.5 m from Edge	Surface	<2000	<2000	64350	<2000	<2000	2920	1920	600	<2000
G98	WS 3.5 m from Edge	Surface	<1000	<500	30200	<1000	<1000	3840	3320	220	<1000
G99	WS 3.5 m from Edge	Surface	<1000	140	34400	<1000	<1000	1960	1340	260	<1000
G100	WS 3.5 m from Edge	Surface	<2000	<2000	61500	<2000	<2000	1080	1240	360	<2000
G101	WS 3.5 m from Edge	Surface	<5000	<5000	81500	<5000	<5000	<5000	<5000	600	<5000
G102	WS 3.5 m from Edge	Surface	<10000	<10000	206000	<10000	<10000	<10000	<10000	1400	<10000
Sample Number	**Sample Location[2]**	**Sample Depth, cm**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**	**DNA**
Composite Samples Prior to Detonation of Bomb											
GC27	10 m from	Surface	<26	<34	602	<28	<19	34	60	8	
GC28	10 m from	Surface	<26	<34	10	<28	<19	53	63	6	
GC29	5 m from	Surface	<26	<34	320	<28	<19	270	348	<16	
GC30	5 m from	Surface	<26	4	199	<28	6	180	254	9	
GC31	3 m from	Surface	18	134	4170	20	<19	808	990	98	48
GC32	3 m from	Surface	44	36	21900	42	54	2070	2720	228	
Sample No.	**Sample Location[3]**	**Sample Depth, cm**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**	**DNA**

Composite Samples after Bomb Detonation with C4											
GC51	3 m from	Surface	<26	<34	118000	146	96	1560	1730	878	120
GC52	3 m from	Surface	<26	<34	28000	<28	<19	740	840	220	<DL[4]
GC53	5 m from	Surface	<26	<34	13300	<28	<19	354	368	108	20
GC54	5 m from	Surface	<26	118	7010	<28	<19	246	704	84	16
GC55	10 m from	Surface	<26	<34	1120	<28	<19	50	44	<16	<DL
GC56	10 m from	Surface	<26	64	760	<28	<19	60	82	<16	<DL

[1] The following undetected analytes were excluded from the table: NG, PETN, DNB, Tetryl. All shaded data were generated using RP- HPLC analysis. All other data were generated using GC-ECD.
[2] Sample location is in reference to low order 500-lb bomb; D = Down slope, ES = Edge of shell.
[3] Sample location is in reference to crater; C = Center, NR = North Rim, ER = East Rim, SR = South Rim, WR = West Rim, S = South, WS = Wheel Sample, SW = Southwest.
[4] Less than detection limit. Co-elutes with NB; therefore, detection limits are uncertain.

Table 13
Explosives Concentrations in Soils near UXO Items Before and After Detonation with C4, Camp Guernsey[1], µg kg-[1]

Sample No.	Munitions /Target	Sample Location[2]	HMX	RDX	TNT	2,4DNT	2,6DNT	2ADNT	4ADNT	TNB
Discrete Surface Samples Prior to Detonation with C4										
G29	UXO 1, 155-mm[3]	3 m	<26	<3	6	<0.8	9	279	316	<3
G30	UXO 1, 155-mm	3 m	<26	<3	14	15	20	445	520	4
G31	UXO 1, 155-mm	5 m	<26	<3	15	<0.8	<0.8	84	106	<3
G32	UXO 1, 155-mm	5 m	<26	<3	7	<0.8	<0.8	36	58	<3
G33	UXO 1, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	6	12	<3
G34	UXO 1, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	9	16	<3
G35	UXO 2, 155-mm	3 m	<26	6	<1	<0.8	<0.8	<2.5	<1.6	<3
G36	UXO 2, 155-mm	3 m	<26	47	<1	<0.8	<0.8	<2.5	<1.6	<3
G37	UXO 2, 155-mm	5 m	4	<3	<1	<0.8	<0.8	4	7	<3
G38	UXO 2, 155-mm	5 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G39	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G40	UXO 2, 155-mm	10 m	2	<3		<0.8	<0.8	5	6	<3
G57	UXO 3, 155-mm, 81-mm	3 m	134	45	21	<0.8	<0.8	34	47	<3
G58	UXO 3, 155-mm, 81-mm	3 m	86	34	4	<0.8	<0.8	52	77	<3
G59	UXO 3, 155-mm, 81-mm	5 m	51	330	4	<0.8	<0.8	38	64	<3
G60	UXO 3, 155-mm, 81-mm	5 m	43	29	8	<0.8	<0.8	40	59	<3
G61	UXO 3, 155-mm, 81-mm	10 m	41	20	3	<0.8	<0.8	33	45	<3
G62	UXO 3, 155-mm, 81-mm	10 m	9	26	3	<0.8	<0.8	15	23	<3
Sample Number	**Munitions /Target**	**Sample Location[4]**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**
Discrete Surface Samples after Detonation with C4										
G79	UXO 1, 155-mm	70 cm N	24200	173000	38600	<0.8	<0.8	<2.5	<1.6	<3
G80	UXO 1, 155-mm	70 cm E	20800	184000	50200	<0.8	<0.8	<2.5	<1.6	<3
G81	UXO 1, 155-mm	70 cm S	13000	118000	29700	<0.8	<0.8	<2.5	<1.6	<3
G82	UXO 1, 155-mm	70 cm W	32400	225000	84700	<0.8	<0.8	<2.5	<1.6	<3
G83	UXO 1, 155-mm	C	82800	541000	294000	<0.8	<0.8	<2.5	<1.6	<3
G84	UXO 1, 155-mm	3 m SW	19400	124000	84800	<0.8	<0.8	<2.5	<1.6	<3
G85	UXO 1, 155-mm	3 m SW	2120	19100	9620	<0.8	<0.8	<2.5	<1.6	<3
G86	UXO 1, 155-mm	5 m SW	10600	77800	25600		<0.8	<2.5	<1.6	<3
G87	UXO 1, 155-mm	5 m SW	8840	46300	17200	<0.8	<0.8	<2.5	<1.6	<3
G88	UXO 1, 155-mm	10 m SW	3240	22000	11700	<0.8	<0.8	<2.5	<1.6	<3
G89	UXO 2, 155-mm	10 m SW	6000	36200	17600	<0.8	<0.8	<2.5	<1.6	<3
G20	UXO 2, 155-mm	50 cm N	<26	<3	7	<0.8	<0.8	<2.5	<1.6	<3
G21	UXO 2, 155-mm	50 cm E	2	9	<1	<0.8	<0.8	2	6	<3
G22	UXO 2, 155-mm	50 cm S	33	<3	101	<0.8	<0.8	6	6	<3
G23	UXO 2, 155-mm	50 cm W	55	5	26	<0.8	<0.8	4	6	<3
G73	UXO 2, 155-mm	3 m	<26	<34	2040	102	<19	<38	<32	<16
G74	UXO 2, 155-mm	3 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G75	UXO 2, 155-mm	5 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G76	UXO 2, 155-mm	5 m	<26	4	281	<0.8	<0.8	56	50	<3
G77	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G78	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
G9	UXO 3, 155-mm, 81-mm	NR	708	540	518	<28	<19	202	156	50
G10	UXO 3, 155-mm,	ER	111	928	78	<0.8	<0.8	<2.5	<1.6	<3

	81-mm									
G11	UXO 3, 155-mm, 81-mm	SR	91	180	153	<0.8	<0.8	145	163	<3
G12	UXO 3, 155-mm, 81-mm	WR	304	155	35	<28	<19	59	75	<16
G13	UXO 3, 155-mm, 81-mm	3 m	500	120	24700	<28	<19	1680	1720	240
G14	UXO 3, 155-mm, 81-mm	3 m	254	158	1340	<28	<19	1480	1540	28
G15	UXO 3, 155-mm, 81-mm	5 m	173	356	111	<0.8	<0.8	90	98	<3
G16	UXO 3, 155-mm, 81-mm	5 m	278	204	5740	<28	<19	332	456	48
G17	UXO 3, 155-mm, 81-mm	10 m	101	41	296	<0.8	<0.8	72	91	<3
G18	UXO 3, 155-mm, 81-mm	10 m	762	98	18	<0.8	<0.8	114	190	<3
Sample Number	**Munitions /Target**	**Sample Location[2]**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**
Composite Surface Samples Prior to Detonation with C4										
GC9	UXO 1, 155-mm	3 m	<26	3	8	5	<0.8	194	267	<3
GC10	UXO 1, 155-mm	3 m	<26	<3	76	<0.8	5	145	179	<3
GC11	UXO 1, 155-mm	5 m	<26	16	10	<0.8	<0.8	250	268	5
GC12	UXO 1, 155-mm	5 m	<26	<3	18	5	<0.8	118	145	<3
GC13	UXO 1, 155-mm	10 m	<26	<3	7	<0.8	3	67	89	<3
GC14	UXO 1, 155-mm	10 m	<26	<3	210	<0.8	4	154	177	<3
GC15	UXO 2, 155-mm	3 m	<26	2	<1	<0.8	<0.8	4	6	<3
GC16	UXO 2, 155-mm	3 m	<26	3	<1	<0.8	<0.8	4	6	<3
GC17	UXO 2, 155-mm	5 m	<26	4	<1	<0.8	<0.8	9	12	<3
GC18	UXO 2, 155-mm	5 m	193	2	<1	<0.8	<0.8	8	6	<3
GC19	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	5	7	<3
GC20	UXO 2, 155-mm	10 m	<26	2	<1	<0.8	<0.8	7	7	<3
GC21	UXO 3, 155-mm, 81-mm	3 m	173	103	4	<0.8	<0.8	58	70	<3
GC22	UXO 3, 155-mm, 81-mm	3 m	66	39	29	<0.8	<0.8	43	61	<3
GC23	UXO 3, 155-mm, 81-mm	5 m	176	89	20	<0.8	<0.8	119	161	<3
GC24	UXO 3, 155-mm, 81-mm	5 m	530	299	551	4	3	222	436	11
GC25	UXO 3, 155-mm, 81-mm	10 m	216	70	128	<0.8	<0.8	84	119	6
GC26	UXO 3, 155-mm, 81-mm	10 m	324	92	40	<0.8	<0.8	111	147	<3
Sample Number	**Munitions /Target**	**Sample Location[3]**	**HMX**	**RDX**	**TNT**	**2,4DNT**	**2,6DNT**	**2ADNT**	**4ADNT**	**TNB**
Composite Surface Samples after Detonation with C4										
GC45	UXO 1, 155-mm	3 m	17200	121000	60800	98	<0.8	110	98	<3
GC46	UXO 1, 155-mm	3 m	9800	89200	23500	84	<0.8	<2.5	112	<3
GC47	UXO 1, 155-mm	5 m	9000	72800	39100	64	<0.8	178	198	<3
GC48	UXO 1, 155-mm	5 m	8300	92300	19400	46	<0.8	92	22	<3
GC49	UXO 1, 155-mm	10 m	1530	1010	5741	<0.8	<0.8	<2.5	<1.6	<3
GC50	UXO 1, 155-mm	10 m	1870	8940	3060	<28	<19	54	80	26
GC39	UXO 2, 155-mm	3 m	3	3	145	8	3	10	12	<3
GC40	UXO 2, 155-mm	3 m	10	2	77	5	<0.8	5	6	<3
GC41	UXO 2, 155-mm	5 m	<26	<3	92	5	<0.8	7	10	<3
GC42	UXO 2, 155-mm	5 m	<26	<3	73	3	<0.8	6	10	<3
GC43	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3
GC44	UXO 2, 155-mm	10 m	<26	<3	<1	<0.8	<0.8	<2.5	<1.6	<3

GC33	UXO 3, 155-mm, 81-mm	3 m	520	1000	844	<28	<19	286	290	34
GC34	UXO 3, 155-mm, 81-mm	3 m	152	174	29400	<28	<19	586	550	<16
GC35	UXO 3, 155-mm, 81-mm	5 m	3200	5480	6200	<28	<19	478	514	74
GC36	UXO 3, 155-mm, 81-mm	5 m	602	113	93	<28	<19	100	139	<16
GC37	UXO 3, 155-mm, 81-mm	10 m	180	80	38	<28	<19	57	85	<16
GC38	UXO 3, 155-mm, 81-mm	10 m	79	77	40	<28	<19	65	93	<16

[1] The following undetected analytes were excluded from the table: NG, TNB, PETN, DNA, DNB, Tetryl. All shaded data were generated using RP-HPLC analysis. All other data were generated using GC-ECD.
[2] Sample location is relative to the round.
[3] The 155-mm is an artillery round; the 81-mm is a mortar round.
[4] Sample location is relative to crater after detonation; N = North, E = East, S = South, W = West, C = Center, SW = Southwest.

Table 14
Geochemistry of Groundwater at Camp Guernsey Springs, mg L^{-1}

Sample Location	Ca	Fe	Mg	Mn	NO_2/NO_3	SO_4	Cl
Deer Corn Springs	55.3	<0.120	25.2	<0.004	1.1	28	6.8
Ryan Springs	56.4	0.400	22.5	0.058	0.030 J	9.4 J	6.5
Sawmill Springs	56.9	0.130	25.8	0.002 J	0.96	18 J	5.1
Pet Springs	49.7	0.093 J	24.3	0.001 J	0.98	27	5.3

Table 15
Firing Record of the Most Commonly Fired Munitions for 1999-2001 at Yakima Training Center [1]

Round	DODIC Number [2]	1999	2000	2001 [3]	Total
60-mm HE M720	B652	1049	116	1552	2717
66-mm rocket HE M72	H557	448	100	--	548
Sum 81-mm HE	C228, C236, C256	2634	1850	1904	6388
Sum 84-mm HE	C382, C383, C995	418	227	238	883
90-mm HE	C280, C282	165	--	--	165
105-mm HE M1	C445	1413	2534	1918	165
106-mm HE AT M344A1	C650	36	--	--	36
Sum 107-mm (4.2-in) HE	C697, C699	412	--	77	489
Sum 120-mm HE	C379, C623, C787, C788	2663	1385	1923	5971
Sum 155-mm HE	D510, D544, D563, D579	3530	2866	2686	9082

[1] Records include data from the RFMS database acquired from January 1999 through September 2001 as provided by SFC Antonio Felix.
[2] Department of Defense Identification Code.
[3] Data through September 2001 only.
[4] Indicates no record of firing this ammunition type during this year.

Table 16
Firing Record of the Most Commonly Fired Munitions for 1996-2001 at Guernsey Training Center [1]

Round	DODIC Number [2]	1996	1997	1998	1999	2000	2001 [3]	Total
Sum 60-mm HE	B632, B642	204	368	453	250	72	-- [4]	1347
81-mm HE M374	C256	46	373	191	300	184	300	1394
90-mm HEAT M371A1	C282	--	413	--	--	--	--	413
105-mm HE M1	C445	1250	2	--	--	2060	--	3312
107-mm (4.2-in) HE M392A2	C697	1842	240	800	2175	--	--	5057
Sum 155-mm HE	D510, D544	6681	2540	2573	5447	5684	2713	25638
8-in HE M106	D680	1201	--	--	1	1	--	1203

[1] Records include data provided by Mr. Guy Mosier, Camp Guernsey Training Center.
[2] Department of Defense Identification Code.
[3] Data through October 2001 only.
[4] Indicates no record of firing this ammunition type during this year.

Table 17
High Explosive Load Carried by Munitions Items Commonly Fired at Yakima Training Center and Camp Guernsey[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	
M72	H557	(213 HMX)[4]	90.7	-	-	Tetryl	5.60	-	-	
M106	D680	-	16,465	TNT	134	-	-	-	-	16,465
60-mm	B632	-	156	-	-	Tetryl	259	Tetryl	4.76	188
60-mm	B642[5]	114	74	-	-	RDX	7.9	HMX	144	354
81-mm	C236[5]	571	372	-	-	-	-	-	-	943
81-mm	C256[5]	571	372	-	-	RDX	23	RDX	0.14	943
84-mm	C382	-	-	-	-	-	-	-	-	-
84-mm	C383	-	-	-	-	-	-	-	-	-
84-mm	C995	-	-	-	-	-	-	-	-	-
90-mm	C280	-	934	-	-	Tetryl	351	Tetryl	3.8	934
90-mm	C282[5]	467	304	-	-	Tetryl	7.9	Tetryl	0.95	771
105-mm	C445	-	2086	TNT	136	-	-	-	-	2086
105-mm	C445[5]	1251	814	TNT	132	-	-	-	-	2086
106-mm	C650[5]	759	494	-	-	RDX	8.0	-	-	1253
107-mm	C699[5]	1565	1017	TNT	136	-	-	-	-	2582
107-mm	C697[5]	1565	1017	TNT	136	-	-	-	-	2582
120-mm	C623[5]	1790	1170	?[6]	?	RDX	7.9	HMX	1.89	2990
120-mm	C787[7]	?	-	-	-	-	-	-	-	?
120-mm	C788	-	2100	-	-	RDX	12.5	-	-	2100
155-mm	D510[5]	4014	2609	-	-	-	-	-	-	6623
155-mm	D544[5]	4191	2725	TNT	136	-	-	-	-	6916
155-mm	D544	-	6622	TNT	136	-	-	-	-	6622
155-mm	D563	2805	-	-	-	-	-	-	-	2805
155-mm	D579[5]	4082	2653	TNT	136	-	-	-	-	6735

[1] Sources of data are the Munitions Items Disposition Action System (MIDAS); personal communication Mr. Mark Serben, Office of the Product Manager for Mortar Systems, TACOM, Picatinny Arsenal, NJ, March 19, 2000; U. S. Army (1994).
[2] Department of Defense Identification Code.
[3] High explosive.
[4] HMX, not RDX.
[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.
[7] Composition A3 (91 %, 9 % wax). Mass of the HE was unavailable.

Table 18
Mean Dud and Low Order Detonation Rates for Munitions Items Commonly Used at Yakima Training Center and Camp Guernsey[1]

Round	DODIC[2]	Items Tested	DUDs, %	Low Orders, %
M72	H557	2,722	4.52	0.04
M106[3]	D680	160	0	0
M720	B652	3,838	1.07	0
60-mm[4]	B632	7,792	3.35	0
60-mm	B642	3,838	1.07	0
81-mm[5]	C228	16,435	2.28	0.08
81-mm[5]	C236	16,435	2.28	0.08
81-mm[6]	C256	9,122	2.16	0.02
84-mm	C382	U[7]	U	U
84-mm	C383	U	U	U
84-mm[8]	C995	658	0	0.15
90-mm	C280	838	13.8	0
90-mm	C282	870	2.76	0.80
105-mm[9]	C445	10,003	4.39	0.07
106-mm	C650	1,065	3.66	0
107-mm	C699	1,518	2.24	0.02
120-mm	C379	U	U	U
120-mm	C623	U	U	U
120-mm	C787	U	U	U
120-mm	C788	270	2.59	0
107-mm	C697	U	U	U
155-mm	D510	U	U	U
155-mm	D544	6,216	2.75	0.02
155-mm	D563	U	U	U
155-mm[10]	D579	1,152	0	0

[1] Values based on test data acquired by U. S. Army Defense Ammunition Center, McAlester, OK (Dauphin and Doyle 2000).
[2] Department of Defense Identification Code.
[3] Dud and low order rates depend upon kind of fuze. With the M582 fuze the dud rate was 5.11% (9 fired) and the low order rate was zero. With other fuzes the dud and low order rates were zero.
[4] Three models were tested. Values are derived from combining data for all models.
[5] This specific DODIC numbered item was not tested. Values are derived from sum of all 81-mm mortars tested.
[6] Four models were tested. Values are derived from combining data for all models.
[7] Data were unavailable
[8] Two models were tested. Values are derived from combining data for both.
[9] One model was tested with nine fuzes. Values are derived from combining data for all.
[10] Various models and fuzes were tested. Values are derived from combining data for all.

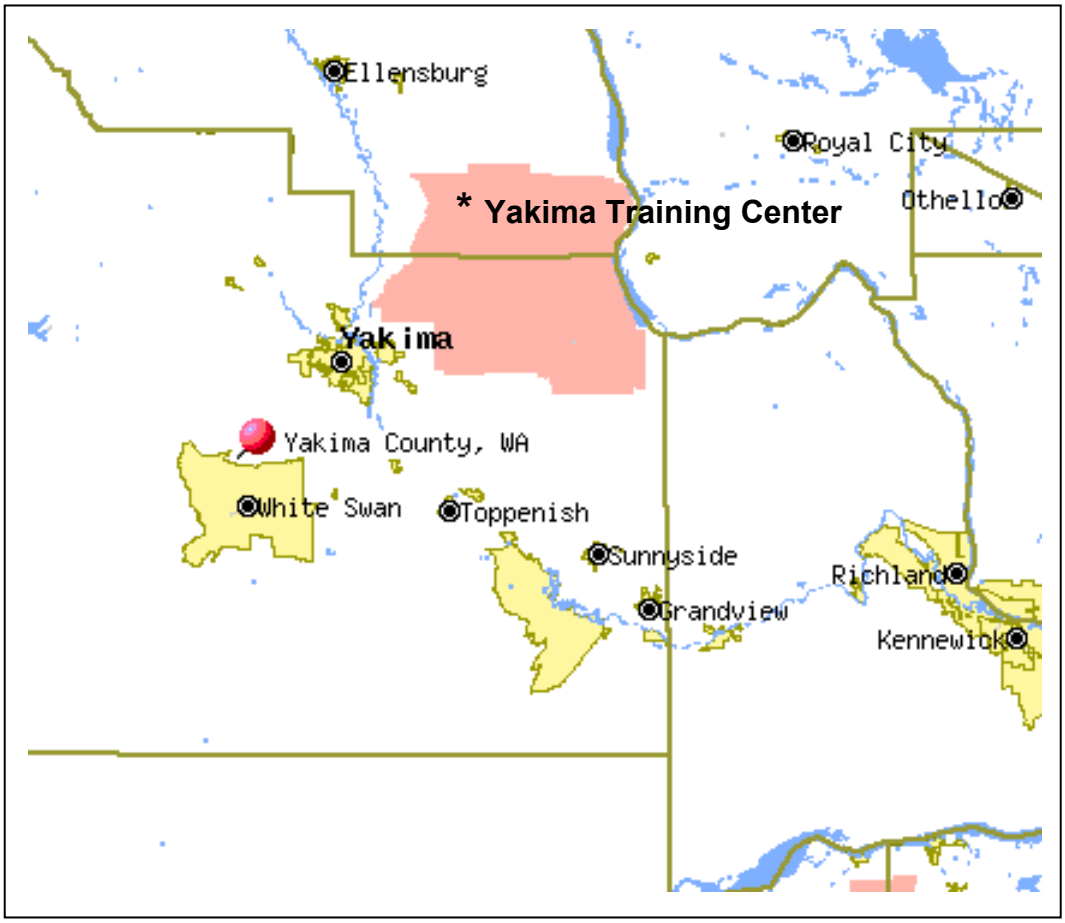

Figure 1. Location of Yakima Training Center, Washington

Figure 2. Antitank Range at Yakima Training Center, Washington, soil sampling near an armored personnel carrier target.

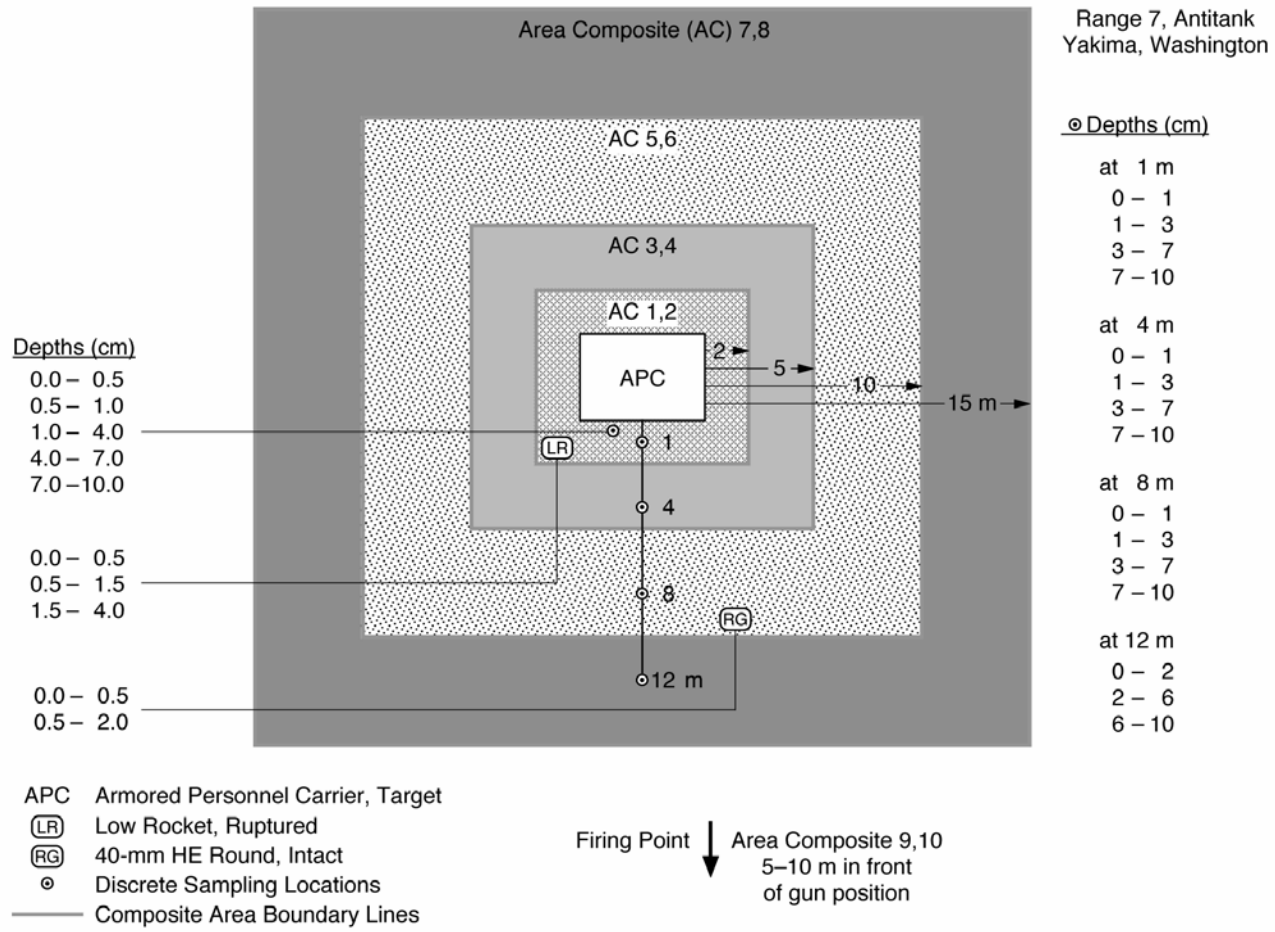

Figure 3. Soil sampling locations around armored personnel carrier target at Yakima Antitiank Range.

Figure 4. Ruptured LAW Rocket at Yakima Antitiank Range.

Figure 5. MPRC tank firing range at Yakima Training Center.

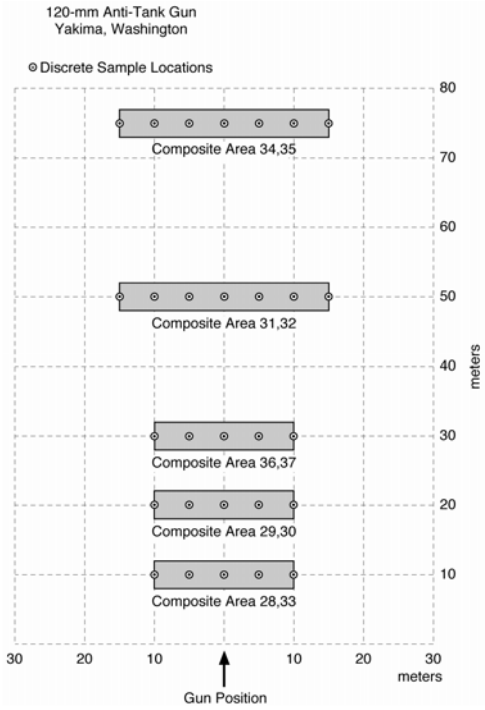

Figure 6. Soil sampling locations at tank firing point on MPRC Range at Yakima Training Center.

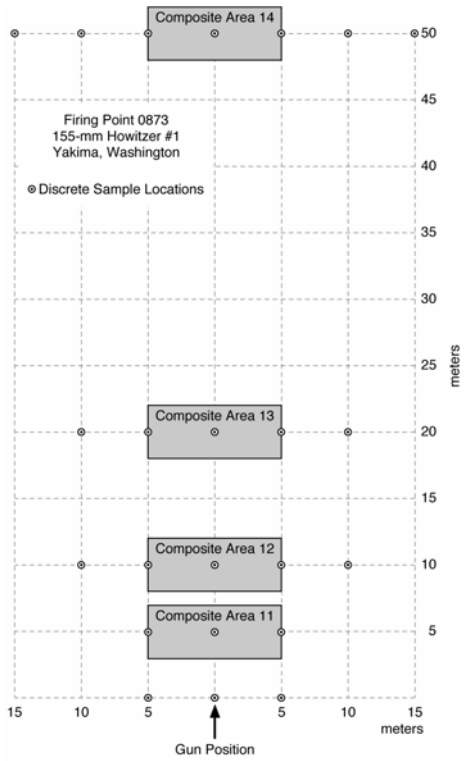

Figure 7. Soil sampling locations at the firing point of 155-mm howitzers at Yakima Training Center.

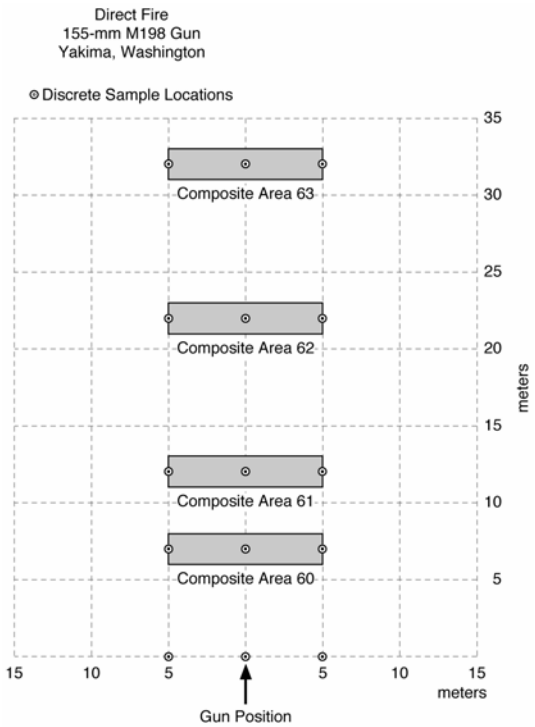

Figure 8. Soil sampling locations at a direct fire 155-mm howitzer firing point, Yakima Training Center.

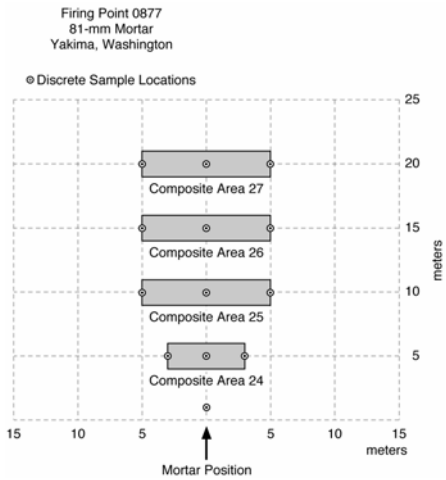

Figure 9. Soil sampling locations at a firing point for 81-mm mortars at Yakima Training Center.

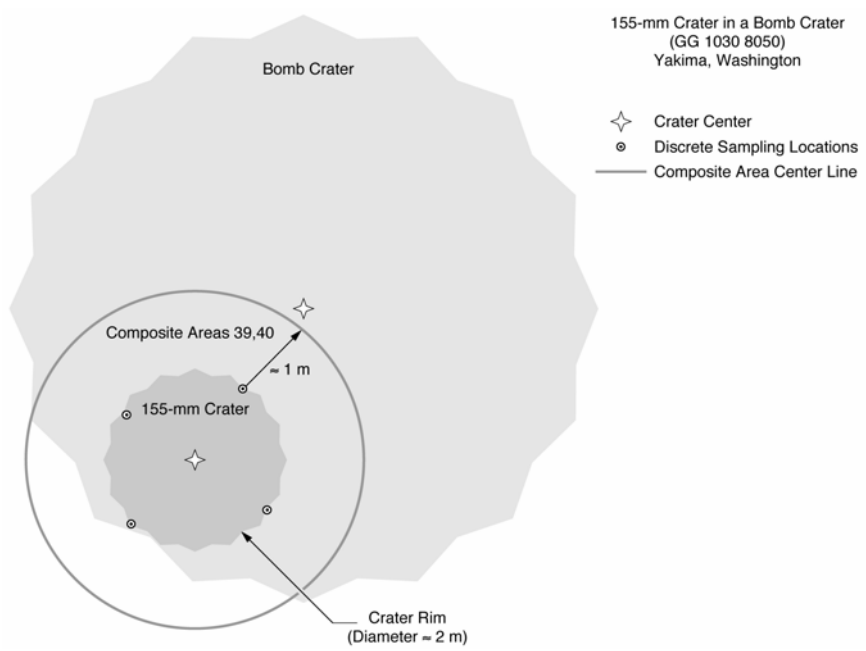

Figure 10. Soil sampling locations in an area of the Central Impact area at Yakima Training Center. Samples were collected within a bomb crater that also had a 155-mm crater within.

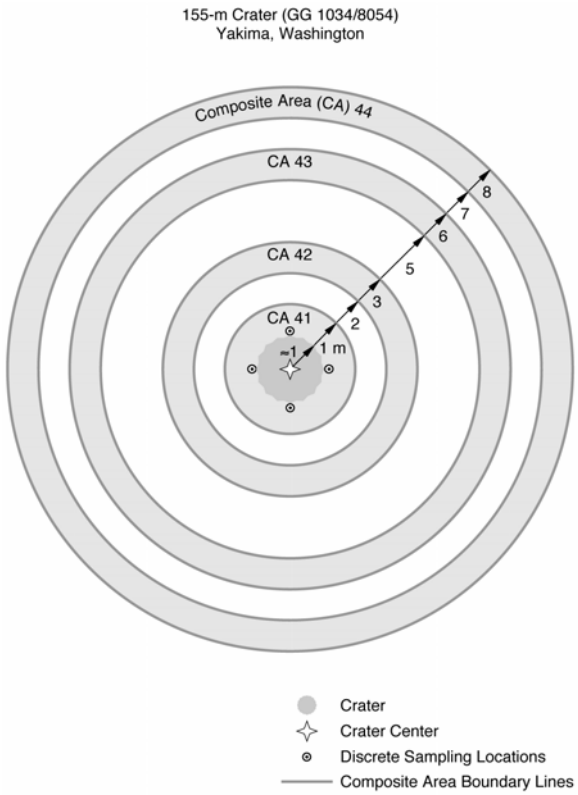

Figure 11. Soil sampling locations around a 155-mm crater at the Central Impact area at Yakima Training Center.

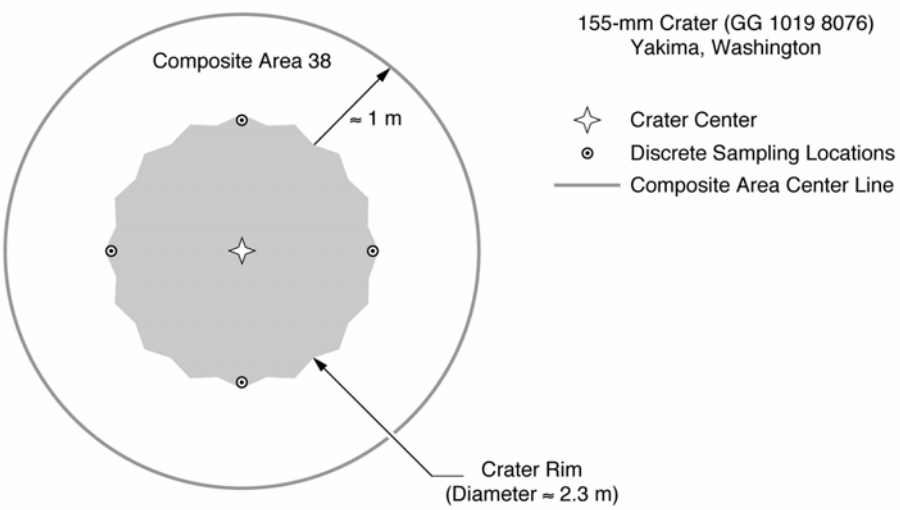

Figure 12. Sampling locations in an area of the Central Impact Area Yakima Training Center, samples collected around a 155-mm crater and next to an illumination round.

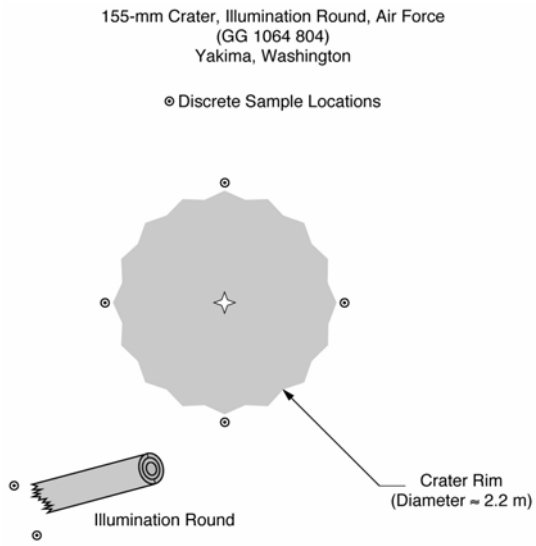

Figure 13. Sampling location in an area of the Central Impact Area, Yakima Training Center, composite sample collected around a 155-mm crater

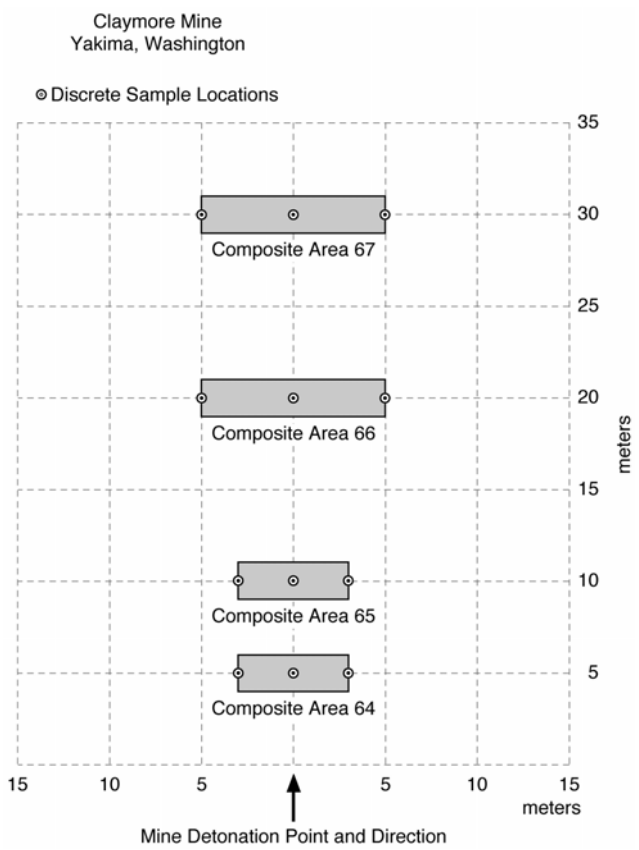

Figure 14. Soil sampling locations in front of the location where a Claymore mine had been detonated at the Yakima Training Center.

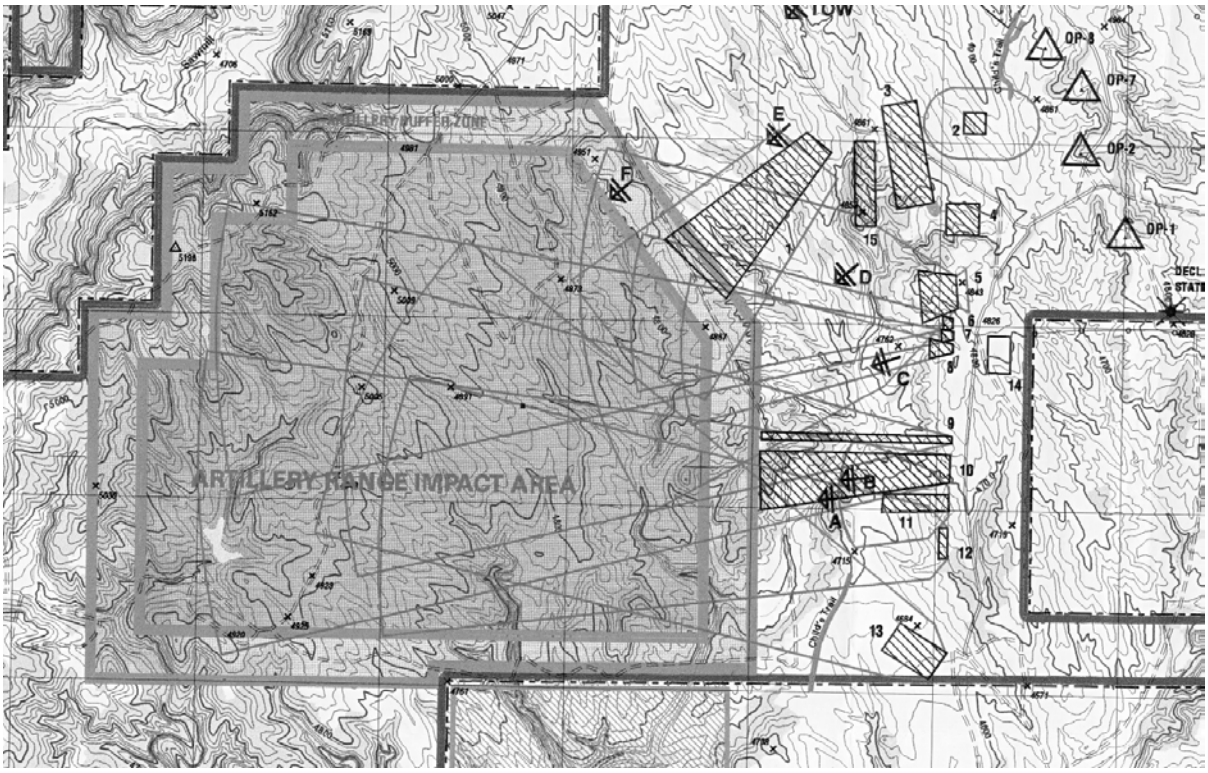

Figure 15. Map of artillery impact area at Camp Guernsey, Wyoming.

Figure 16. Artillery target at Camp Guernsey, Wyoming.

Figure 17. A 500-lb bomb that had undergone a low order detonation, at the central impact area at Camp Guernsey, Wyoming.

Figure 18. Soil samples collected in a wheel pattern at the artillery impact area at Camp Guernsey, Wyoming.

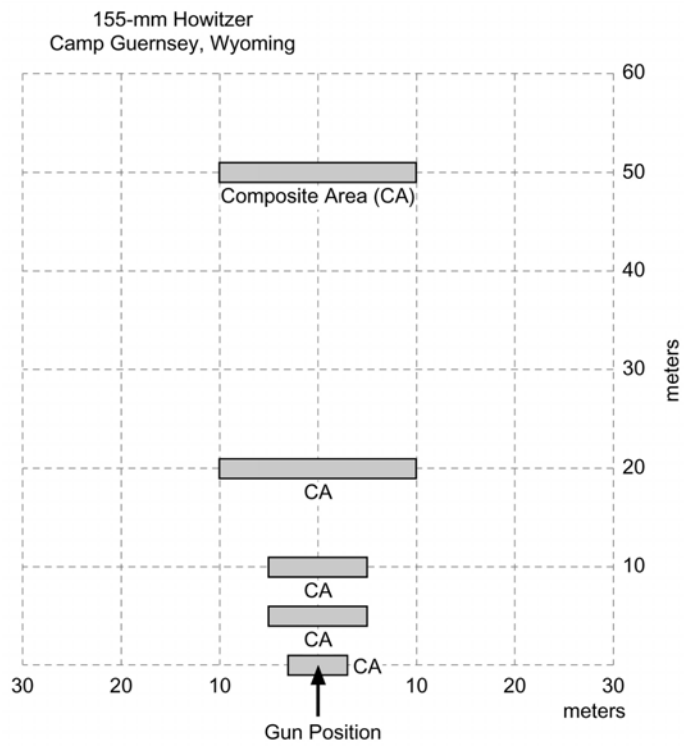

Figure 19. Soil sampling locations in front of firing point for 155-mm howitzers at Camp Guernsey, Wyoming.

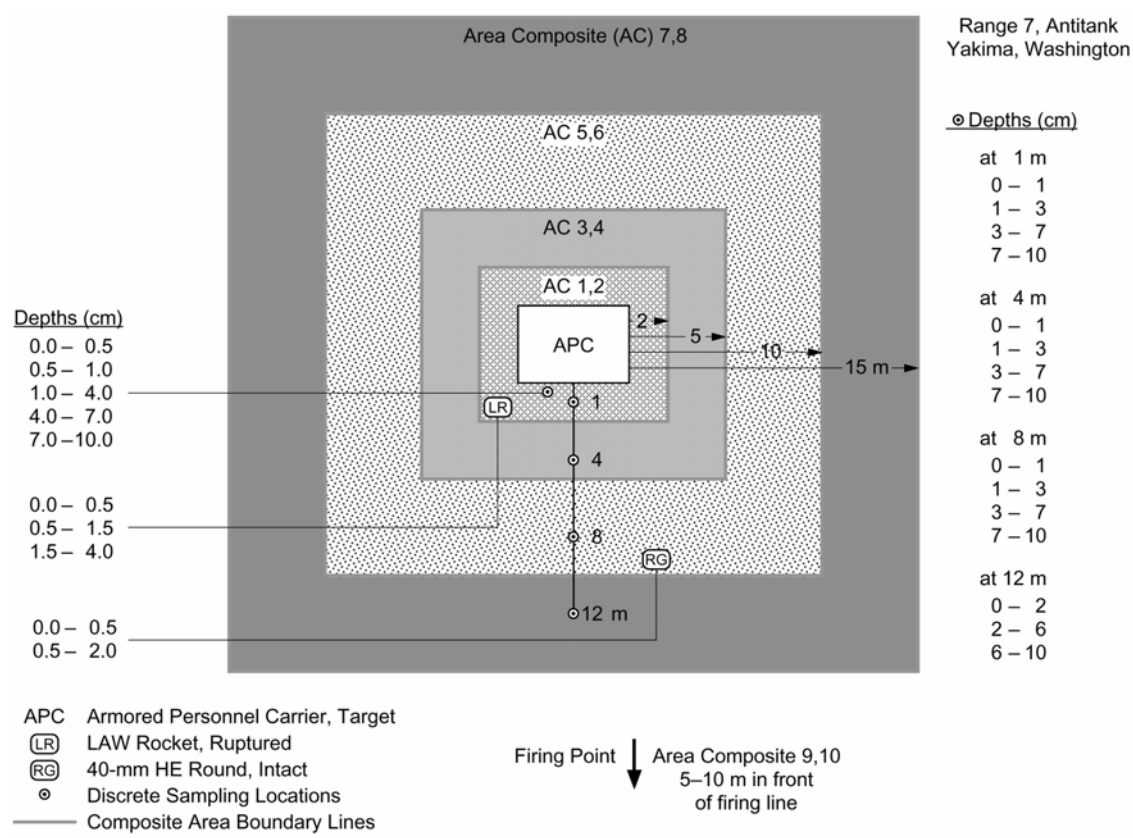

Figure 20. 40-mm HE grenade found on antitank range at Yakima Training Center, Washington.

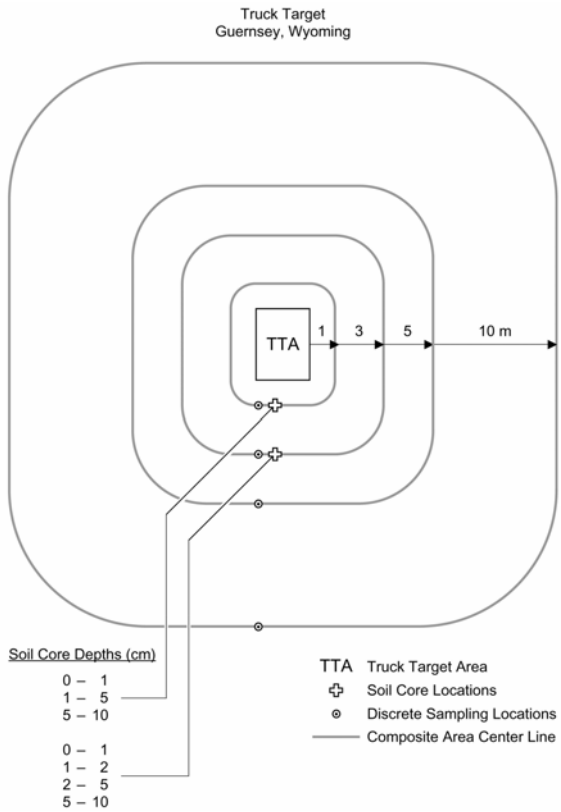

Figure 21. Soil sampling locations around truck target at artillery impact area at Camp Guernsey, Wyoming.

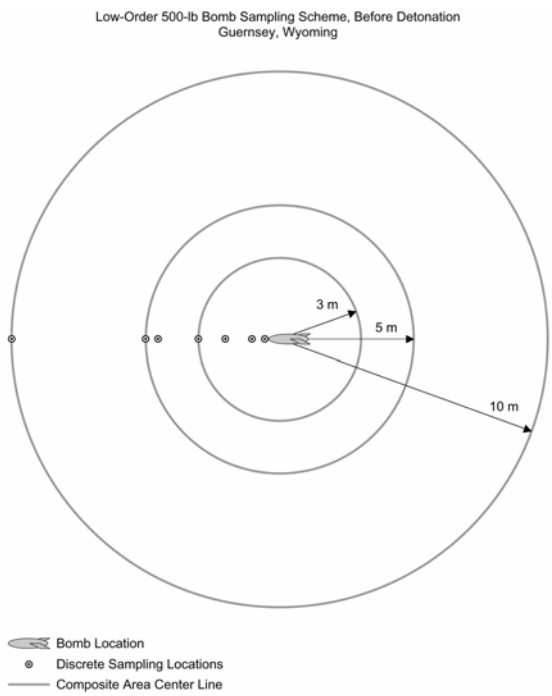

Figure 22. Soil sampling locations around low-order 500-lb bomb at Camp Guernsey, Wyoming.

3 Assessment of CFB Shilo Training Areas Contamination by Explosives and Other Contaminants

Introduction

A comprehensive environmental assessment was conducted at Canadian Forces Base (CFB) Shilo during the month of September 2001(Phase II). Soil, biomass, groundwater and surface water were all tested for a wide variety of contaminants. This report will outline the work performed and should provide the reader with both an understanding of the methodology of the sampling campaign, and the historical context of the contamination.

Range History

Canadian Forces Base Shilo was established in 1910 when the rapid influx of settlers onto the prairies persuaded the Militia Department (now the Department of National Defence) to secure areas of the prairies for military exercises. Initially called Sewell Camp, Shilo was established about 200 km west of Winnipeg on 96 000 acres of rolling prairie. Its size and location were carefully chosen to be appropriate for use as an artillery training range, as well as for all arms maneuvers.

World War one saw the camp explode in size, reaching a peak of 30,000 all-ranks in 1917. However, following the war it was reduced in size and again became seasonal. It was only in 1940 that a permanent camp was constructed in preparation for the renewal of hostilities, and the base as it exists today began to take shape. Following WWII, Shilo became the permanent home to the Royal Canadian Artillery, and the Royal Canadian School of Artillery was established in 1960.

In 1965-66, a West German artillery unit carried out cold weather trials on their equipment at Shilo. This marked the beginning of a long relationship with the German military. In 1974 mechanized troops from the Federal Republic of Germany began training at Shilo under the GATES (German Army Training Exchange Shilo) agreement. The closure of GATES in 2000 prompted an environmental study, conducted by Defence Research Establishment Valcartier (DREV), to assess the impact that 25 years of intensive armoured training had on the prairie ecosystem. Of particular concern were the MILAN missiles that the Germans trained with as these contained Thorium 232, a radioactive element used as a tracer in the guidance system.

The ammunition expended since 1910 is nothing less than astounding, and gives an excellent idea of the magnitude of the Unexploded Ordnance (UXO) challenge. Canadian expenditures are estimated at 2,185,000 rounds, and German expenditures at 299,000 rounds for a total of nearly 2.5 million rounds. Given a conservative dud rate of 5%, 125 000 rounds of dud munitions are left over an area of 96,000 acres. The majority of the ammunition that has been fired is either 105 or 155 mm artillery rounds and 105 mm tank rounds. These munitions are all quite large and contain several kilograms of explosive filling. Even if level one clearance is done on a regular basis, the casual observer at Shilo will find several unexploded munitions in the course of a day. As it is reasonable to assume that most of the dud rounds are buried, the potential environmental impact is obvious. Therefore, the potential for the contamination of the soils, biomass or groundwater by explosive is considered relatively high.

It should also be pointed out that prior to 1970, records were not kept with the same accuracy as they are today, and in fact the numbers quoted here could be even higher. As well, experimental trials have been conducted at CFB Shilo by both the Canadian and German military. These secret trials left no record of either the number or the type of rounds that were fired.

There are thousands of unexploded rounds at CFB Shilo as a legacy of 90 years of military training. The goal of the present study was to identify the environmental impacts these munitions are causing, including the potential for explosive contamination of the training ranges and their surroundings.

Environmental assessment

In 2000, an environmental assessment of Canadian Forces Base Shilo was tasked to Defence Research Establishment Valcartier by DGE, prior to the GATES closure. The first characterization of the Shilo battleruns was accomplished in the fall of 2000 following the departure of Germans in order to establish the impact of the past training activities on the environment. This initial work was done under

considerable time and funding constraints and indicated that a more extensive and detailed assessment was necessary. This second phase of the characterization of Shilo training ranges was conducted in September 2001 and is the subject of this report. Dr Guy Ampleman, Dr Sonia Thiboutot, Mr. Jeff Lewis and André Marois from DREV were on site and led the characterization work. Dr Richard Martel, Jean-Marc Ballard and Catherine Gauthier from Institut National de la Recherche Scientifique (INRS) led the hydrogeological characterization work. Eight Defence Construction Canada employees were on site to assist the field work and to lead the sub-contractors involved for the drilling of piezometers, proofing of the drilling locations by electromagnometers (EM-61) and the analysis of samples for other parameters than energetic materials.

Distinguishing between an environmental assessment and environmental remediation is important. The work done at Shilo was purely a measurement of the contaminants present in the environment at CFB Shilo. The purpose of this work was simply to identify the problem if present prior to any cleanup. While assessments can be done in weeks or months, remediation efforts usually require years. This environmental evaluation was initiated primarily to determine Germany's share in any clean up or remediation activities. Now the goal is more oriented to understanding and sustaining the training activities as well as understanding the fate of explosives in the training area environment.

This assessment addressed four areas of concern, the contamination of surface soils, of the aquifer, of the biomass and of the surface water. The contamination patterns of surface soils around targets and in battleruns were evaluated. The unconfined aquifer underlying the training area was assessed (hydrostratigraphy, hydraulic conductivity, groundwater flow direction) and the groundwater quality were characterized. The extent of biomass contamination in the worst-case scenario locations (around targets) and in battleruns was assessed and finally, the surface water quality was evaluated.

In previous DREV studies, surface soils were contaminated by energetic materials and metals in training ranges, especially in anti-tank ranges. On the other hand characterizing the groundwater quality is also critical, especially on such a large range. Metals and energetic materials are both mobile in sandy environments and may, therefore, migrate with the groundwater, thus presenting a threat to human health and the environment. Moreover, combined with groundwater quality, groundwater flow had to be carefully assessed to determine its velocity and direction to evaluate the amplitude of a potential problem. This groundwater serves as a drinking water source for the base, is used to sustain aquatic ecosystems, and also serves for irrigation. Consequently, any contamination could impact human health, the irrigated crops and the aquatic ecosystems. In fact, groundwater flowing under CFB Shilo discharges into surface

water in many springs southeast of the range discharging into the Assiniboine River and into the Marsh Creek to the north of the range. Both are highly sensitive areas of potential wildlife and humans receptors. Epinette Creek to the north is also used for irrigation. Biomass, such as prairie grass, has proven to bio-accumulate both metals and energetic materials. Therefore, prairie grass could represent a high potential intake source of these compounds for wildlife. Finally, the surface water quality had to be verified since wildlife has access to it and it can also be used for irrigation.

Sampling strategies

Soil and biomass sampling was conducted under DREV's supervision while surface water and groundwater sampling was conducted with the guidance of INRS. DREV and INRS have both developed expertise in the characterization and the environmental fate of energetic materials in Canadian Forces training ranges and open detonation ranges. For this particular sampling campaign, Defence Construction Canada (DCC) was supporting DREV and INRS during the phase II by hiring the drillers, all the necessary personnel, supplying materials, etc. Funding was provided mainly from Defence Land Force Requirement (DLFR) for the hydrogeologic portion of the study and from Stategic Environmental Research and Development Programme (SERDP) for the surface soil and biomass sampling portion of the study. The phase I of the Shilo characterization was performed during September-October 2000 following Germans' departure and the phase II was performed during September 2001. Drs. Judy Pennington and Thomas Jenkins were supposed to attend the sampling campaign in mid-September, but due to the September 11th events they were unfortunately not able to travel to Canada

Soils

The Germans conducted the majority of their training at five battleruns at CFB Shilo. Three of these battleruns were sampled during the first characterization (phase I)(Berlin, Deilinghofen and Essen). These battleruns were the focus of the soil and biomass sampling campaigns. During the second phase, the two remaining battleruns, Aachen and Cologne, rifle ranges, grenade ranges and a small part of Essen named Klein Essen were sampled for biomass and soils. Since a pattern of contamination was observed around targets in the battleruns during the first phase, more efforts were done during phase II to sample biomass and soils around targets. A battlerun is a loosely defined area approximately 5 km long and up to 2 km wide where tanks and other armoured vehicles conduct mounted exercises. Various types of targets were used, most of them were pop-up targets not designed to stop the rounds. Therefore, these rounds could end up landing just about anywhere. If live firing leads to the accumulation of contaminants in soils, higher levels should be found at the end of battleruns since the ammunition fired should end up

towards the far end. Therefore, the sampling involved the collection of linear composite samples at 20, 40, 60, 100 and 120 % of the length of each ranges as illustrated in figure 1. The start point for each of the linear composite samples was pinpointed using a GPS, cross-referenced with a topographic map of the base. From the start point, small amounts of soil were collected randomly while walking perpendicularly across the battlerun. Each sample was normally approximately 1 kg, and was composed of a minimum of 20 discrete samples. A large effort was also dedicated to the identification of specific "hot-spots" such as broken UXOs. Soil and biomass samples were then collected around these potential "hotspots", such as near UXOs that had broken open. Few of such hotspots were found. This can be explained by the type of training conducted in battleruns. Pop-up targets do not stop rounds, which is quite different to the situation on anti-tank training ranges. Anti-tank rocket ranges usually use static targets – often WW II vintage tanks – and these massive targets often cause dud rounds to break open on impact. The situation with pop-up targets is arguably better than that on anti- tank ranges because the explosive content of the shell is not spread into the environment. A circular sampling strategy used around targets to collect biomass and soil samples consisted in building composite samples out of 20 sub-samples of soils or biomass collected at specific distances such as 0-1, 1-3, 3-5, 5-10 m as illustrated in figure 2.

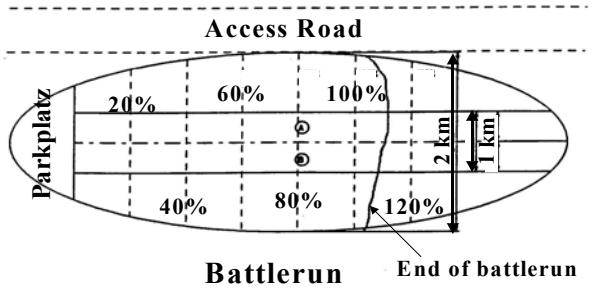

Figure 1: Linear sampling used in battleruns for soils sampling

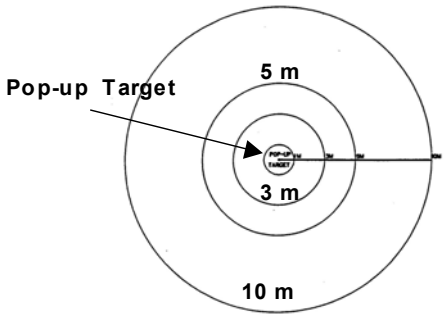

Figure 2: Circular sampling around target in battleruns for soils and biomass sampling

Finally, specific soil samples were collected for thorium analyses in suspected areas where Milan missile debris was found. In these instances, missile debris was used as sources for the circular sampling strategy. When soils were taken as background samples, they were collected in a random manner, in a circular pattern of approximately 20 meters. A minimum of 30 sub-samples was collected to form each background sample.

Biomass

As mentioned earlier, biomass samples were simply composite samples of different plant species. Given the prairie ecosystem at Shilo, most of the plants collected were grasses or small shrubs. Only the aboveground parts of the plant were sampled, no roots were included. Each composite sample was composed of many different discrete samples taken in a roughly 10-meter diameter area. One composite sample was generally around one litre in volume of compacted biomass. During Phase II, no biomass sample was collected in the battleruns using the linear sampling strategy since no pattern of contamination was observed during Phase I. Our efforts for biomass sampling during Phase II were concentrated in backgrounds, around hot spots, around targets in battleruns, in rifle and grenade ranges.

Biomass provides a powerful indicator of whether contaminants are entering the food chain. Herbivorous animals will consume contaminants, either in the cellular structure or on the surface of plants. These contaminants will be concentrated in body tissues, and passed on to the carnivorous animals that prey on the plant eaters, where they are concentrated again. The classic example of this process is the peregrine falcon, which was pushed to the brink of extinction due to extremely high tissue levels of the pesticide DDT.

No standard guidelines for the presence of various contaminants in biomass exist. Different plants will absorb different levels of a given contaminant, making guidelines virtually impossible. However, the simple presence of a contaminant in plant tissues gives a reasonable indication that the contaminant may be in the food chain, and it may cause damage higher up the chain where it becomes more concentrated.

Metals that could be either inside the plants following bio-accumulation (phytoremediation) or on the plant (accumulated by deposition of dust) were evaluated by digesting the biomass samples or a portion of the biomass samples was leached in distilled water and analysed. This was used to discriminate

the metal that was found in or on the plants. For energetic materials, lyophilisation of the entire biomass material was done so the concentrations represent the total amounts in and on the plants.

Groundwater

Monitoring wells were installed according to the ASTM-D5092-90 standard. These wells were placed according to available groundwater flow data obtained during phase I, and were spread throughout the base to complete the piezometric map. Prior to sampling, each well was thoroughly developed. Development involves the removal of the fine sedimentary particles in the soil which are present at the level of the aquifer, and which would otherwise contaminate the sample. Once developed, water samples were taken to test for explosive residues and thorium as well as more common contaminants such as heavy metals and solvents.

Slug tests were done on all developed wells for an estimation of hydraulic conductivity of the sand formation. This was done by injecting compressed air into the well in order to drop the water table between 30 and 70 cm below its natural static level. After an instantaneous pressure release the rise in water table was recorded with a Level Logger pressure gauge (from Solinst). Data interpretation was done with the Bower Rice method to evaluate the hydraulic conductivity. As well, the horizontal component of groundwater velocity and direction was measured *in situ* with a flowmeter (*Geoflo 40L*). The *Geoflo 40L* is a probe with eight thermistors placed around a heat source. The instrument measures the propagation and the deformation of a heat pulse in the groundwater. In dynamic systems like an aquifer, the heat pulse propagates with an elliptic shape and the long-axis is oriented in the groundwater flow direction.

Water level measurements were made after well development. An electronic measuring tape (RST) with a precision of ± 0.5 cm was used to record the water depth in every well in relation to the top of the PVC tubing. As well, pH, conductivity, and redox potential were measured electronically at each well. The position and elevation of the top of each well PVC casing was determined using the two GPS technique. The GPS locations (northing and easting) of monitoring wells and the elevations of the top of the PVC tubing served to construct the piezometric map. The error associated with GPS location is ± 2 m whereas the precision on elevation was ± 0.01 m with this technique.

Surface Water

Surface water was sampled from streams, rivers and springs, both on the base and outside its boundaries as background samples. Surface water from these sources is replenished largely from

subsurface sources. Therefore, surface water can provide useful information without having to drill and develop monitoring wells. In addition, samples can be taken in areas which otherwise could not be sampled – such as on private land when the owners would be unlikely to authorize the drilling of a well. Conductivity, redox potential and pH were measured at each site. The same series of samples were taken as for subsurface groundwater, in order to allow the same testing.

Parameters monitored and analytical methods

Soil and biomass samples were analyzed for metals, energetic materials and specifically for thorium-232. Groundwater and surface water samples were analyzed for heavy metals, anions, thorium, energetic materials and other more common contaminants and parameters such as dissolved solids. As opposed to Phase I, no parkplatz (staging area for fueling/refueling vehicles, tanks) was sampled, so no petroleum, VOCs and BTEX were analysed in soils and groundwater. Metals were analysed by Inductively Coupled Plasma Mass Spectrometry, (ICP/MS) and all the parameters available by this method were included in the study. Energetic materials for soils and groundwater were analysed at DREV by Gas Chromatography/ Electron Capture Detector, a method that leads to 1 ppb detection limit for explosives. INRS conducted the following on site groundwater measurements: pH, electrical conductivity, temperature, dissolved oxygen and Eh. Furthermore, water level measurements, in situ permeability tests and groundwater flow direction and velocity measurements were also conducted. Thorium-232 was analysed by the Geological Survey of Canada using ICP/MS with a detection limit of 5 ppt for aqueous samples. All the results coming from these analyses are presently being compiled, analysed and will soon be available in the final report.

Magnitude of the study

During the first phase of the characterization done in September 2000, a total of 83 soil (8 background), 34 biomass (4 background), 34 groundwater (3 background) and 11 surface water (2 background) samples were collected. Background soil samples are critical for establishing the anthropogenic contribution versus the natural contribution for all parameters. A total of 18 background soils samples were also planned for collection. However, due to the same limiting factors mentioned earlier, only 8 background samples were collected, all in the southern part of the Shilo training area. All these samples were collected mainly in three battleruns and in parkplatz, soils were sampled at each of the five battleruns for traces of volatile organic compounds (VOCs) and BTEXs. Two composite samples were randomly collected at each parkplatz and named samples

A and B. The composite samples were formed of a minimum of 20 sub-samples. For thorium-232, the target areas for the MILAN missiles were identified and the approach using the circular pattern was applied to collect soil samples. 41 boreholes were drilled and observation wells were installed. Out of these, because of the bad weather, only 36 wells were developed and groundwater was collected in only 34 wells.

Soil sample results were compared to Canadian Council Ministers of Environment (CCME) soil threshold criteria and also with the mean value of background sample results for some representative metals. None of the soil samples collected exhibited contamination levels higher than any of the CCME threshold criteria, even for agricultural soils. This indicated no major soil contamination at either surface or sub-surface levels.

The analytical results for the parameters tested in all types of samples showed no major environmental impacts related to the training activities. In soils, the accumulation of some heavy metals associated with ammunitions was observed around pop-up targets, but did not reach levels of concern. Neither surface nor sub-surface soil samples showed levels of metals higher than agricultural CCME criteria. Our study clearly demonstrated that no major problems are associated with soil contamination. The fact that higher levels of contaminants were encountered around targets proved that the firing activity caused an accumulation of contaminants locally, but not at levels of concerns. However, radioactive thorium accumulated near targets in both soils and groundwater presenting a concern. Soil samples near targets presented statistically higher results for ^{232}Th, while results for groundwater showed ppb levels of radioactive compound, close to identified impacted area with MILAN missiles. This highlights the fact that measurable impacts were found related to the use of the missiles. Levels are still very low, both in soils and groundwater, but considering the very long half-life of this particular contaminant, measurable traces of this element are a matter of great concern. ^{232}Th has accumulated around target impact area and, even if this element has a very low solubility, the trace levels found in the groundwater might migrate off range in a long-term scenario. Therefore, MILAN missile firings was recommended to be discontinued at CFB Shilo. Collection and disposal of MILAN missile debris according to an existing procedure for radioactive materials was also recommended.

All the analyses for explosives revealed no contamination in soils, groundwater and biomass

samples. Energetic materials analyses showed only traces levels of energetic residues, which were under our quantification limits, in some water samples. This will be confirmed when a 1 ppb detection and quantification levels will be obtained and will allow the certification that no traces level of explosives are found in the Shilo groundwater. Confirmation of the absence of energetic residues in the groundwater is still very important and will be completed in phase II.

Results obtained from the biomass samples, both for metals concentrations in plants (extracts) and the metals dust on the plants (leachates) showed no levels of concerns for metals in battleruns when compared to the biomass background mean values. Only five hits were encountered in the Berlin range where some metals showed concentrations higher than for the background samples. These hits were not considered critical. Higher levels of chromium and aluminium were found in the 80 and 120 % transects where the highest concentrations of UXOs were expected to be found. No hits were observed in the Essen or in the Deilinghofen battleruns.

No biomass samples were collected around targets for which systematic soil sampling was carried out. This decision was based on discussions with range controls who believed that the targets should not present the highest levels of UXOs concentration. Since the targets were pop-up targets more than 90 % of the munitions fired at them did not stop, but continued towards the end of the battleruns. The fact that we did not collect plants around targets was unfortunate, since a trend in accumulation of metal was observed for soils and could have also been observed for the biomass. This was corrected in phase II where many biomass samples were collected around targets.

For some groundwater and surface water samples, Al, Mn, Fe, Cr, Ag and Se exceeded CCME threshold criteria. However, iron and manganese were found in background samples at high levels and, therefore, were not considered as threats to the environment. Aluminum was found in trip blanks (empty container sent along with the other samples to evaluate if contamination is occurring during transportation of the samples to the lab) and field blanks at level as high as 60 ppb. Therefore, levels lower than 60 ppb should be considered insignificant. Silver was detected at high levels as outliers in some isolated replicates, but the remaining data revealed no detections indicating that these high values were false. Chromium and selenium were detected at low levels exceeding the lower limit interval of the aquatic threshold criteria and, therefore, should not be considered a threat in groundwater media.

At the end of phase I, further work was recommended to fully characterize this very large site. One should keep in mind that this study was made at a regional scale and that the sampling was, therefore, not representative of the whole area. Point sources at the local scale could still be found in the future. The training area can be considered as a weak source with various modes of transportations for contaminants with no measurable impacts on environmental receptors outside of the range.

Phase II was dedicated mainly to complete the work initiated during the first phase. This resulted in more background sampling, more soil and biomass sampling around the targets to better assess the pattern of contamination, more thorium sampling in suspected areas, sampling soils and biomass in rifle and grenade ranges and completing the sampling of the two remaining battleruns. During this phase, 162 soils samples including 23 as backgrounds, 64 biomass samples including 18 as backgrounds were collected. Forty supplementary wells were drilled and installed to complete the piezometric map of the base. All the 80 wells were sampled for groundwater analyses and more surface water samples were collected around the base. 132 groundwater samples including 12 as backgrounds were collected and surface water samples were also collected to evaluate what is going out of the ranges. All these results are being compiled and analysed for the writing of the final report.

Conclusion

The task of environmentally assessing a large area is enormous. This effort represents one of the first efforts worldwide to comprehensively assess an active training base. The situation in battleruns using pop-up targets is completely different from the one encountered in anti-tank training. The enormous density of unexploded ordnance presents a huge environmental challenge, both in the immediate physical danger of unexpected detonations and in the longer-term biological damage caused as the explosive and metallic components of the munitions enter the environment. The nature of munitions as contamination point sources makes the task of identifying all contaminated sites extremely difficult. The task of assessing military sites is challenging, but must be done in the interest of sustaining the training activities in the long-term.

4 Transport Parameters for Firing Range Residues

Background

Dissolution of explosives residues from free product contained in cracked or partially fragmented munitions is the primary method by which nonvolatile explosives contaminate firing ranges. Yet, dissolution rates of explosives components of munitions have not been measured (Brannon et al., 1999). Soils analysis show concentration gradients for HMX and TNT that are consistent with kinetic limitations on solubilization (Jenkins et al. 1997). However, the information available on dissolution kinetics of explosives residues is limited to a small amount of unpublished data by Jenkins that show pronounced differences in the rates of TNT, RDX, and HMX movement into solution over time. Thiboutot et al. (1998) show that for octol, the dissolution rates of TNT and HMX differ substantially. Gilcrease, Murphy, and Reardon (1996) reported that surface area and mixing rate effects TNT dissolution rate. Accurate dissolution rate kinetics for explosives and the main explosives formulations used in munitions are key parameters for describing the fate and transport of explosives residues from firing ranges into groundwater.

The main factors affecting fate and transport of explosives residues after they dissolve from solid phase residues are adsorption, transformation and irreversible soil binding (Brannon and Myers 1997). The fate and transport process descriptors are required for describing the movement of explosives residues through soil and into groundwater are the adsorption coefficient and the transformation rate coefficient. Process descriptors mathematically depict the impacts of interactions between soil and water on explosives concentrations in water and soil. The adsorption coefficient is a mathematical expression that describes the distribution of a chemical compound between soil and water when they are at equilibrium. When transformation or irreversible sorption is significant, equilibrium is not attained and the transformation rate coefficient is used to describe the fate and transport of an explosive contaminant. The transformation rate coefficient is a kinetic parameter that describes the removal of a compound from solution by transformation and sorption. The transformation rate coefficients generally follow first-order kinetics (Brannon and Myers 1997). The amount of available data on fate and transport process descriptors for explosives residues varies greatly. Most studies have been directed at TNT and its transformation products, RDX, and to a lesser extent, HMX.

This chapter reports progress on development of environmental fate and transport parameters for selected energetic residuals for which data are currently lacking or that have been detected on firing ranges. Fate and transport parameters are used to evaluate the migration of explosives residues from the solid phase residue into solution during rainfall events (dissolution kinetics) and the interactions of explosives residues in solution with firing range soils that then occurs. This chapter presents new process data leveraged with the Army Installation Restoration Research Program (IRRP) work unit titled "Fate and Transport of Explosives Contaminants" (A835/309E/RE004) which provided 90% of the funding for this effort. When completed, the dissolution data will be published as a separate "thesis" ERDC report.

Objectives

The objectives of this study were (1) to evaluate dissolution kinetics for the explosives formulations Composition B, octol, and LX-14, (2) to determine dissolution kinetics and solubility for TNT, RDX, and HMX, and (3) to determine process descriptors for selected explosives residues for which data are lacking. Fate and transport process parameters were determined for nitroglycerine and the mono-, di-, and tri-nitroso transformation products of RDX (MNX, DNX, TNX). In addition, site specific process descriptors were determined for TNT, RDX, and HMX in Ft. Lewis soils.

Materials and Methods

Explosives Dissolution: Kinetics

Three military grade explosives selected for this study were 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). TNT is a nitroaromatic explosive while RDX and HMX are classified as nitramines (Figure 1). The TNT used in this study is identified as Type I flake, the RDX is Type II, Class 3 crystals, and the HMX is Grade B, Class 2 crystals. Military grade high explosives were used to replicate the nature of explosives expected in a field environment (i.e. age, composition) and were deemed more representative than pure individual compounds. These explosive compounds were used separately and in the preparation of the non-bound explosive mixtures to compare with the explosive compounds in the formulations Composition B, octol, and LX-14.

Environmental variables. The choice of experimental variables was based on key terms in Fick's First Law

$$V\frac{dC}{dt} = \frac{D}{h}a\left(C_s - C_b\right) \qquad (1)$$

where dC/dt = the change in concentration over time (mg $s^{-1} \cdot L^{-1}$), V = volume of solvent (L), D = diffusion coefficient (cm^2 s^{-1}), a = surface area (cm^2), C_s = solubility (mg cm^{-3}), C_b = concentration in bulk liquid (mg cm^{-3}); and h = stagnant layer thickness (cm).

This expression can be reduced to a zero order equation where the approximation of the $\frac{D}{h}$ term under different environmental conditions is possible. To approximate a zero order equation, several of the variables in Eq. (1) were assumed constant. In dilute solutions, C_b is small with respect to C_s and is assumed negligible. Sampling intervals were therefore arranged to be complete before the predicted C_b/C_s ratio reached 0.2. Experiments were also controlled so that changes in solvent volume (averaging a 1% loss from total sampling) and explosive compound surface areas (averaging a 5% loss from dissolution) would be negligible. The need to maintain a dilute solution affected run times, ranging from 4.3 minutes for HMX at 30 ^oC (solubility less than 3 mg L^{-1}) to 120 minutes for TNT at 10 ^oC (solubility greater than 70 mg
L^{-1}).

The three temperatures selected for this study (10, 20, 30 ^oC) are representative of the range of ambient conditions where unexploded explosive compounds might be found in the environment.

Approximation of explosive surface areas was necessary because of the heterogeneity of particle sizes and shapes (ranging from less than 0.04 mm in diameter for HMX crystals to greater than 4 mm in length for TNT flakes). Surface areas for RDX and HMX were estimated using mass to surface area ratios for each explosive based on military specifications for acceptable granulation distribution. These nominal surface areas do not account for surface roughness that was seen microscopically on the explosives. Based on a desired separation of approximately 20 % among the three sample surface areas (to provide sufficient separation yet fit within the conditions of this study), RDX quantities that produced sample surface areas of approximately 8, 10, and 12 cm^2 were measured out using an estimated RDX surface area to mass ratio of 100.4 cm^2 g^{-1}. Similarly, sufficient HMX was used to produce sample surface areas of approximately 5, 6, and 7 cm^2 based on an HMX surface area to mass ratio estimate of 598.5 cm^2 g^{-1}. Surface area effects on dissolution rate were normalized by dividing the dissolution rate

(mg min^{-1}) by the nominal explosive surface area used in the run (cm^2), resulting in a rate with units of mg min^{-1} cm^{-2}.

Measuring TNT flake areas under a microscope and then weighing these sets of flakes on a balance yielded a reproducible surface area to mass ratio. This method yielded a surface area to mass estimate of 23.28 cm^2 g^{-1}. Sufficient TNT was used to produce sample surface areas of approximately 5.8 cm^2, 7.3 cm^2, and 8.7 cm^2.

The stagnant layer thickness represents the gradient zone in the solution between the surface of the solid explosive (where the solution concentration is at the solubility limit) to a point in the solution where the concentration equals that of the rest of the bulk solution. Since dissolution is affected by the rate of transport from the surface of the explosive compound to the bulk solution, rates would increase if the layer were thinner and the gradient steeper (Stumm and Morgan 1996). This condition can be achieved by energy input in the form of agitation or stirring. Mixing rates of 90, 150, and 250 rpm were selected to examine effects of mixing rate on dissolution rates.

Experimental design. To determine the impact of each variable on dissolution rate, one of the variables was allowed to change while the other two were held constant. To limit TNT photolysis (Townsend and Myers 1996), experiments were performed under limited light conditions and samples were stored in the dark. The experimental design is based on dissolution tests described in the United States Pharmacopeia Convention, Inc. (1990).

Initially, 500 ml of demineralized (reverse osmosis) water in 600 ml beakers were covered with aluminum foil and allowed to equilibrate for 15 hours to temperature in a water bath. The water temperature was regulated using a Fisher Scientific Isotemp Refrigerated Circulator and insulated by a floating layer of 20-mm hollow plastic balls.

Stirring propellers from overhead mounted Yamato Scientific StedFast Digital Lab Stirrers were centered and lowered into the beakers, adjusted to the desired rpm, and raised to a height of 2.5 cm above the beaker bottom. Once these conditions were achieved, the desired amount of dry explosive compound was added to each beaker. While continuing to stir, five one-milliliter samples were periodically pipetted from a zone midway between the surface of the solution and the top of the stirring propeller and midway between the beaker wall and the propeller shaft.

Analytical methods. Pipetted 1 ml samples were immediately filtered using a disposable 3 ml Luer-Lok syringe with attached Millex Millipore Filter unit (0.45 µm pore size). The filtrates were combined with an equal volume of 0.45 µm-filtered acetonitrile, and capped in a 4 ml vial. The vial was vortexed for five seconds and then stored quiescently for at least 25 minutes. Samples were analyzed using a Waters High Performance Liquid Chromatograph (HPLC) following Method 8330 (USEPA, 1994).

Effects of pH on explosives solubility and dissolution

The Holston Army Ammunition Plant, Kingsport, Tennessee, provided experimental quantities of TNT and the explosive formulations octol and composition B. Picatinny Arsenal, Picatinny, New Jersey, provided experimental quantities of LX-14, RDX, and HMX. Demineralized water (reverse osmosis with a pH of approximately 5.7) was used with the pH adjusted lower by addition of H_2SO_4 and HNO_3 or higher by the addition of Na_2CO_3 and NaOH. These chemicals were selected to replicate acid rain and basic conditions expected in the natural environment.

Environmental variables. Environmental factors such as temperature and pH can affect solubility and therefore chemical fate and toxicity (Huang et al. 2000). If ideal conditions are assumed, solubility can be estimated using the equation (Atkins 1982):

$$\ln x_B = -\left(\frac{\Delta_{fus} H}{R}\right)\left(\frac{1}{T} - \frac{1}{T^*}\right) \qquad (2)$$

where x_B = mole fraction of solute, $\Delta_{fus}H$ = enthalpy of fusion of solute, R = ideal gas constant, T = absolute temperature, and T^* = solute melting temperature. Aqueous solutions of explosive compounds are not ideal, but the general equation remains similar following the form

$$\ln S = A - \frac{B}{T} \qquad \text{or} \qquad S = A * \exp\left(\frac{-B}{T}\right) \qquad (3)$$

where S = solubility, A and B = arbitrary constants, T = absolute temperature.

Taylor and Rinkenbach (1923) conducted one of the earliest studies on TNT aqueous solubility over the temperature range 0 to 100 ^{o}C, but did not evaluate the effect of pH. Spanggord et al. (1983) reported expressions for TNT and RDX solubility based on measurements at 10, 20, and 30 ^{o}C, but also did not investigate pH. Ro et al. (1996) reported aqueous solubilites for TNT at differing pH levels and

temperatures. They proposed a solubility correlation and found that temperature had the greater impact on solubility and that solubility varied widely at higher pH. Phelan and Barnett (2001) reported TNT pH independent aqueous solubility values that agree with those reported by Spanggord et al. (1983). None of the predictive solubility correlations were similar to the others. Townsend and Myers (1996) and Gibbs and Popolato (1980) list solubilities from the literature for TNT, RDX, and HMX as a function of temperature and independently of pH. These values will be shown later in figures compared with results from this study. Here we re-evaluate TNT solubility as a function of temperature and pH, and add evaluations of RDX and HMX solubility as a function of these same variables.

Dissolution is the primary mechanism allowing for transformation and transport of nonvolatile explosive compounds. Dissolution rate and solubility control the persistence of the explosive at the source and the degree of contamination at some distance away from this source. Fick's Law can be used to predict the concentration of explosive compounds dissolved in water as well as the time required to reach solubility limits.

$$\frac{dC}{dt} = K_L a\left(C_s - C_b\right) \tag{4}$$

where dC/dt is the dissolution rate, $K_L a$ = overall mass transfer coefficient, C_s = solubility, and C_b = concentration in bulk liquid. If the dissolution rate is known, equation 4 (Tchobanoglous and Schroeder 1987) can be integrated to identify the concentration, C_t, at any time:

$$C_t = C_s\left(1 - e^{(-K_L a)t}\right) \tag{5}$$

Information on high explosive dissolution rates is sparse. Gilcrease et al. (1996) reported that increasing stirring rate increased dissolution of TNT and surface area by grinding of the particles during mixing. The effects of pH have not been addressed. The zero-order, multivariable dissolution rate (dC/dT) equations (in units of mg dissolved per minute) are

TNT

$$\frac{dC}{dt} = \left(9.82E-6\left[\frac{mg}{\min - C - cm^2 - rpm}\right] * temp[C] - 4E-5\left[\frac{mg}{\min - cm^2 - rpm}\right]\right) * sa\left[cm^2\right] * rpm \tag{6a}$$

RDX

$$\frac{dC}{dt} = \left(1.49E-6\left[\frac{mg}{\min - C - cm^2 - rpm}\right] * temp[C] - 6.1E-6\left[\frac{mg}{\min - cm^2 - rpm}\right]\right) * sa\left[cm^2\right] * rpm \quad (6b)$$

HMX

$$\frac{dC}{dT} = \left(4.46E-6\left[\frac{mg}{\min - C - cm^2 - rpm}\right] * temp[C] - 7.8E-7\left[\frac{mg}{\min - cm^2 - rpm}\right]\right) * sa\left[cm^2\right] * rpm \quad (6c)$$

where temp = temperature, sa = nominal surface area, and rpm = stirring rate in the experimental design.

Experimental design. Aqueous solutions with pH values of 4.2, 5.7, and 6.2 were used as the solvent for the solid explosive dissolution experiments. An excess amount of solid explosive was added to 200 ml of pH adjusted water in a 250 ml Erlenmeyer flask wrapped in aluminum foil to minimize photolysis (Townsend and Myers 1996).

A magnetic stir bar was added to the flask, which was then sealed with parafilm. The solution was stirred on a magnetic stirrer at a rate sufficient to maintain a deep vortex. Experiments were performed in duplicate and at temperatures of 3.1 ± 0.8, 21.1 ± 1.4, and 33.3 ± 3.0 ^{o}C. Samples were taken in replicate seven and 14 days after stirring began. Samples were immediately passed through a 0.45 µm pore size membrane filter and combined with an equal volume of 0.45 µm-filtered acetonitrile. Procedures for dissolution rates, equipment, and analytical methodologies were as previously described.

Dissolution rates of military formulations

Experimental quantities of weapons grade RDX, HMX, and TNT were provided by the Environmental Processes and Engineering Division, Environmental Laboratory, of the US Army Corps of Engineers Engineer Research and Development Center, Vicksburg, Mississippi. These explosive compounds were used separately and in the preparation of the non-bound explosive mixtures for comparative purposes with the explosive compounds in the formulations.

Three samples of TNT and eight samples each of Composition B and octol were melt-poured at the Holston plant into 5.5 cm diameter disk-shaped molds with an average thickness of 0.88 ± 0.08 cm^2. Octol is the formulation name given to a mixture of HMX and TNT (Gibbs and Popolato 1980). The octol consisted of 70% HMX and 30% TNT by weight. Composition B is a mixture of TNT and RDX

that might also include a wax desensitizer (Gibbs and Popolato 1980). Composition B consisted of 59.5% RDX, 39.5% TNT, and 1% wax by weight. Both octol and Composition B are prepared by stirring the other components of the formulation into melted TNT and, after mixing, allowing the resulting formulation to solidify. LX-14 is a plastic-bonded explosive consisting of 95.5% HMX and 4.5% polyurethane by weight (trademarked as Estane). The components of LX-14 are bonded together using a pressurization process.

The procedure for the dissolution rate experiments were as outlined previously for the pure compounds with one modification. The width of the formulation disks required that the mold be added first to the beaker and the 500 ml of water subsequently added at time zero while the stirring propellers were turning.

Explosives partitioning

Adsorption kinetics

An aquifer soil, LAAP –D, and two surface soils with different physical characteristics, Yokena Clay and Picatinney, were used to measure adsorption kinetics (Table 1). The tests were conducted under nitrogen in a glove box to simulate anaerobic aquifer conditions. Sufficient soil (4 g) and distilled, deionized, deoxygenated water (16 mls) were added to 25 ml glass centrifuge tubes to make a soil-to-water ratio of 1:4. For nitroglycerine testing, the distilled water added to the soil contained 1.47 mg L^{-1} nitroglycerine. The transformation products of RDX (MNX, DNX, and TNX) were spiked by adding 16 mls of a solution of either TNX or a mixture of MNX and DNX. The solution for MNX and DNX was a mixture of the two compounds because they cannot be chemically separated at this time. The initial concentration of TNX was 3 mg L^{-1}, while the initial concentration of the mixture of MNX and DNX was 1.01 mg L^{-1} MNX and 1.71 mg L^{-1} DNX. Samples were placed on a reciprocating shaker at 180 excursions per minute. At predetermined sampling times (0.5, 1, 6, 12, 24, 72, 120, and 168 hrs for nitroglycerine and 1, 6, 24, 48, 72, 96, and 120 hrs for MNX/DNX and TNX), triplicate tubes were removed and centrifuged at 8,288 RCF for 30 minutes. Two mls of the aqueous sample was removed and 2-mls acetonitrile was added. The diluted samples were analyzed by HPLC using EPA SW846 Method 8330 (USEPA 1994).

Adsorption partitioning

Adsorption partitioning was conducted with LAAP D, Yokena Clay, and Picatinney soils in a 1:4 ratio of soil to water in 25-ml glass centrifuge tubes. TNX samples were spiked at concentrations of 1.1, 2.8, 5.6, 8.3, and 11.1 mg L^{-1}. The DNX/MNX samples were spiked at 0.4, 1, 2, 3, and 4 mg L^{-1} DNX and 0.2, 0.5, 1.1, 1.6, and 2.1 mg L^{-1} MNX. Nitroglycerine was spiked at concentrations of 1, 1.5, 2.0, 2.5, and 2.0 mg L^{-1}. Triplicate samples for nitroglycerine testing were shaken for 72 hrs for LAAP D soils and 120 hrs for Picatinney soils on a reciprocating shaker at 180 excursions/min, centrifuged at 8,288 RCF for 60 minutes, and the aqueous phase removed and analyzed for nitroglycerine as previously described for the kinetics tests. Yokena clay soil was not tested because steady-state nitroglycerine solution concentrations were not attained. Triplicate TNX and DNX/MNX samples were shaken for 1 hr on a reciprocating shaker at 180 excursions/min prior to centrifugation, preparation, and analysis as previously described.

Desorption kinetics

Fort Lewis soil (Table 1) from the hand grenade range contained 2.6 mg Kg^{-1} TNT, 22.5 mg Kg^{-1} RDX, and 3.5 mg Kg^{-1} HMX. Tests were prepared by loading 2.5 gms soil into 25 ml centrifuge tubes and adding 10 mls of water. Samples were placed on a reciprocating shaker at 180 excursions per minute. At sampling times (0.5, 1, 6, 24, and 48 hrs), duplicate tubes were removed and centrifuged at 8,288 RCF for 30 minutes. Two mls of the aqueous sample was supplemented with 2 mls acetonitrile, then analyzed by HPLC for TNT, RDX, and HMX using EPA SW846 Method 8330 (USEPA 1994).

Desorption partitioning

Soil from the hand grenade range at Ft. Lewis (2.5 g) was loaded into two 25-ml centrifuge tubes. Ten mls of water was added to the centrifuge tubes, shaken on a reciprocating box shaker at 180 excursions/min for 24 hours, and centrifuged at 8,288 RCF for 30 minutes. A 2-ml aqueous aliquot was removed, 2 mls of acetonitrile were added to the aqueous aliquot and the samples were analyzed for TNT, RDX, and HMX as previously described. Excess water was removed and replaced by 10 mls of fresh water and the shaking and analytical procedures repeated three more times.

Results and Discussion

Dissolution of primary explosives

Analysis of the dissolution data showed that linear regression adequately described explosives dissolution. The mean r^2 and standard deviation from the mean for each explosive dissolution rate experiment was 0.986 and 0.008 for TNT, 0.989 and 0.014 for RDX and 0.746 and 0.096 for HMX,

respectively. Ten individual runs each were analyzed at 10 and 30 ^{o}C. Six individual runs were analyzed at 20 ^{o}C for each explosive.

If the surface area approximations were reproducible, an evaluation of dissolution rate normalized for surface area (mg min^{-1} cm^{-2}) should yield similar rates if performed under the same conditions. To check this premise, dissolution rates for the three explosives are shown in Figure 2. Results indicate that the surface area estimation procedures were similar and reproducible. Dissolution rates as a function of surface area at 150 rpm and 10, 20, and 30 ^{o}C are summarized in Table 2.

Dissolution rates as a function of temperature (mg min^{-1} ^{o}C^{-1}) at 150 rpm and at specified explosive surface areas are summarized in Table 3. Changes in temperature have the greatest effect on TNT and the smallest effect on RDX dissolution rates. Dissolution rate increases with increases in temperature, suggesting that dissolution of these explosives is an endothermic process.

The activation energies of dissolution were calculated using a form of the Arrhenius equation (Henry and Heinke 1996):

$$E_a = \frac{R \ln\left(k_1 / k_2 \right)}{\left(1/T_1 - 1/T_2 \right)} \qquad (7)$$

where E_a = activation energy, $k_{i=1,2}$ = dissolution rate at conditions $_1$ and $_2$, R = universal gas constant, $T_{i=1,2}$ = temperature in ^{o}K at conditions $_1$ and $_2$. Activation energies for TNT, RDX, and HMX were calculated to be 55.6, 55.4, and 40.7 kJ mol^{-1}, respectively. In agreement with the Arrhenius prediction that dissolution rate doubles with a 10 ^{o}C increase in temperature, the experimental dissolution rates increased by approximately 2.2 times for TNT and RDX and 1.8 times for HMX.

Dissolution rates as a function of mixing rpm at 10 and 30°C and an explosive compound surface area equal to 7.3 cm^2 for TNT, 10 cm^2 for RDX and 6 cm^2 for HMX are shown in Figure 3. Dissolution rate correlations as a function of mixing rate are presented in Table 3. Given that zero agitation equates to diffusion, linear regression trend lines of the data were not forced through zero. These y-intercepts in Table 4 allow comparison of the "relative" diffusion rates of the three explosive compounds with TNT having the apparent slowest diffusion rate followed by RDX and HMX with the highest diffusion rate. Changes in stirring rate have the greatest effect on TNT and the smallest effect on HMX dissolution rates.

Using the mixing rates of 90, 150, and 210 rpm for HMX resulted in a linear regression trend line with an r^2 of only 0.58. This non-linearity suggested that increases in mixing speed over the experimental range had reduced effects on increasing HMX dissolution rate. In theory, there should be a limit to how much the stagnant layer thickness can be decreased as a result of increased energy input. A second experiment using mixing rates of 35, 65. 95, and 150 rpm at 10°C and a surface area of 6 cm^2 for HMX was performed to test this theory. The resulting r^2 for this correlation improved to 0.97 and is included in Figure 3.

To relate rpm-based dissolution rates in a beaker to terms that are used in a process or natural setting, mixing speed was correlated to two different terms. The first is the ε term (a mass normalized energy dissipation rate) in the Levins- Glastonbury (1972b) correlation

$$\varepsilon \approx \frac{N^3 D_s^{\,5}}{D_T^{\,2} H} \tag{8}$$

where N = stirrer speed, D_s = stirrer diameter, D_T = tank diameter, H = height of liquid. This term has been used in tank reactors and is relevant in an equation to be presented later when comparing TNT dissolution rate results of this study to that of Gilcrease et al. (1996).

The second correlation relates the power driven mixing rate to the "R" term (rainfall erosivity index) in the Revised Universal Soil Loss Equation (RUSLE) (USDA 2001). The reason for pursuing this relationship was to relate rainfall energy impinging on explosives in the field to the energy input variable in the experimental design. This would permit the calculation of dissolution rates and contaminant persistence resulting from rain falling on explosive compounds exposed on the soil surface. The R term, a yearly average, is in units of hundreds foot tons-force inch $acre^{-1}$ $hour^{-1}$ $year^{-1}$, or energy times a rainfall rate over an area (Simanton 2000[1]). The experimental design has similar units with power input (energy/time) over an area (beaker area) in a certain depth (height of liquid in beaker). Mixing power requirements assuming turbulent flow were estimated using the equation (Tchobanoglous and Schroeder 1987):

$$p = k\rho n^3 d_i^{\,5} \tag{9}$$

where p = power requirement, k = arbitrary constant estimated as 1 (Borsella, 2000[2]), ρ = liquid density, n = rotational speed, d_i = diameter of mixer impeller.

[1] Simanton, R. 17 July 2000. Agricultural Research Service, Tucson, AZ.
[2] Borsella, J. July, 2000. Yamato Scientific America, Inc., Orangeburg, NY.

After equating units, R-values in the RUSLE program (ranging from the 20s in Nevada to the 350s in Florida) were similar to the experimental energy input values selected for this study. For example, an R-value of 250 hundred foot tons-force inch acre^{-1} hour^{-1} year^{-1} (representative of Tennessee) from the RUSLE compares well to a mixing speed of approximately 120 rpm in the experimental design using the equation

$$\text{rpm} = 60\left(R * \frac{1.182\text{x}10^{-6}\,\frac{\text{Watt}\cdot\text{cm}}{\text{cm}^2}\,\Pi D_T^{\,2}}{k\rho d_i^{\,5} H} \right)^{1/3} \qquad (10)$$

with units for R = 100 foot-ton-force inch acre^{-1} hour^{-1} year^{-1}, D_T = cm, d_i = m, ρ = kg m^{-3}, and H =cm.

Besides evaluating individual variable effects on explosive dissolution rates, the combination of temperature, surface area, and mixing speed into a single correlation was investigated using three different approaches. The first approach built on the single variable dissolution rate approach and involved a series of linear regressions incorporating an additional variable at each regression, ultimately yielding an expression for dissolution rate with units of mg min^{-1} cm^{-2} rpm^{-1} ^{o}C^{-1}. Of the possible combinations, the sequence of variables addition and regressions used in this study was from dissolution rate expressed as mg min^{-1} to mg min^{-1} cm^{-2} to mg min^{-1} cm^{-2} rpm^{-1} to mg min^{-1} cm^{-2} rpm^{-1} ^{o}C^{-1}. All regressions except the last forced the y-intercept to zero. Other sequences for variable addition did not yield a multi-variable equation that closely fit the experimental data. With respect to the variables employed in this study, ranking from greatest to least impact on dissolution rate is temperature (^{o}C), followed by surface area (cm^2), and then mixing speed (rpm). The multi-regression, multivariable equations, whose solutions yield a dissolution rate in units of mg min^{-1}, are presented below. The average percent difference between raw data dissolution rates expressed as mg minute^{-1} and those calculated by the multivariable equation averaged less than 10% for TNT and RDX and less than 15% for HMX.

TNT

$$\frac{dm}{dt} = \left(1.0\text{E}-5\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}-^{o}\text{C}} * T - 4.3\text{E}-5\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}} \right) * a * m \qquad (11a)$$

HMX

$$\frac{dm}{dt} = \left(4.75\text{E}-6\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}-^{o}\text{C}} * T - 2.4\text{E}-6\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}} \right) * a * m \qquad (11b)$$

RDX

$$\frac{dm}{dt} = \left(1.49\text{E}-6\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}-^{o}\text{C}} * T - 6.5\text{E}-6\,\frac{\text{mg}}{\text{min}-\text{cm}^2-\text{rpm}} \right) * a * m \qquad (11c)$$

A second approach avoided the multiple regressions in favor of a single linear regression of normalized dissolution rates and one variable. Dissolution rates were normalized by dividing each run's initial mg min^{-1} rate by two of the variable conditions used in that particular run (i.e. surface area and rpm). These normalized rates were then regressed against the remaining variable (in this case temperature). These linear regressions were not forced through zero. The first row in Table 5 identifies the dissolution rate equation for the example given. This process was then repeated two more times, once for rpm as the last included variable (row 2, Table 5) and again using surface area as the independent variable (row 3, Table 5). Again, those correlation trend lines where temperature served as the independent variable had the best fit to the data. This indicates that temperature has the greatest impact on dissolution rate employing the units used in this study. The means of the average percent difference between the described correlations and the experimental data for all the explosive compounds with temperature as the independent variable was 10%, for surface area it was 15%, and for mixing speed it was 450%.

Results from the multiple linear regression methodology for determining a correlation with multiple variables are very similar to the single linear regression approach. Two validation runs were performed for each explosive compound using different temperatures (15 and 25°C), surface area (6 cm^2), and mixing rate values (180 and 120 rpm) from those generating the correlations. The single regression correlation line is included with the multiple regression correlation line for comparison with experimental HMX data in Figure 4 as are the validation data points. All TNT (not shown) and HMX data and validation points fell within the 99% confidence bands while all RDX data (not shown) and validation points fell within the 95% confidence bands.

The last method for determining a multivariable dissolution rate expression used a correlation developed by Levins and Glastonbury (1972a) describing spherical particle-liquid hydrodynamics and mass transfer in a stirred vessel

$$\frac{kd_p}{D_v} = 2 + 0.47\left(\frac{d_p^{\,4/3}\varepsilon^{1/3}}{\nu}\right)^{0.62}\left(\frac{D_S}{D_T}\right)^{0.17}\left(\frac{\nu}{D_v}\right)^{0.36} \qquad (12)$$

where k = mass transfer coefficient, d_p = particle diameter, D_v = diffusivity, □ = energy dissipation rate/unit mass, □ □kinematic viscosity, D_S = stirrer diameter, and D_T = tank diameter. Gilcrease, Murphy, and Reardon (1996) used this method in their evaluation of TNT dissolution in reactors containing either water or a water/Teflon bead slurry.

Comparisons between the Levins and Glastonbury (1972a) correlation and the experimental data obtained in this study can be made by expressing the "k" term in EQ(12) in milligrams dissolved per minute and comparing it to the rate determined from the data of each run. The dissolution rates for data from this study, rates predicted by the multivariable equation derived in this study, and rates predicted by the Levins and Glastonbury (1972a) correlation for TNT mixed at 150 rpm and 10 ^{o}C (lower set of data) and 30 ^{o}C (upper set of data), are compared and presented in Figure 5. The average percent difference between actual rates and those predicted using the Levins and Glastonbury correlation are slightly greater than those based on the multivariable equation.

Gilcrease, Murphy, and Reardon. (2001) noted that the effectiveness of the k term in EQ(12) depended on selecting an appropriate effective diffusivity value. Gilcrease, Murphy, and Reardon (1996) successfully used the Levins and Glastonbury (1972a) approach in describing the dissolution of solid TNT in both deionized water and in a Teflon chip/water slurry. For the best fit to their experimental design, Gilcrease, Murphy, and Reardon (1996) selected a TNT diffusivity of 7.4E-6 cm^2 s^{-1} at 25 C. For our study, a diffusivity of 6.71E-6 cm^2 s^{-1} at 25 ^{o}C (Townsend and Meyers 1996) was used.

The Levins and Glastonbury correlation did not prove as accurate in predicting dissolution rates for either RDX or HMX compared to the multivariable equations developed in this study. Average percent differences between prediction and actual rate exceeded 20% for each explosive compound, even after modifying diffusivity values from those reported in the literature. Best-fit diffusivity values at 25 ^{o}C were 2.2 E-6 cm^2 s^{-1} and 1.5E-4 cm^2 s^{-1} for RDX and HMX, respectively (vs. 7.15 E-6 and 6.02 E-6 cm^2 s^{-1}, reported by Townsend and Meyers, 1996 at 25 ^{o}C). The "relative diffusivities" in Figure 3 show similar orders of separation among explosives as those presented here.

Estimating a single particle diameter for RDX and HMX from a heterogeneous mix of crystal sizes may have had a major impact on the applicability of the Levins and Glastonbury (1972a) correlation. A comparison of rates among our experimental data, the temperature-based multivariable equation, and the Levins and Glastonbury correlation k term is shown in Table 6. Use of an estimated single particle size may also account for the discrepancies in the best-fit diffusivities.

Dissolution rates for TNT, RDX, and HMX as a function of temperature, surface area, and power input are best represented by the first row of equations in Table 5 where temperature was the final variable in rate determination. These equations can provide insight to expected changes in explosive

dissolution rates given changing seasonal temperatures and remaining explosive surface area. To predict rainfall affects on expected dissolution rates, use EQ(10) which relates the RUSLE "R" term to mixing rpm. EQ(8) can be used to relate study rpm to stirred reactors.

Limits exist for the use of these correlations, however. First, dissolution rates cannot exceed the solubility limit of the explosive. Second, extrapolation outside the limits of the study boundaries is not recommended. Third, as demonstrated by the HMX results, a point is reached where increased power input results in only minimal changes in dissolution rate.

Effects of pH and temperature

Solubility. The temperature range studied (3.1 ^{o}C to 33.3 C) is representative of ambient conditions in most areas of the Continental United States where explosives residues are typically found. The pH range was based on maximum and minimum pH values reported for rainfall in the Continental United States (National Atmospheric Deposition Program, 1998). The experimental solubility data for the three high explosives at three pH values and temperature are summarized in Table 7. To conform to the format in equation 3, data were plotted as ln[S] versus 1 $^{o}K^{-1}$ and linearly regressed. Solubility of TNT, RDX, or HMX at different pH values did not differ significantly ($p < 0.05$).

Solubilities for TNT compare favorably with those reported by Spanggord et al (1983) and Phelan and Barnett (2001) (Figure 6). Solubilities for TNT were found to be less than those reported by Taylor and Rinkenbach (1923), but higher than those reported by Ro et al (1996). Solubilities for RDX (Figure 7) again compare favorably with Spanggord et al. (1983) though generally less than those values reported in the literature. Solubilities for HMX agree well with those values reported by Townsend and Meyers (1996) (Figure 8). A correlation was made for solubilities reported by Spanggord et al. (1982) and cited in Townsend and Meyers (1996) and plotted on this figure for comparative purposes. Composite correlations that utilize all TNT, RDX, and HMX data to predict solubility are presented in Figure 9.

Dissolution. Evaluation of pH effects on dissolution rate was conducted at 30 ^{o}C because of higher solubility values for each explosive at this temperature. Samples were taken at a rate and over a time period selected so that sample concentrations would be well below solubility maxima, hence keeping the solution dilute. The pH did not affect the dissolution rate of TNT, RDX, or HMX (Figure 10). In general, TNT had the fastest dissolution rate, followed by HMX and RDX. Composite dissolution rates

incorporating all pH data for TNT, HMX, and RDX (Table 5) compared well to those predicted by equation 10.

A reducing environment at pH 7 had a pronounced impact on TNT, RDX, and HMX stability in soil (Price, Brannon, and Hayes 1997, Price, Brannon, and Yost 1998). Remediation strategies that rely on high alkalinity (Heilmann, Wiesmann, and Stenstrom 1996) may be related to a reducing environment by the Nerst equation where an increase in pH corresponds to a decrease in redox potential (Stumm and Morgan, 1996), but the pH required (pH $\geq$ 10) exceeds those normally encountered in the environment.

The combined ability to predict solubility and dissolution rate at a given temperature permits the prediction of solution concentration at any given time using equation 5. This equation was used here to confirm that solubility had been reached prior to the seventh day of stirring. Using a conservative mixing rate of 210 rpm and 30 ^{o}C, HMX attained saturation in less than half a day, RDX in less than five days, and TNT was 99.996% of saturation in seven days.

Dissolution rates of formulations

The dissolution rates for all analytical runs were recorded in units of mg cm^{-2} sec^{-1} to normalize for the variations in solid surface area. TNT, RDX, and HMX were run independently in addition to the formulations and mixtures to serve as a basis for dissolution rate comparison. The dissolution rates for the formulations at 150 rpm and 20 ^{o}C are presented in Figures 11, 12, and 13 for TNT, HMX, and RDX, respectively. Both the melt-pour process used in the preparation of octol and composition B and the pressure binding process used in the production of LX-14 appear to have caused the inherent explosive compounds to dissolve at rates lower than those of the pure compounds. TNT dissolution rates from octol and Composition B molds were lower than those from a pure TNT mold (Figure 11). HMX dissolution from LX-14 and octol were orders of magnitude lower than dissolution rates from pure HMX (Figure 12). RDX showed a more than 50% decrease in dissolution rate from Composition B compared to the pure compound (Figure 13).

Explosives partitioning

Adsorption kinetics and partitioning

Solution nitroglycerine concentrations decreased over time when exposed to all tested soils (Figure 14). Partitioning coefficients are not provided for Yokena Clay because steady-state conditions did not develop. Half lives for nitroglycerine were 335 hrs, 84 hrs, and 7.3 hrs for LAAP D, Picatinney,

and Yokena Clay soils, respectively. Results suggest that nitroglycerine will be degraded and strongly adsorbed in both aquifer and surface soils.

Concentrations of the RDX transformation products MNX (Figure 15), DNX (Figure 16), and TNX (Figure 17) were generally stable in all three soils. Notable exceptions were MNX and DNX in Yokena Clay soil. The half-lives shown in Figures 15 and 16 for Yokena Clay reflect first order transformation coefficients of 0.225 h^{-1} ($r^2 = 0.754$) and 0.333 h^{-1} ($r^2 = 0.76$) for MNX and DNX, respectively. Partitioning coefficients for LAAP D soil ranged from 0.29 to 0.85 L Kg^{-1} for MNX, DNX, and TNX (Figure 18). This compares to a value of 0.33 L Kg^{-1} for RDX in LAAP D soil (Pennington et al. 1999). These results indicate that adsorption coefficients for the major RDX transformation products are similar to that of the parent compound. Partition coefficients for nitroglycerine were similar in the two soils for which K_ds could be determined (Figure 19).

Desorption kinetics and partitioning

Concentrations of TNT, RDX, and HMX desorbed from the Ft. Lewis soil reached steady-state concentrations in 6 hours (Figure 20). These results indicate that TNT, RDX, and HMX are rapidly desorbed and mobilized from the soil. No decrease in solution concentrations was observed over the course of two days following establishment of steady-state concentrations.

Partitioning coefficients were highest for HMX (3.5 ± 0.6 L Kg^{-1}), intermediate for TNT (1.6 ± 0.8 L Kg^{-1}), and lowest for RDX (0.6 ± 0.2 L Kg^{-1}). These results indicate that transport will be greatest for RDX in this soil.

Summary and Conclusions

Dissolution rates of explosives increase with increases in surface area, temperature, and mixing rate. Under the same experimental conditions, the order of dissolution rate (fastest to slowest) was TNT, HMX, and RDX. Calculated activation energies for dissolution of TNT, RDX, and HMX in kJ mol^{-1} were 55.6, 55.4, and 40.7, respectively. Dissolution rates approximately double with every 10 ^{o}C increase in temperature. Surface area estimates were reproducible and the RUSLE "R" values and experimental energy input were comparable. At 25 ^{o}C and using the Levins-Glastonbury (1972a) correlation, diffusivities were estimated at 6.71 E-6 cm^2 s^{-1} for TNT, 2.2E-6 cm^2 s^{-1} for RDX, and 1.5E-4 cm^2 s^{-1} for HMX.

The use of combined variable equations, such as those presented in Table 5 and EQ (10), are representative of observed dissolution rates under various environmental conditions. Predicting dissolution rates by performing multiple regressions of data was no improvement over normalizing these data into the appropriate units for dissolution and performing a single regression. Regressing dissolution in units of mg min^{-1} cm^{-2} rpm^{-1} versus temperature in ^{o}C provides the best multi-variable equation fit to experimental data. The Levins-Glastonbury correlation was a viable method of estimating dissolution rates when diffusivities were known and explosives were of uniform particle diameter. The relationships developed in this study will serve as a first/worst case approximation of expected dissolution rates in a field environment.

Solubilities and dissolution rates of TNT, RDX, and HMX were not significantly affected by pH over the pH range (4.2 to 6.2), but were significantly affected by temperature over the range (3.1 ^{o} C to 33.3 C) studied. TNT was the most soluble and had the highest dissolution rate, while RDX had the second highest solubility, but exhibited the slowest dissolution rate. Composite correlations incorporating all pH data were presented to predict explosive solubility as a function of temperature and to identify dissolution rates using specified variables. These equations can be used to predict the solubility of TNT, RDX, and HMX, their dissolution rates, and solution concentrations over time.

The production process affects dissolution rates of the explosive compounds in the formulations. Dissolution rates of explosives compounds are suppressed in LX-14, Composition B, and octol.

Adsorption kinetics and partitioning studies showed that nitroglycerine was degraded and strongly adsorbed in both aquifer and surface soils. Therefore, it is not expected to persist in the environment. The RDX transformation products, MNX, DNX, and TNX, were generally stable in all tested soils. Adsorption coefficients for the RDX transformation products were similar to that of the parent compound. Desorption partitioning with Ft. Lewis soil showed that steady-state solution concentrations of TNT, RDX, and HMX were reached within six hours. RDX partitioned to this soil less than TNT and HMX, indicating that RDX transport would be greatest.

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Table 1
Properties of soils used in adsorption and desorption testing

Soil	TOC, %[1]	CEC[2], meq $100g^{-1}$	pH	Clay, %	Sand, %	Silt, %
LAAP D	0.02	5.5	5.5	7.5	85	7.5
Yokena Clay	2.4	38.9	6.4	48.75	13.75	37.5
Picatinney	0.634	9.8	6.1	5	62.5	32.5
Ft. Lewis	0.26	6.8	6.8	9.9	82.3	7.8

[1] Total organic carbon
[2] Cation exchange capacity

Table 2
Dissolution rates as a function of surface area at 150 RPM and different temperatures

	10 C		20 C		30 C	
	mg $min^{-1}cm^{-2}$	r^2	mg $min^{-1}cm^{-2}$	r^2	mg $min^{-1}cm^{-2}$	r^2
TNT	0.009	0.996	0.014	0.908	0.041	0.958
RDX	0.001	0.988	0.003	0.718	0.006	0.992
HMX	0.006	0.999	0.013	0.995	0.020	0.992

Table 3. Dissolution rates as a function of temperature at 150 RPM and different explosive surface areas

		Mg min^{-1}			Mg min^{-1}			Mg min^{-1}	
	cm^2	C^{-1}	r^2	cm^2	C^{-1}	r^2	cm^2	C^{-1}	r^2
TNT	5.800	0.008	0.955	7.300	0.009	0.964	8.700	0.012	0.953
RDX	8.000	0.0015	0.961	10.000	0.0018	0.960	12.000	0.0023	0.957
HMX	4.800	0.003	0.996	6.000	0.004	0.999	7.100	0.005	0.998

Table 4
Dissolution Rates, r (mg min^{-1}) as a Function of Mixing Rate, m (rpm), Using Middle Value Surface Areas and Specified Temperatures. Note how selection of study rpm values affects correlation r^2 for HMX.

	10°C		30°C	
	Correlation	**r^2**	**Correlation**	**r^2**
TNT	r = 5.0E-4 *m – 1.1E-2	0.99	r = 2.0E-3 * m – 2.9E-2	0.96
RDX	r = 1.0E-4 * m – 6.7E-3	0.89	r = 5.0E-4 * m – 8.5E-3	0.99
HMX	r = 1.0E-4 * m + 8.7E-3	0.97	r = 3.0E-4 * m + 7.4E-2	0.58

Table 5
Zero-order pH-related explosive dissolution rates measured at 30 °C, 150 rpm, and normalized solid explosive surface area.

Method	**Dissolution rate/mg/cm^{-2} s^{-1}**	**R^2**	**Av % diff[a]**
TNT			
Eq 5	= 0.00063	n/a[b]	
Composite	= 0.00069	0.984	9.1
HMX			
Eq 5	= 0.00032	n/a[b]	
Composite	= 0.00029	0.628	9.8
RDX			
Eq 5	= 0.000097	n/a[b]	
Composite	= 0.000096	0.991	1.0

Table 6
Average percent difference comparisons between data from this study, the multiple regression multiple variable equation, the single regression multiple variable equation, and the Levins and Glastonbury (1972a) correlation for RDX dissolution rates

Run ID	Surface Area/rpm/°C[1]	Dissolution Rate mg min^{-1} Study Data	Dissolution Rate mg min^{-1} Multiple Variable Eqn	Avg % Diff	Dissolution Rate mg min^{-1} Single Variable Eqn	Avg % Diff	Dissolution Rate Mg min^{-1} Levins Glastonbury Correlation	Avg % Diff
M	S/150/10	0.010	0.011	-6.3	0.011	-10.5	0.014	-29.2
O	M/150/10	0.012	0.013	-3.5	0.013	-7.6	0.016	-26.4
P	L/150/10	0.015	0.015	-2.1	0.016	-6.2	0.019	-25.16
R	M/90/10	0.008	0.008	9.1	0.008	4.9	0.012	-34.0
S	M/210/10	0.026	0.018	38.4	0.019	34.3	0.020	28.8
R1	S'/150/20	0.015	0.014	4.0	0.014	2.5	0.015	-2.5
R2	M'/150/20	0.015	0.018	-13.6	0.018	-15.1	0.019	-20.1
R3	L'/150/20	0.019	0.021	-8.7	0.021	-10.2	0.023	-15.1
R8	S/150/30	0.047	0.046	1.6	0.047	0.6	0.055	-15.0
R6	M/150/30	0.057	0.058	-1.0	0.058	-2.0	0.068	-17.6
R9	L/150/30	0.071	0.069	2.2	0.070	1.2	0.082	-14.4
R4	M/90/30	0.034	0.035	-2.9	0.035	-3.9	0.050	-39.4
R5	M/210/30	0.088	0.081	8.9	0.081	8.0	0.083	5.5

[1] S=8, M=10, L=12 S'=4, M'=5, L'=6 cm^2

Table 7
Solubilities of High Explosive Compounds At Specified pH and Temperature

TNT						RDX						HMX					
pH 4.2		pH 5.7		pH 6.2		pH 4.2		pH 5.7		pH 6.2		pH 4.2		pH 5.7		pH 6.2	
Tmp[1]	Sol[2]	Tmp	Sol	Tmp	Sol	Tmp	Sol	Tmp	Sol	Tmp	Sol	Tmp	Sol	Tmp	Sol	Tmp	Sol
°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}	°C	mgL^{-1}
2.3	49.5	2.3	54.5	2.4	55.9	2.7	13.5	2.5	12.6	2.1	13.1	2.7	0.81	2.5	0.77	2.1	0.77
2.3	50.5	2.3	54.2	2.4	56.4	2.7	13.0	2.5	12.8	2.1	13.5	2.7	0.80	2.5	0.77	2.1	0.77
2.6	54.9	2.3	47.5	2.4	54.9	2.7	13.3	2.6	13.8	2.6	12.9	2.7	0.76	2.7	0.77	2.6	0.60
2.6	55.7	2.3	47.3	2.4	55.4	2.7	13.2	2.6	13.7	2.6	13.3	2.7	0.78	2.7	0.78	2.6	0.65
4.2	57.6	4.1	47.9	4.7	56.7	2.8	13.5	2.7	13.2	2.9	13.7	3.6	0.92	3.6	1.01	3.6	0.98
4.2	57.7	4.1	48.2	4.7	57.4	2.8	12.9	2.7	13.2	2.9	13.9	3.6	0.91	3.6	0.95	3.6	0.93
4.2	45.7	4.6	58.1	5.2	56.7	3.2	13.9	3.5	13.6	3.9	14.1	3.6	0.89	3.7	0.90	3.6	0.93
4.2	48.4	4.6	59.1	5.2	56.1	3.2	14.0	3.5	13.9	3.9	13.5	3.6	0.91	3.7	0.99	3.6	0.94
20	100.7	20	96.7	20	99.6	20.1	38.9	20	37.7	20	37.5	22.6	3.82	22.7	3.84	22.5	3.88
20	99.0	20	98.7	20	100.2	20.1	36.8	20	37.8	20	37.6	22.6	3.84	22.7	3.82	22.5	3.88
20	99.2	20.1	98.9	20.1	99.5	20.1	38.6	20.2	38.0	20	38.2	22.8	3.68	22.8	3.88	22.7	3.80
20	101.7	20.1	100.6	20.1	96.3	20.1	38.3	20.2	38.0	20	38.8	22.8	3.68	22.8	3.89	22.7	3.79
20.1	96.3	20.2	98.8	20.1	99.5	20.2	35.8	20.4	35.4	20.4	35.5	23.1	3.87	23	3.94	23.4	3.93
20.1	95.9	20.2	99.8	20.1	99.8	20.2	35.7	20.4	35.6	20.4	35.3	23.1	3.85	23	3.95	23.4	3.72
20.1	96.0	20.2	97.5	20.2	94.6	20.2	36.0	20.4	35.1	20.4	36	23.7	3.94	23.5	3.90	23.7	3.75
20.1	97.8	20.2	100.4	20.2	97.2	20.2	36.3	20.4	35.6	20.4	36.1	23.7	3.97	23.5	3.94	23.7	3.89
36	211.7	35.7	208.5	35.9	216.5	31.6	65.1	31.7	62.5	31.7	67.6	28.5	5.35	28.5	5.40	28.5	6.21
36	213.1	35.7	213.5	35.9	213.9	31.6	65.4	31.7	62.2	31.7	68.1	28.5	5.55	28.5	5.43	28.5	6.10

36	208.5	36	215.2	36	212.2	31.9	46.5	32	60.6	32	58.7	28.6	5.74	28.6	5.96	28.6	6.13
36	211.6	36	214.3	36	215.3	31.9	48.5	32	61.8	32	59.8	31.2	7.58	28.6	6.02	28.6	6.66
37.7	219.6	37.7	229.7	37.6	229.4	32.1	65.9	34	73.4	34.1	85.2	31.2	7.74	31.7	7.25	32.3	7.67
37.7	219.4	37.7	230.6	37.6	231.4	32.1	66.3	34	87.8	34.1	86.5	32	7.41	31.7	7.19	32.3	7.75
37.8	218.2	37.7	226.2	38	234.4	32.1	65.6	34.1	86.8	34.2	85.7	32	7.47	32.2	7.39	32.3	7.60
37.8	214.8	37.7	228.3	38	235	32.1	64.1	34.1	85.7	34.2	81.8	ND[3]	ND	32.2	7.39	32.3	7.63
						34.9	92.5										
						34.9	89.95										

[1] Temperature; [2] Solubility; [3] Not Done

Figure Captions

Figure 1. TNT, RDX, and HMX molecular structures

Figure 2. Surface area comparison of explosives at 150 rpm and 10°C (◇ = TNT, □ = RDX, △ = HMX)

Figure 3. Mixing speed comparison of middle-size surface area explosives (◊ = TNT, □ = RDX, △ = HMX, — = 30°C, - - - = 10°C)

Figure 4. Comparison of HMX multiple regression, multiple variable dissolution rate correlation (—) to the HMX single regression, multiple variable dissolution rate correlation (- · -). Note: Correlation data points (○) and validation points (□)

Figure 5. Rate comparisons of study TNT data (□ = 30 °C data, ◊ = 10 °C data) to multiple regression-multiple variable regression line (—) and the Levins-Glastonbury regression line (- - -)

Figure 6. Comparison of literature TNT solubility to this study. (____) Taylor and Rinkenbach (1923), (. . . . .) Spanggord et al. (1983), (_ ... _) Ro et al. (1996), (■) Gibbs and Popolato (1980), (□) Phelan and Barnett (2001), ▒ this study pH 4.2, ▒ this study pH 5.7, ▒ this study pH 6.2.

Figure 7. Comparison of literature RDX solubility to this study. (__+__) Spanggord et al. (1983), (■) Gibbs and Popolato (1980), (□) Townsend and Meyers (1996), (____) this study pH 4.2, (_ _) this study pH 5.7, (.. .. ..) this study pH 6.2.

Figure 8. Comparison of literature HMX solubility to this study. (__*__) Spanggord et al. (from Townsend and Meyers, 1996), (□) Townsend and Meyers (1996), (____) this study pH 4.2, (_ _) this study pH 5.7, (.. .. ..) this study pH 6.2.

Figure 9. Composite explosive solubility prediction correlations. (____, ●) TNT, (. . . . , ▲) HMX, (_ _, ■) RDX.

Figure 10. Comparison of explosive dissolution rates at three pH values. (□) TNT, (▲) HMX, (■) RDX.

Figure 11. Comparison of TNT dissolution rates from pure TNT, Octol, and Composition B at 20 °C and 150 rpm

Figure 12. Comparison of HMX dissolution rates from pure HMX, LX-14, and Octol at 20 °C and 150 rpm

Figure 13. Comparison of RDX dissolution rates from pure RDX and Composition B at 20 °C and 150 rpm

Figure 14. Adsorption kinetics of nitroglycerine in LAAP-D, Picatinney, and Yokena Clay soils.

Figure 15. Adsorption kinetics of MNX in LAAP-D, Picatinny, and Yokena Clay soils.

Figure 16. Adsorption kinetics of DNX in LAAP-D, Picatinny, and Yokena Clay soils.

Figure 17. Adsorption kinetics of TNX in LAAP-D, Picatinny, and Yokena Clay soils.

Figure 18. Partitioning coefficients for MNX, DNX, and TNX in LAAP-D soil.

Figure 19. Partitioning coefficients for nitroglycerine in LAAP-D and Picatinny soils.

Figure 20. Desorption kinetics of TNT, RDX, and HMX in Ft. Lewis soil.

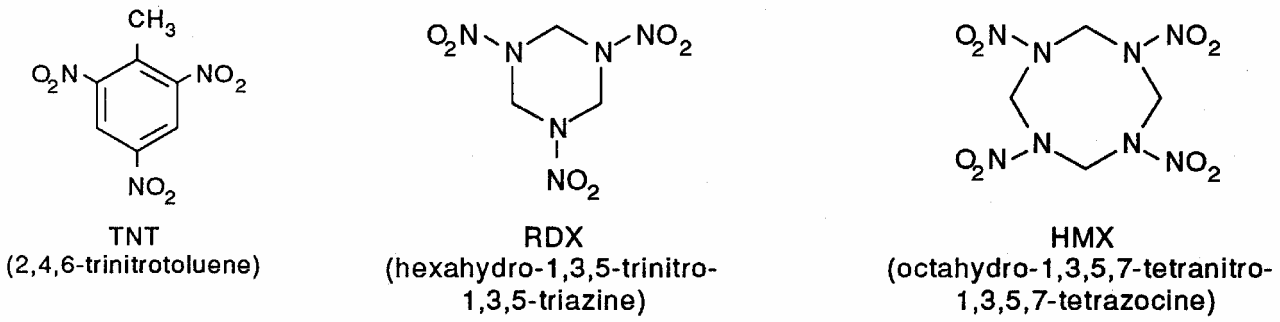

Figure 1. TNT, RDX, and HMX molecular structures

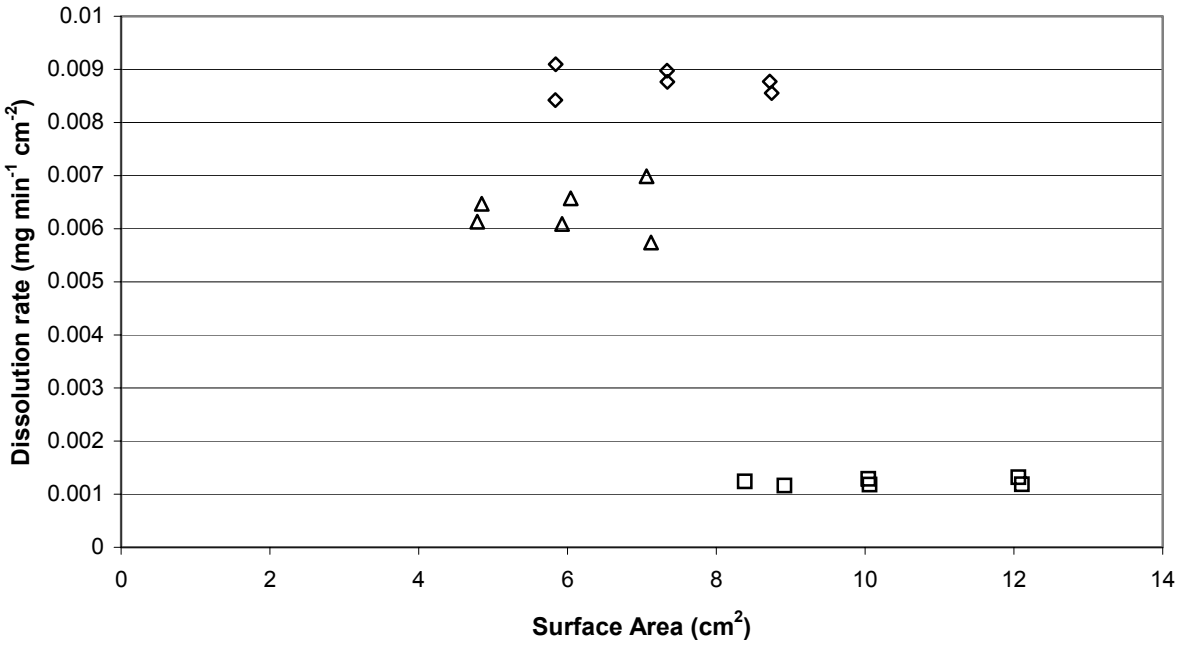

Figure 2. Surface area comparison of explosives at 150 rpm and 10°C (◇ = TNT, □ = RDX, △ = HMX)

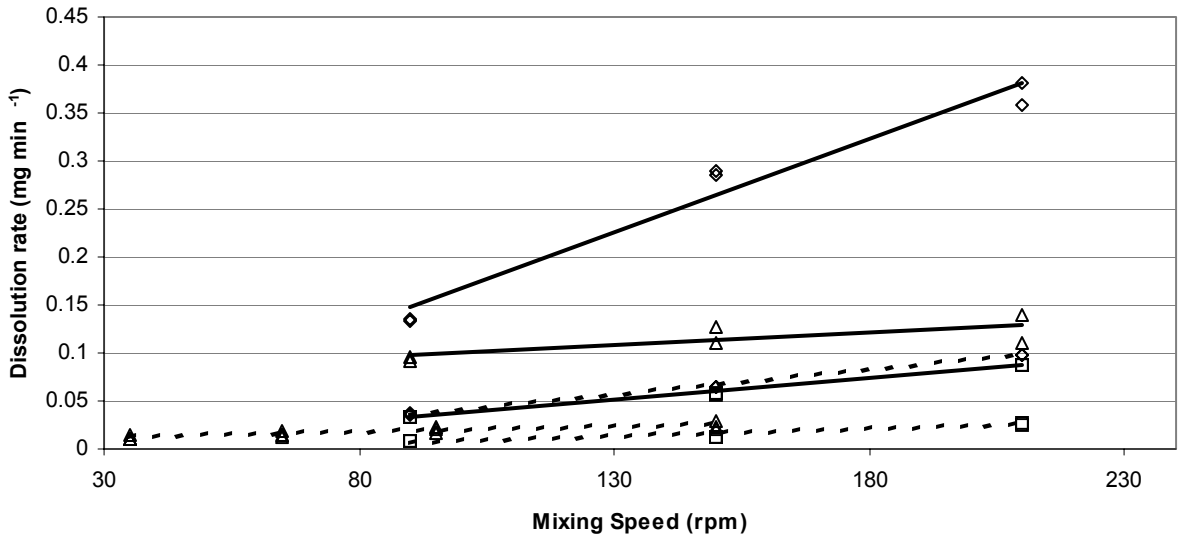

Figure 3. Mixing speed comparison of middle-size surface area explosives (◊ = TNT, □ = RDX, △ = HMX, —— = 30°C, - - - = 10°C)

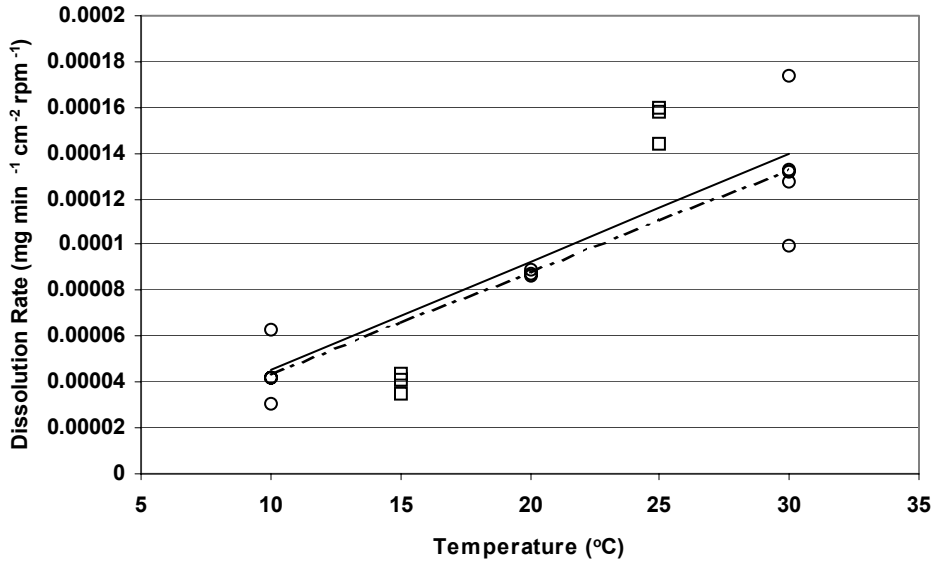

Figure 4. Comparison of HMX multiple regression, multiple variable dissolution rate correlation (—) to the HMX single regression, multiple variable dissolution rate correlation (-·-). Note: Correlation data points (○) and validation points (□)

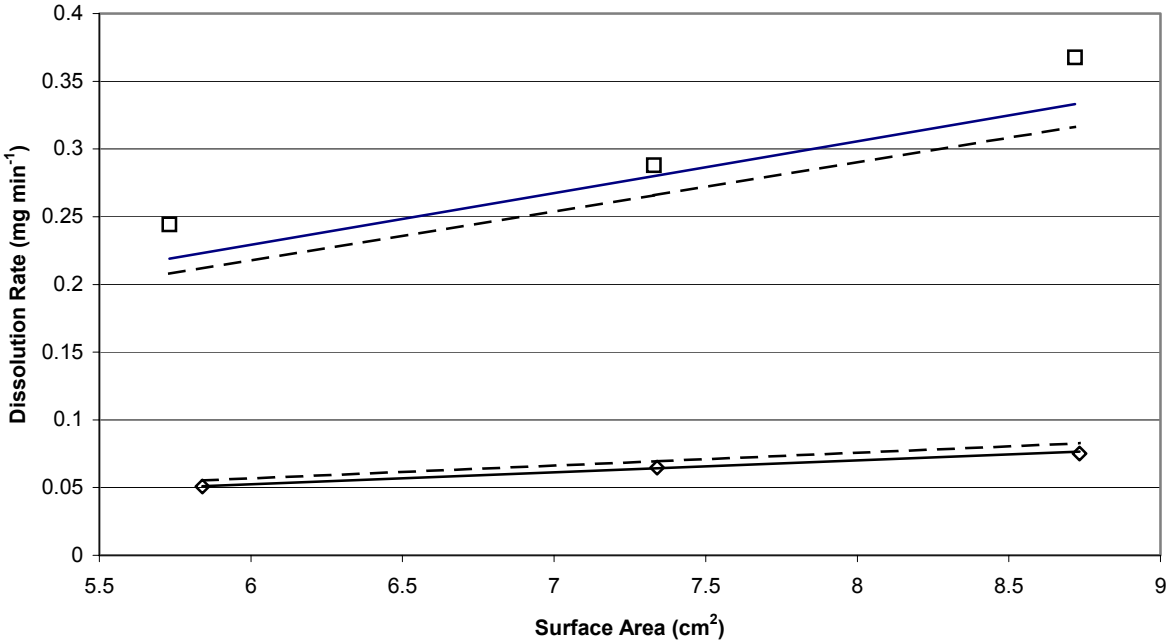

Figure 5. Rate comparisons of study TNT data (□ = 30 °C data, ◊ = 10 °C data) to multiple regression-multiple variable regression line (—) and the Levins-Glastonbury regression line (- - -)

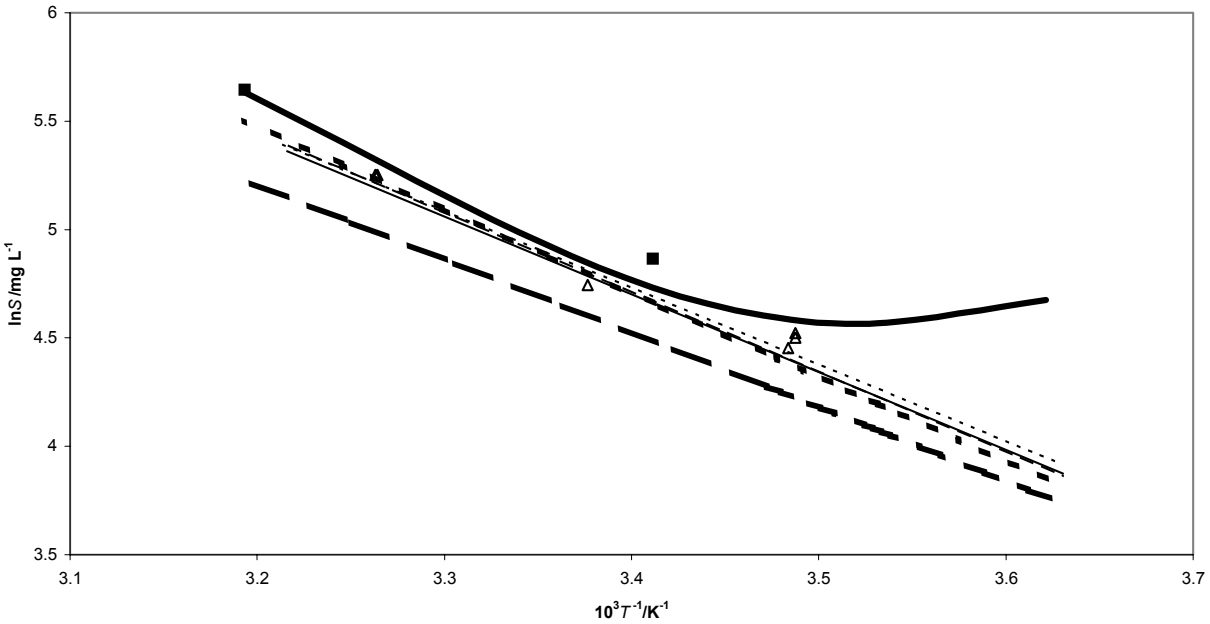

Figure 6. Comparison of literature TNT solubility to this study. ▬▬ Taylor and Rinkenbach (1923), ▪▪▪▪▪ Spanggord et al. (1983), ▬ ··· ▬ Ro et al. (1996), ■ Gibbs and Popolato (1980), △ Phelan and Barnett (2001), ── this study pH 4.2 [ln (S/ mg L^{-1}) = 16.895 – 3586.4 K/T, R^2=0.9822]; – – this study pH 5.7 [ln (S/ mg L^{-1}) = 17.263 – 3691.3 K/T, R^2=0.9837], ·· ·· ·· this study pH 6.2 [ln (S/ mg L^{-1}) = 16.777 – 3542.5 K/T, R^2=0.9785].

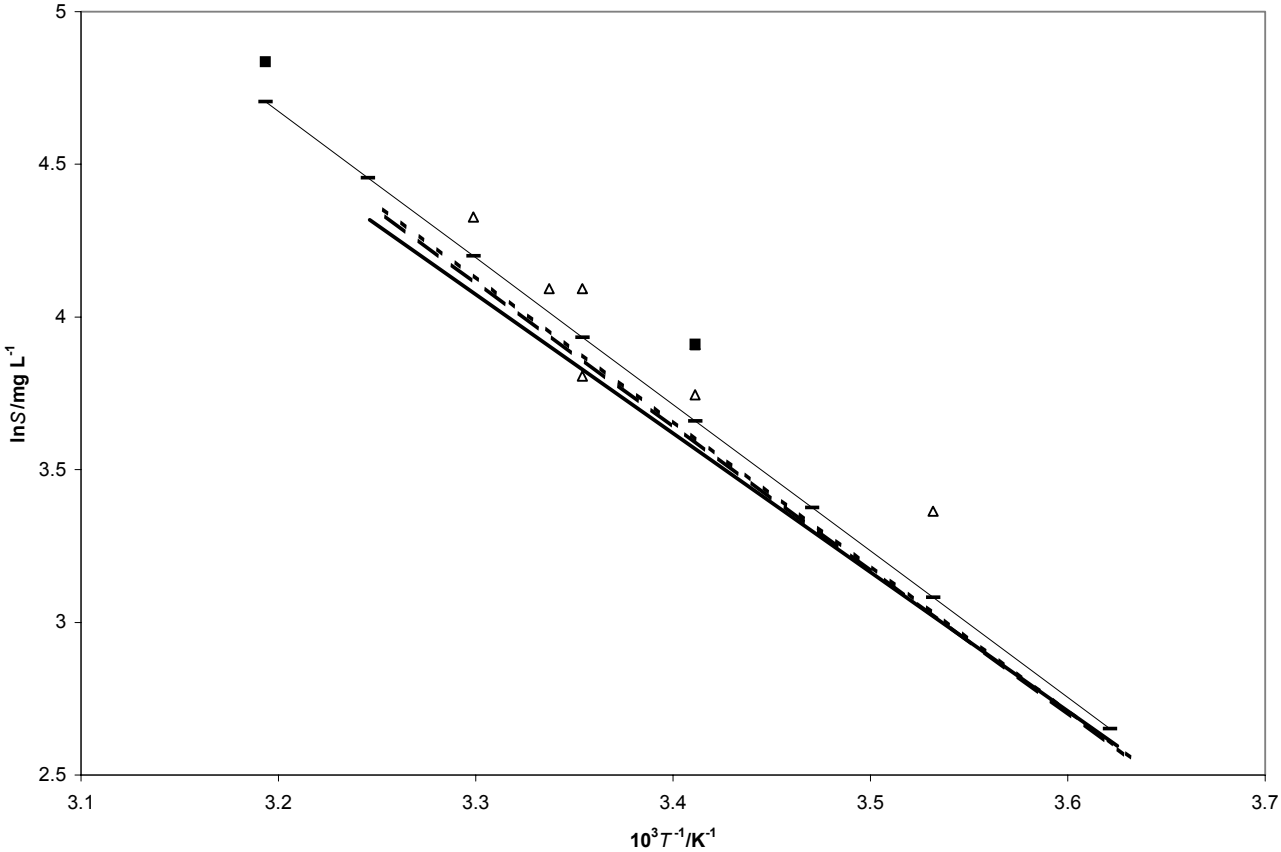

Figure 7. Comparison of literature RDX solubility to this study. —+— Spanggord et al. (1983), ■ Gibbs and Popolato (1980), △ Townsend and Meyers (1996), — this study pH 4.2 [ln (S/ mg L^{-1}) = 19.087 – 4549.1 K/T, R^2=0.987], - - this study pH 5.7. [ln (S/ mg L^{-1}) = 19.718 – 4727.8 K/T, R^2=0.995],, ····· this study pH 6.2 [ln (S/ mg L^{-1}) = 19.818 – 4753.2 K/T, R^2=0.995].

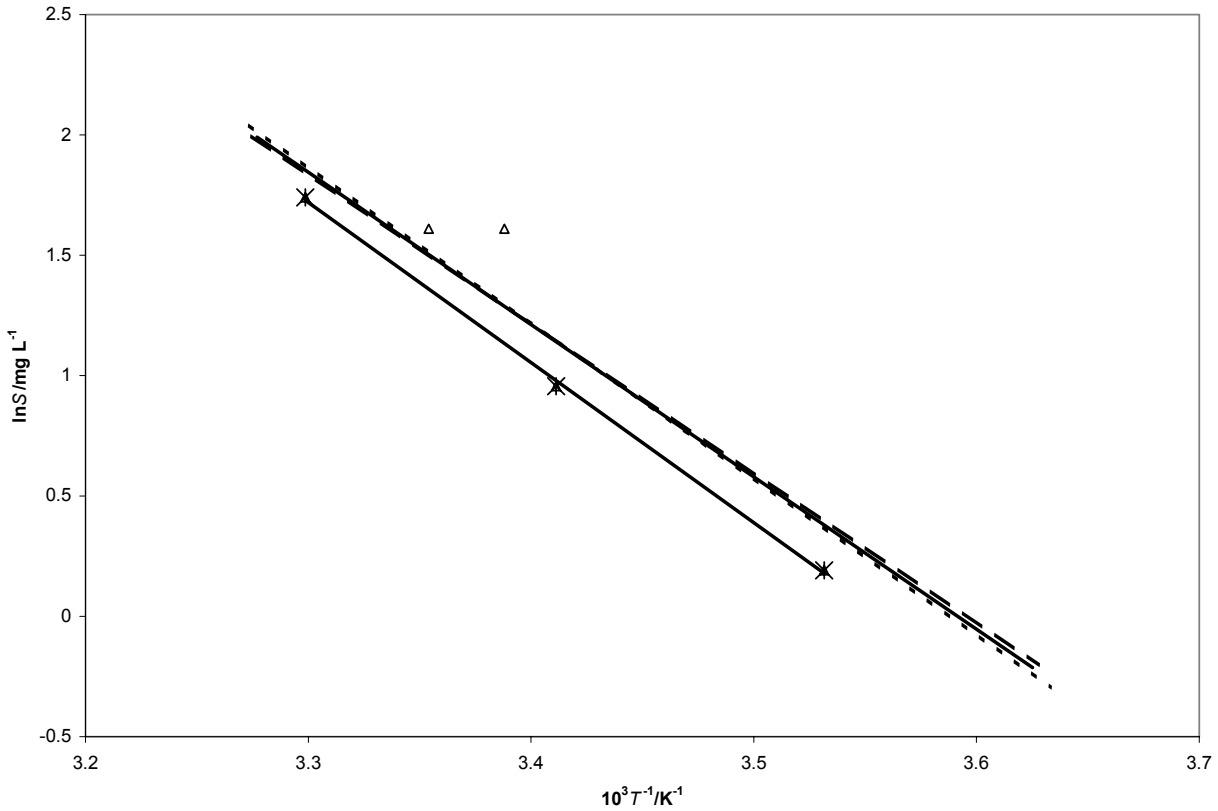

Figure 8. Comparison of literature HMX solubility to this study. —*— Spanggord et al. (from Townsend and Meyers, 1996), △ Townsend and Meyers (1996), —— this study pH 4.2 [ln (S/ mg L^{-1}) = 22.741 – 6332 K/T, R^2=0.9974], – – this study pH 5.7 [ln (S/ mg L^{-1}) = 22.399 – 6230 K/T, R^2=0.9968]., ¨ ¨ ¨ this study pH 6.2 [ln (S/ mg L^{-1}) = 23.344 – 6506.8 K/T, R^2=0.9901]..

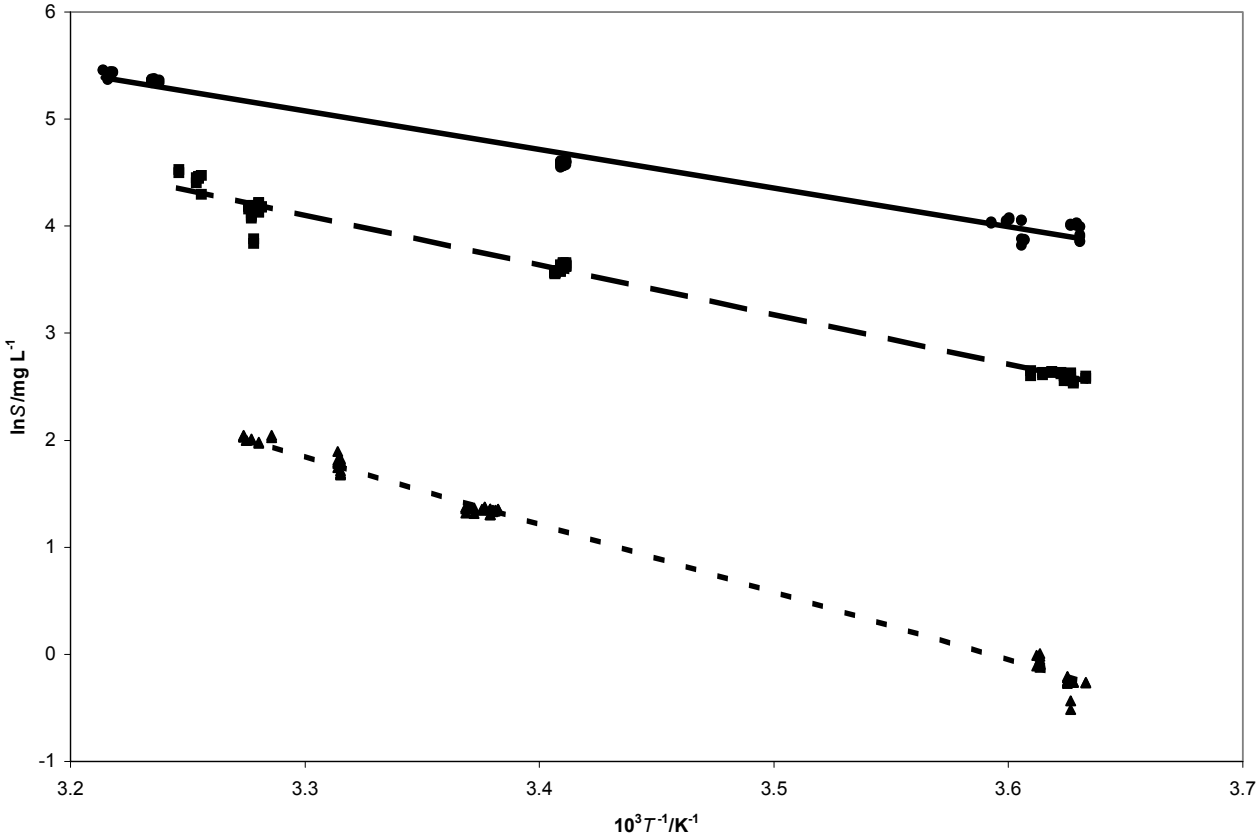

Figure 9. Composite explosive solubility prediction correlations. ——, ● TNT [ln (S/ mg L^{-1}) = 16.981 – 3607.5 K/T, R^2=0.990], ····, ▲ HMX [ln (S/ mg L^{-1}) = 22.825 – 6358.2 K/T, R^2=0.997], – –, ■ RDX [ln (S/ mg L^{-1}) = 19.52 – 4670.9 K/T, R^2=0.992].

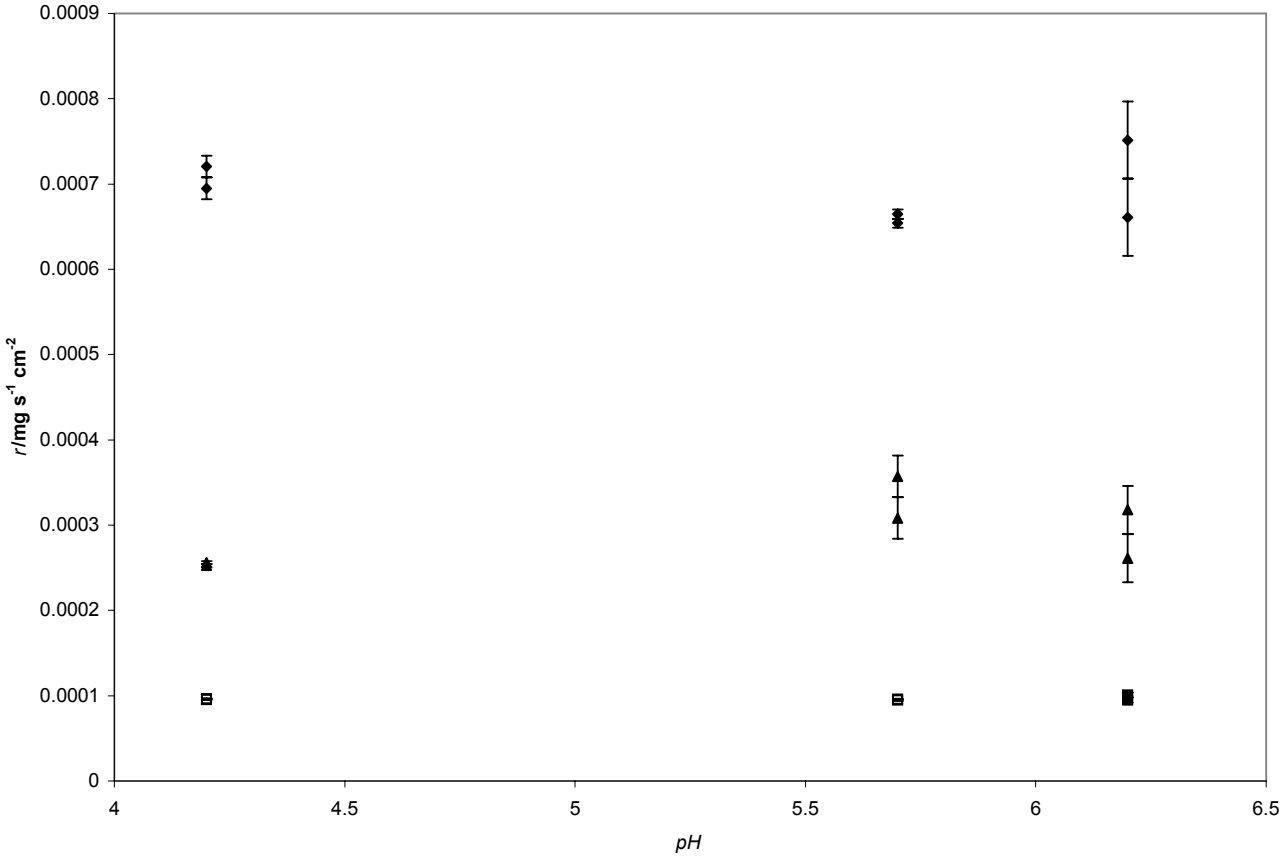

Figure 10. Comparison of Explosive Dissolution Rates at Three pH Values. ◆ TNT, ▲ HMX, ■ RDX.

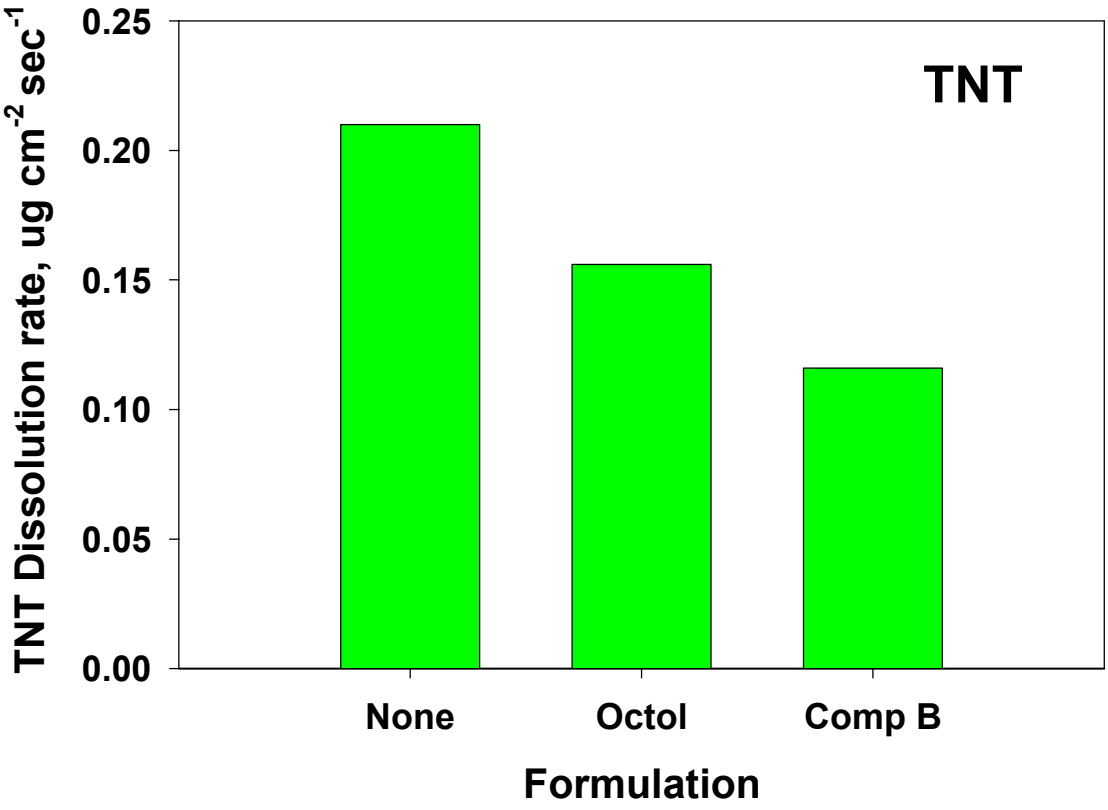

Figure 11. Comparison of TNT dissolution rates from pure TNT, Octol, and Composition B at 20 ^{o}C and 150 rpm

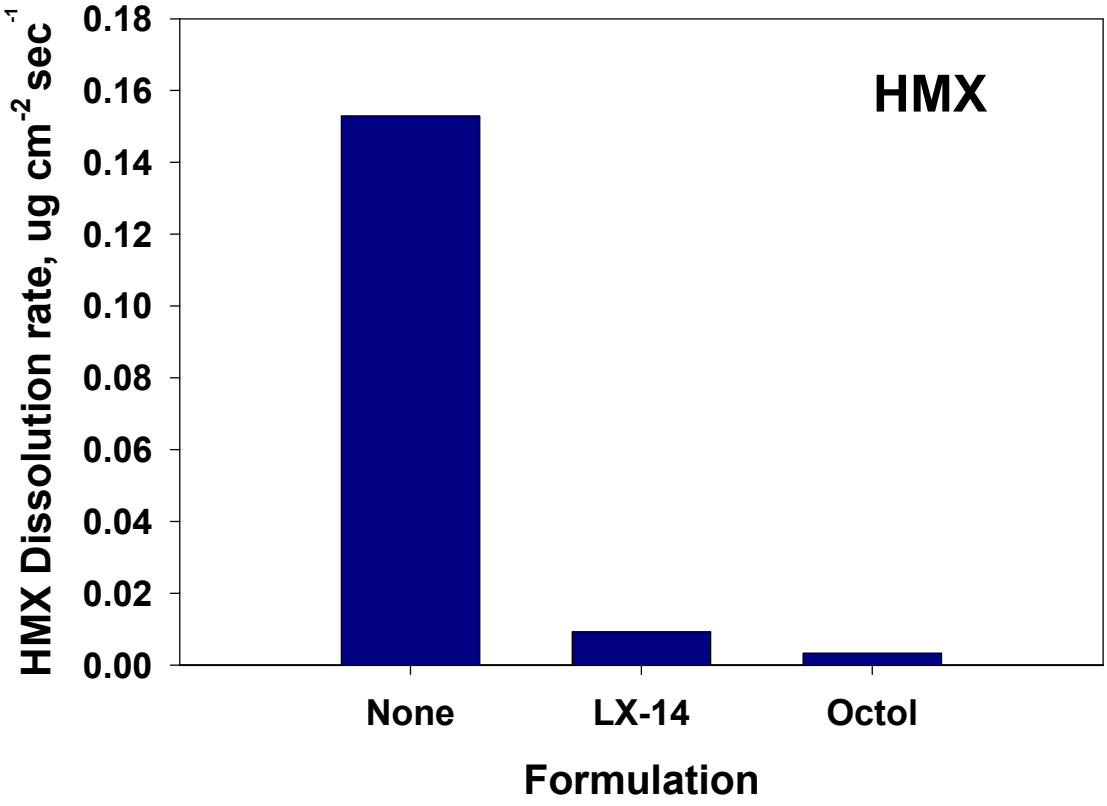

Figure 12. Comparison of HMX dissolution rates from pure HMX, LX-14, and Octol at 20 ^{o}C and 150 rpm

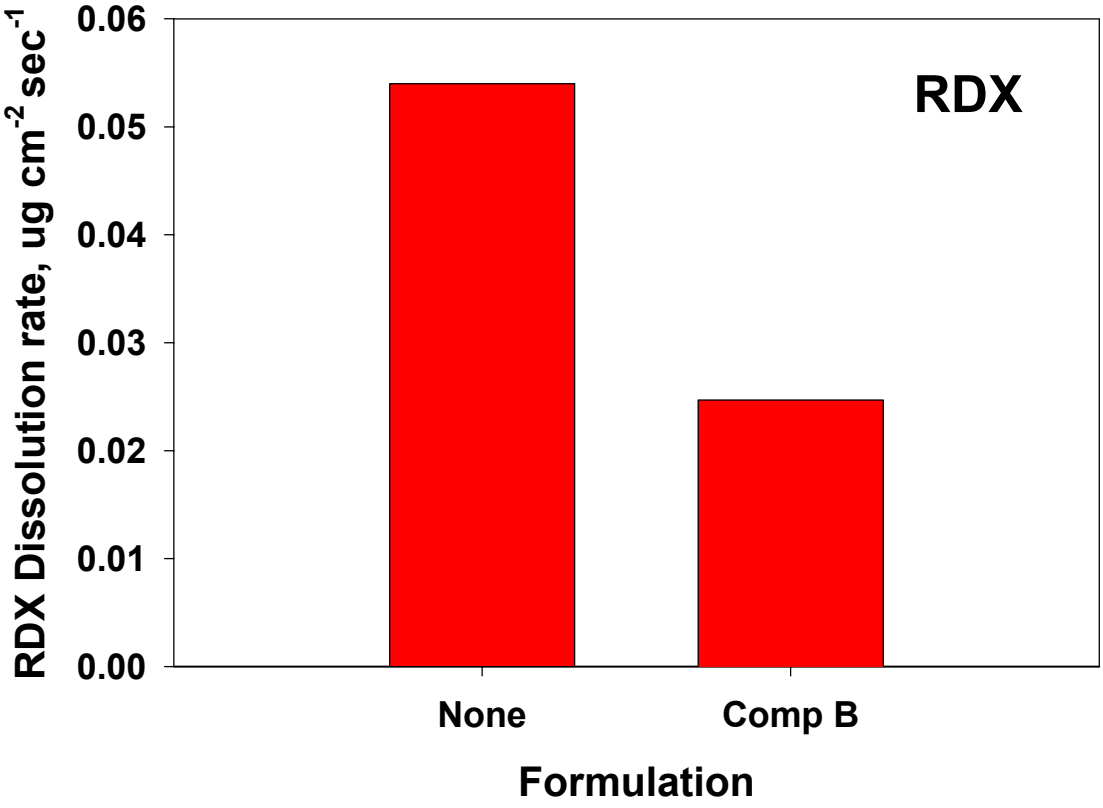

Figure 13. Comparison of RDX dissolution rates from pure RDX and Composition B at 20 ^{o}C and 150 rpm

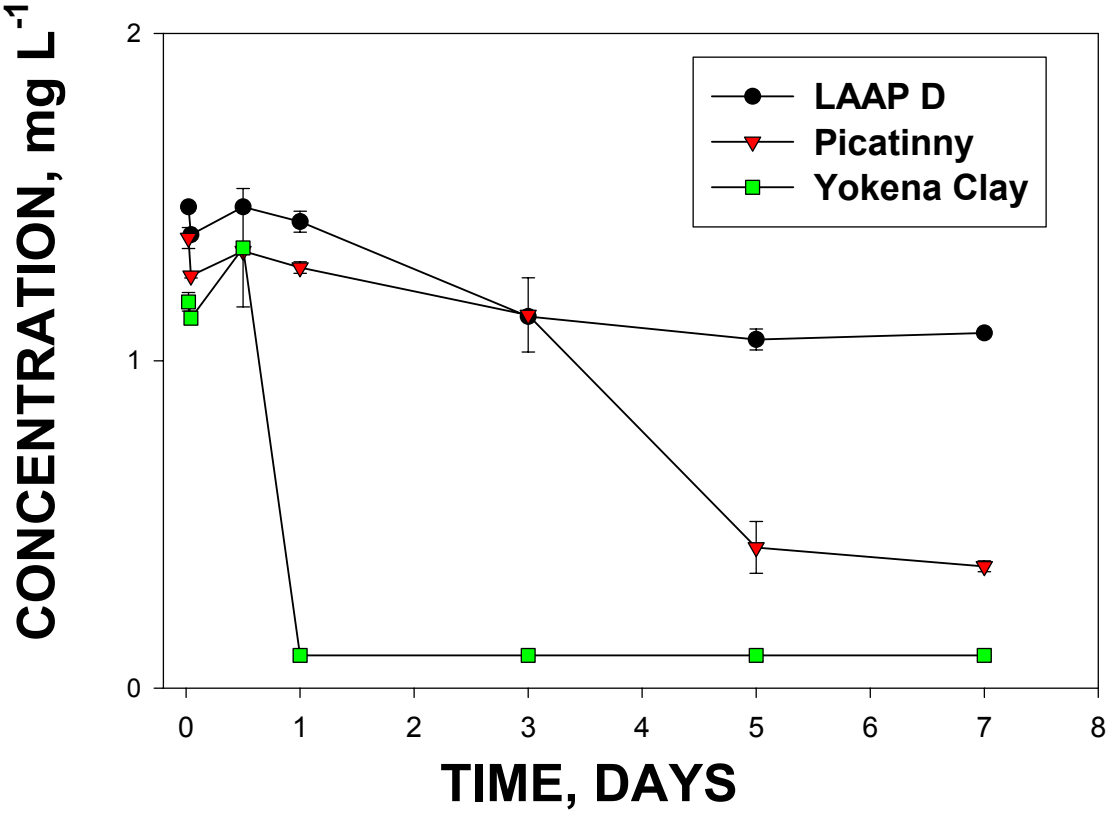

Figure 14. Adsorption kinetics of nitroglycerine in LAAP-D, Picatinny, and Yokena Clay soils.

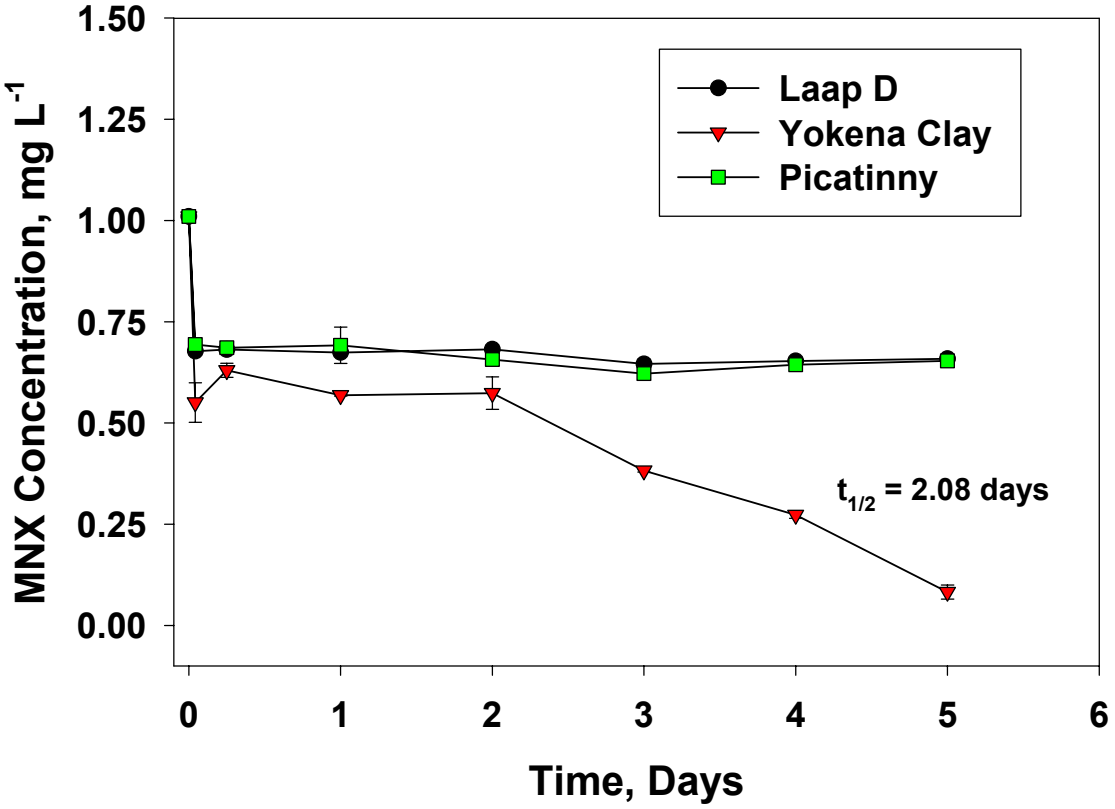

Figure 15. Adsorption kinetics of MNX in LAAP-D, Picatinny, and Yokena Clay soils.

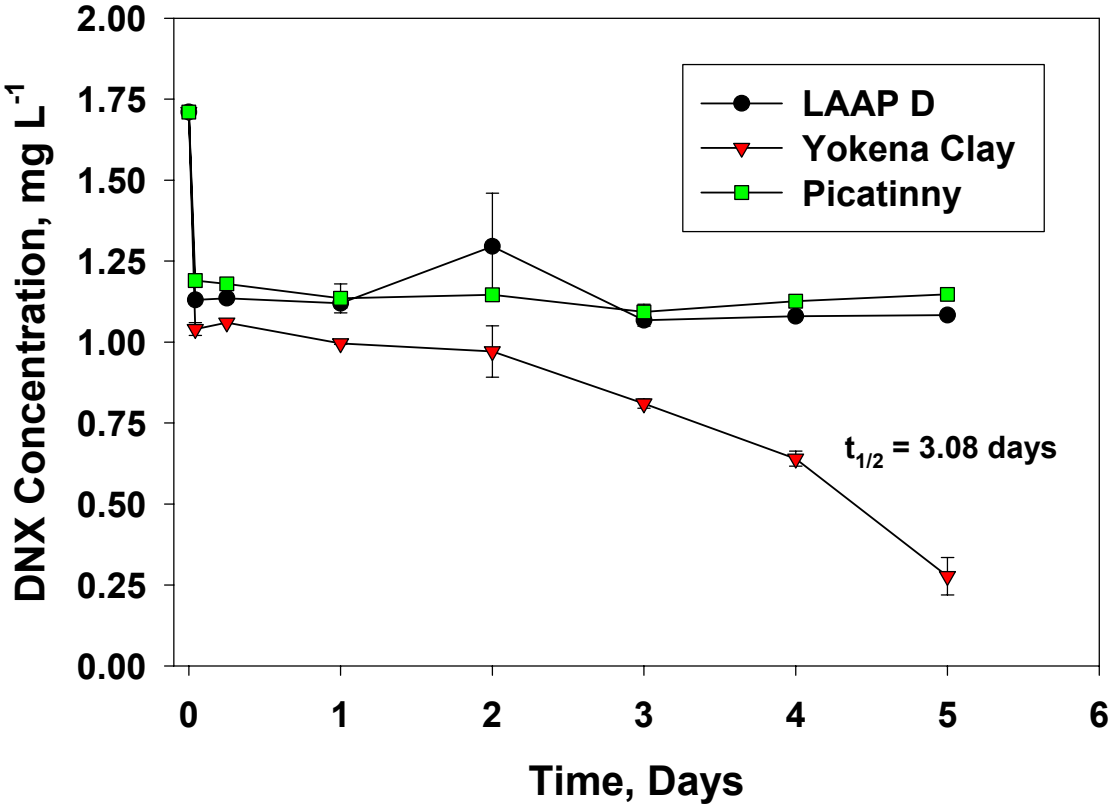

Figure 16. Adsorption kinetics of DNX in LAAP-D, Picatinny, and Yokena Clay soils.

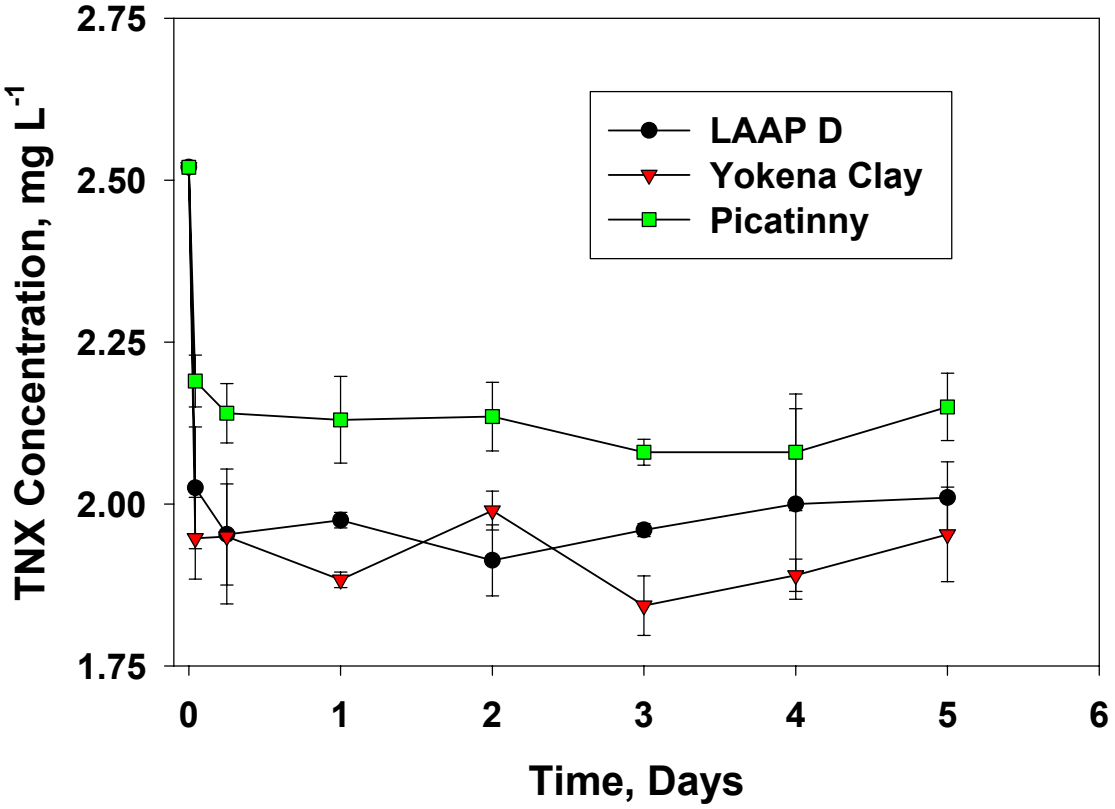

Figure 17. Adsorption kinetics of TNX in LAAP-D, Picatinny, and Yokena Clay soils.

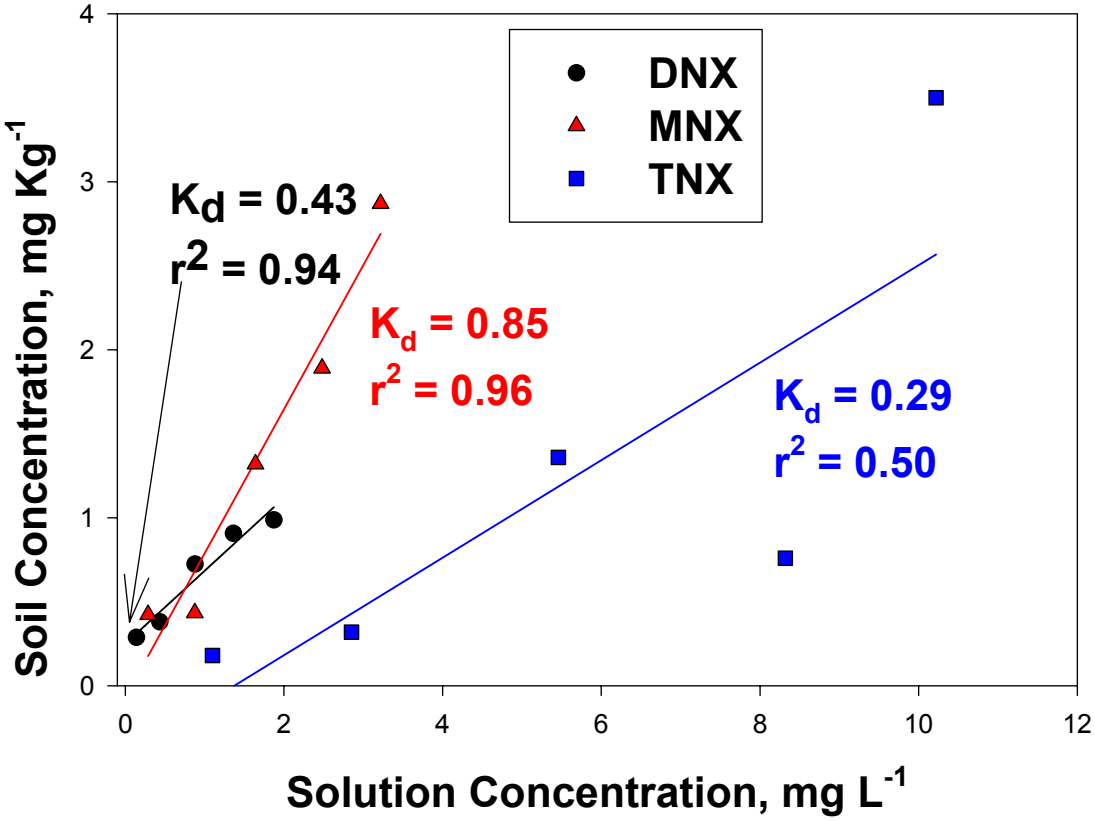

Figure 18. Partitioning coefficients for MNX, DNX, and TNX in LAAP-D soil.

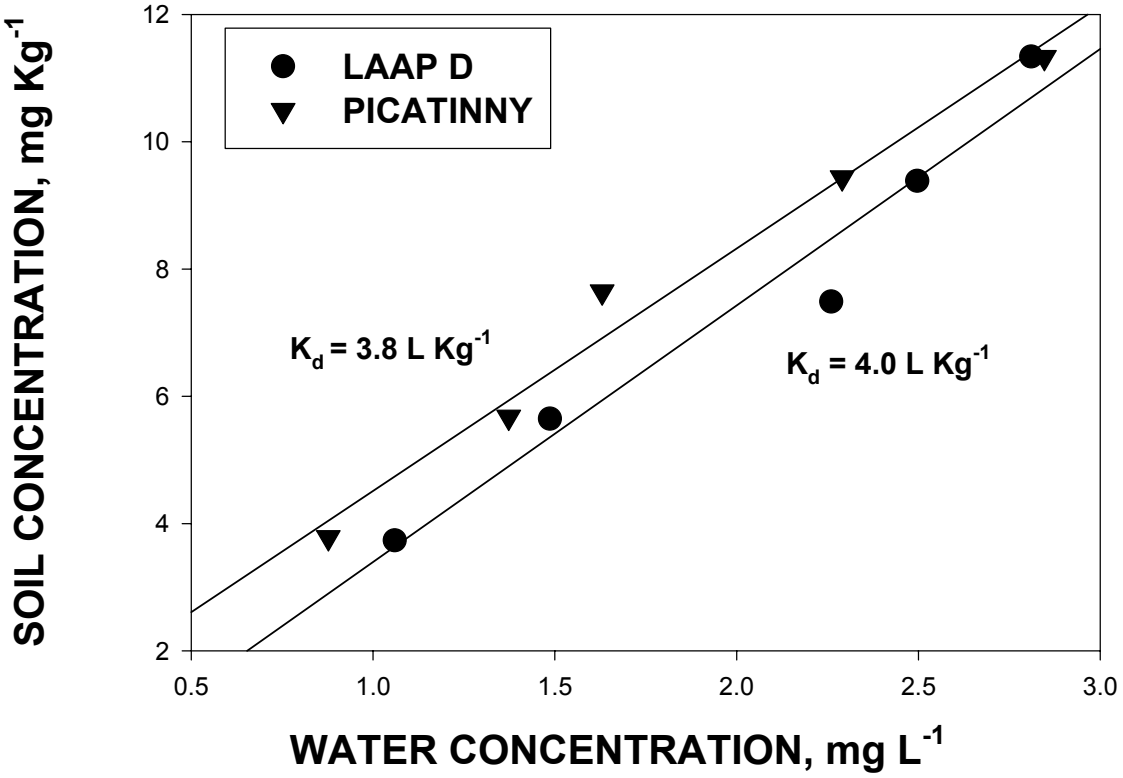

Figure 19. Partitioning coefficients for nitroglycerine in LAAP-D and Picatinny soils.

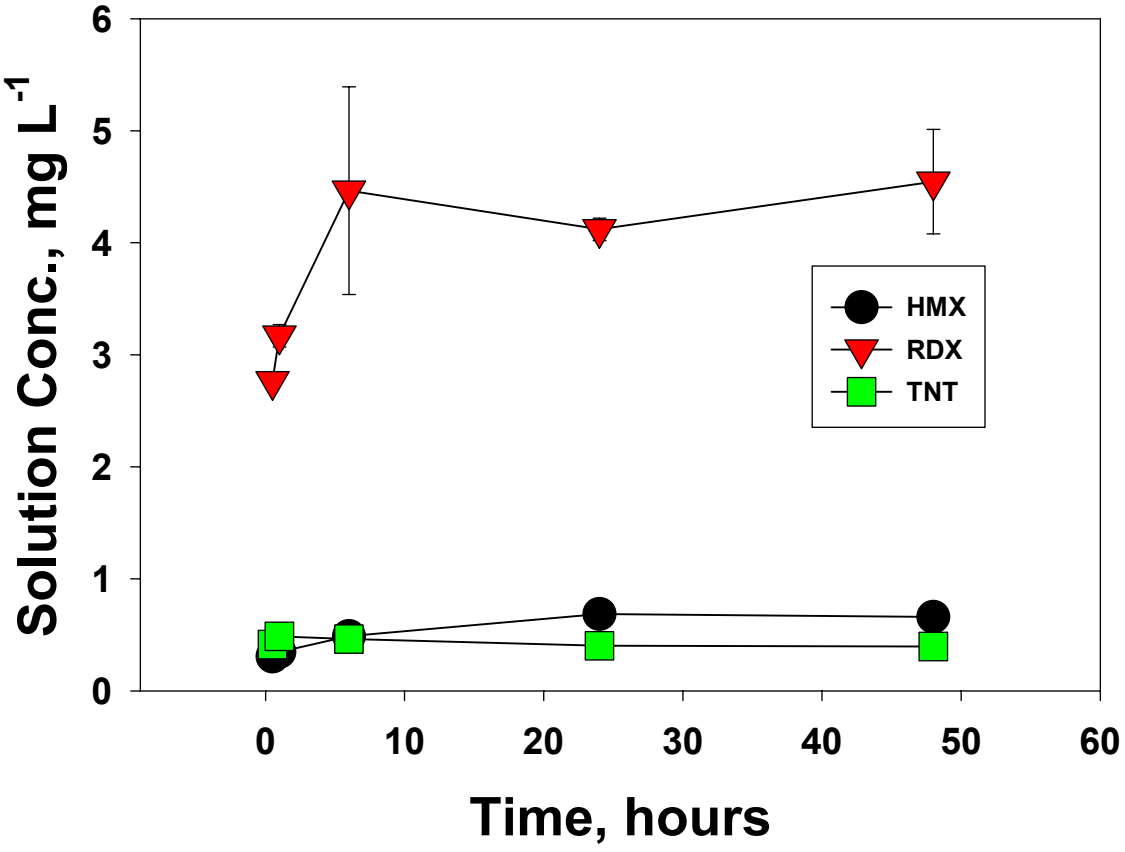

Figure 20. Desorption kinetics of TNT, RDX, and HMX in Ft. Lewis soil.

5 Conclusions

Results of range characterization studies indicate that various types of military testing and training ranges differ in the contaminants present. For example surface soils near targets on anti tank rocket ranges are contaminated with extremely high concentrations (ppms) of HMX, while soils near targets on artillery ranges exhibit extremely low concentrations (ppbs) of RDX and TNT. The contamination associated with battle runs using pop-up targets is completely different from those associated with fixed anti-tank targets. Consistently high concentrations (% levels) of explosives residues were found near ruptured ordnance. Artillery ranges are a potentially very low non-point source of explosives residues with higher point sources randomly scattered across the site. A multi-increment composite sampling strategy is essential to adequately characterize the distribution of contaminants on artillery ranges. Combining 30 individual increments into a composite sample in these studies resulted in adequate reproducibility. The ability to reproduce data with an acceptable level of uncertainty provides confidence that the sample is representative of the area.

The degree of contamination associated with detonation of dud rounds using C4 is a potential concern. The use of C4 can result in incomplete detonations that scatter RDX across the soil. Since RDX is an undesirable groundwater contaminant, consideration should be given to improving the efficiency of blow-in-place disposal of dud rounds.

Dissolution rates of TNT, HMX, and RDX increased with surface area, temperature, and mixing rates. TNT dissolved fastest, followed by HMX and RDX, respectively. Solubility and dissolution rates were unaffected by pH, but increased slightly with temperature. Solubility and dissolution rates were not always consistent with each other for a given analyte. Specifically, of the three primary explosives, TNT, RDX, and HMX, TNT was the most soluble and had the highest dissolution rate, while RDX had the second highest solubility, but exhibited the slowest dissolution rate. Dissolution rates of individual

explosives were suppressed in their formulations, i.e., LX-14, Composition B, and octol. Therefore, explosives formulations would persist longer in surface soils than the parent compounds.

Nitroglycerine degraded rapidly in all soils tested; therefore, it is not expected to persist in surface soils. The RDX transformation products, MNX, DNX, and TNX, were generally stable in all soils tested. These compounds exhibit transport potential consistent with RDX. Transport parameters used to model potential groundwater contamination and to evaluate environmental or human health risk should reflect formulations of the explosives present and the dissolution rates as well as solubilities.

Abstract

Testing and training ranges are essential to maintaining the readiness of the Armed Forces of the United States and Canada. Recently, concerns have arisen over potential environmental contamination from residues of energetic materials at impact ranges. The current state of knowledge concerning the nature, extent, and fate of contamination is inadequate to ensure sound management of ranges as sustainable resources. 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.

The approach included characterization of two U. S. installations, Yakima Training Center, WA, and Camp Guernsey, WY, and one Canadian installation, CFB Shilo. Post blast residues from various heavy artillery munitions were characterized by sampling surface soils associated with firing positions and with craters from both high- and low-order detonations. Where possible, ground and surface water associated with the ranges was also sampled. Vegetation was characterized on the Canadian range. The study also included determination of transport parameters for RDX transformation products, MNX, DNX, and TNX and for nitroglycerin. Dissolution rates and solubilities of TNT, RDX, and HMX were determined on the compound and on three explosives formulations, LX-14, Composition B, and octol.

Results of range characterization studies indicate that various types of military testing and training ranges differ in the contaminants present. Consistently high concentrations (% levels) of explosives residues were found near ruptured ordnance. Artillery ranges are a potentially very low non-point source of explosives residues with higher point sources randomly scattered across the site. A multi-increment composite sampling strategy is essential to adequately characterize the distribution of contaminants on artillery ranges. Contamination associated with demolition detonation of duded rounds using C4 is a potential concern. The use of C4 can result in incomplete detonations that scatter RDX across the soil. Since RDX is an undesirable groundwater contaminant, consideration should be given to improving the efficiency of blow-in-place disposal of duded rounds.

Dissolution rates of TNT, HMX, and RDX increased with surface area, temperature, and mixing rates. Nitroglycerine degraded rapidly in all soils tested; therefore, it is not expected to persist in surface soils. The RDX transformation products, MNX, DNX, and TNX, were generally stable in all soils tested. These compounds exhibit transport potential consistent with RDX. Transport parameters used to model

potential groundwater contamination and to evaluate environmental or human health risk should reflect formulations of the explosives present and the dissolution rates as well as solubilities.