Technical Report

Department of Defense Operational Range Sustainability through Management of Munitions Constituents

April 2014

Thomas Jenkins, PhD
Private Consultant

Catherine Vogel, P.E.
Noblis

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Thomas Jenkins, PhD (Consultant)
Catherine Vogel, P.E. (Noblis)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Thomas Jenkins Environmental Consulting - 43 Gould Road, West Lebanon NH, 03784
Noblis - 1820 Woodland Hills Ave NW, Atlanta Georgia 30318

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14. ABSTRACT
This document aims to illustrate the environmental risks posed from the deposition of MC residue on ranges from live-fire training activities. Moreover, the document describes the state-of-the-art for numerous management technologies designed to slow or halt the migration of energetic compounds in soil and groundwater. This document is provided in two versions: an extended version that provides full descriptions of all background material and technologies, and a compendium document titled, Department of Defense Best Management Practices for Munitions Constituents on Operational Ranges (April 2014), which is intended as a quick reference guide.

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Executive Summary

The Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) has developed this document to provide a reference for DoD range managers and their contractors to assist in the evaluation and application of munitions constituent (MC) management technologies to sustain ranges for future use. This document aims to illustrate the environmental risks posed from the deposition of MC residue on ranges from live-fire training activities. Moreover, the document describes the state-of-the-art for numerous management technologies designed to slow or halt the migration of energetic compounds in soil and groundwater. This document is provided in two versions: an extended version that provides full descriptions of all background material and technologies, and a compendium document titled, *Department of Defense Best Management Practices for Munitions Constituents on Operational Ranges* (April 2014), which is intended as a quick reference guide.

The focus of this document is on energetic compounds (explosives and propellants) on operational land-based ranges including: hand grenade ranges; antitank rocket ranges; artillery, tank, and mortar ranges; air-to-ground bombing ranges; and explosive ordnance detonation sites on operational ranges. This document does not address munitions-related metals or ammonium perchlorate (oxidizer used in solid rocket motor propellant).[1] Further, the document does not discuss technologies applicable to water-based operational ranges or small arms ranges (SARs), with the exception of SAR firing points that may pose problems due to the release of propellants in the environment. Although this document does not present policy recommendations for the design, siting, and construction of new military ranges, the information presented on the environmental behavior of the energetic chemicals of concern should be considered when making such decisions.

This document is not intended to serve as guidance for a thorough site characterization or technology feasibility study. Basic background information is provided on issues associated with energetic compounds on ranges and management technologies that may be implemented to reduce the risks posed by the deposition of MC residues on ranges. References are provided to aid the reader in gathering detailed information on topics covered. This document is divided into sections that address the:

- Rationale for implementing MC management technologies (Section 2).
- Chemical and physical properties of the energetic compounds of primary use in munitions used on training ranges (Section 3).
- Fate and transport of the energetic compounds under various environmental conditions (Section 3).

[1] Information on technologies to address ammonium perchlorate (in groundwater) and munitions-related metals is readily available in numerous other documents (e.g., ITRC, 2008; Stroo and Ward, 2009; Fabian and Watts, 2005; full citations provided in Section 1). Currently there are no validated technologies for managing perchlorate in shallow soils on operational ranges. However, several of the groundwater technologies presented in Section 5.2 are applicable for perchlorate.

- Supporting technologies—surface soil sampling procedures, mass loading estimation techniques, groundwater monitoring, and analytical methods (Section 4).
- Soil mitigation approaches—alkaline hydrolysis, passive *in situ* management approach for shallow soil, plant-based mitigation, *ex situ* soil management technologies, controlled burning, onsite residue collection and destruction, and field-portable burn pans (Section 5).
- Groundwater mitigation approaches—monitored natural attenuation, passive *in situ* mitigation approaches, active *in situ* management approaches, hydraulic control, and constructed wetlands (Section 5).
- Current status of research and development efforts for innovative management technologies (Section 6).
- Description of the risk management approaches used by the Canadian Army to mitigate environmental risks on their operational ranges (Appendix A).

This document does not provide guidance regarding the potential applicability of any environmental laws or regulations to the implementation of any of the management technologies. The environmental and legal staff supporting the range should be consulted to ensure any legal or regulatory requirements are considered when evaluating and implementing these technologies. Additionally, this document is not intended to include discussions of the safety issues associated with sites impacted by unexploded ordnance and energetic residues. Explosive safety procedures and safety precautions should be identified prior to initiating sampling activities or implementation of the BMPs.

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1 Introduction

1.1 Background

Live-fire training is a necessary military function to maintain the mission readiness of our nation's warfighter; however, these training activities can create source zones[2] of munitions constituents (MCs).[3] Depending on the hydrogeologic, geographic, and climatological setting of the range, some of these MCs have the potential to dissolve and/or migrate to reach surface water and/or groundwater.

Department of Defense (DoD) policy (DoD, 2003) requires that environmental issues be considered during the planning and management of ranges and operating areas to help ensure their long-term sustainability. One of the responsibilities outlined in DoD Directive 3200.15[4], Sustainment of Ranges and Operating Areas, requires the DoD to address knowledge and technology requirements necessary for range sustainment through active research, development, testing, and evaluation (RDT&E) programs. The DoD and the Military Services have funded a significant body of basic and applied research to gain a better understanding of the MCs resulting from military training activities on ranges, to characterize the environmental deposition of MCs on military ranges, and to develop technologies to manage or contain MCs in soil and groundwater. The results from these efforts can be found in numerous technical reports and journal articles, but because there is no clearinghouse for this type of information, this information is not readily available to the operational range community. Additionally, there are no guidelines universally accepted by the range managers to implement technological strategies to reduce the dissolution and migration of MCs in environmental media.

1.2 Purpose and Scope

The purpose of this document is to provide a reference tool for Army, Marine Corps, Navy, Air Force and National Guard range managers and their contractors to assist in the evaluation and application of technologies to sustain ranges for future use. Technologies (hereafter referred to as Best Management Practices or BMPs) designed to reduce the risks to human health and the environment from the dissolution and migration of energetic compounds in environmental media are described.

The focus of this document is on:

- ***Energetic compounds*** (explosives and propellants) on
- ***Operational land-based ranges*** including: hand grenade ranges; antitank rocket ranges; artillery, tank, and mortar ranges; air-to-ground bombing ranges; and explosive ordnance detonation sites on operational ranges.

This document does not address:

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[2] A *source zone* is defined as a deposit of chemicals, usually in the surface soil, that under certain conditions may create and sustain a contaminant plume.

[3] *Munitions constituents (MC):* Any materials originating from unexploded ordnance, discarded military munitions, or other military munitions, including explosive and non-explosive materials, and emission, degradation, or breakdown elements of such ordnance or munitions (10 United States Code (U.S.C.) 2710 [e][4]).

[4] DoD Directive (DoDD) 3200.15 was revised and reissued on December 18, 2013.

- ***Ammonium perchlorate*** (oxidizer used in solid rocket motor propellant),
- ***Munitions-related metals***,
- ***Technologies applicable to water-based operational ranges***,
- ***Technologies applicable to small arms ranges (SARs)***, with the exception of SAR firing points that may pose problems due to the release of propellants in the environment, or
- ***Policy recommendations*** for the design, siting and construction of new military ranges, although the information presented on the environmental behavior of the energetic chemicals of concern would be valuable when making these decisions.

Information on technologies to address ammonium perchlorate (in groundwater) and munitions-related metals is readily available in numerous other documents (e.g., ITRC, 2008; Stroo and Ward, 2009; Fabian and Watts, 2005). Currently there are no validated technologies for managing perchlorate in shallow soils on operational ranges. However, several technologies presented in Section 5.2 are applicable for perchlorate contamination in groundwater.

Basic background information is presented on issues associated with energetic chemicals on ranges, to include (1) defining the problem posed by the release of the energetic chemicals, (2) discussing the limitations on the applicability of different sustainment technologies due to range usage and size, and (3) discussing the impact of geographic, geologic, and climatological settings on the dissolution and mobilization of energetic chemicals. This document further describes technologies that remove, degrade, or stabilize energetic chemicals in soil and groundwater. Methodologies and technologies that have been, or are being, tested and validated at the field-scale are presented. The status of technologies currently in development at the laboratory- and pilot-scale are also provided.

1.3 DoD Operational Range BMP Workgroup

A DoD Operational Range BMP workgroup was formed to provide input to and review of this document. Representatives from the Office of the Secretary of Defense, Army, Army National Guard, Marine Corps, Navy, and Air Force involved in operational range environmental issues participated in this workgroup led by the DoD Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) Office.

In developing this document, the authors interviewed the workgroup members to gather information on methodologies and technologies in use or in development by the Military Services that control MCs on ranges. Additionally, information was gathered on the mission-specific challenges in applying such technologies.

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DoD (Department of Defense). 2003. Sustainment of Ranges and Operating Areas (OPAREAs), DoD Directive Number 3200.15. January 10. Revised and reissued on December 18, 2013.

Fabian G, Watts K. 2005. Army Small Arms Training Range Environmental Best Management Practices (BMPs) Manual. U.S. Army Environmental Center Report SFIM-AEC-AT-CR-2006007. February 12. 211 p.

ITRC (Interstate Technology & Regulatory Council). 2008. Remediation Technologies for Perchlorate Contamination in Water and Soil. March. 217 p.

Stroo HF, Ward CH, eds. 2009. *In Situ* Bioremediation of Perchlorate in Groundwater. SERDP/ESTCP Environmental Remediation Technology Monograph Series. Springer Science+Business Media, New York, NY, USA. 250 p.

2 When to Implement Munitions Constituent Management Technologies

2.1 Operational Range Life-Cycle

The development of new operational testing and training ranges and the expansion/upgrading of existing ranges, follow established design guidelines (e.g., USACE, 2004). Typical steps in the range development process, from conception to the first live-fire training event, are shown in Figure 2.1.

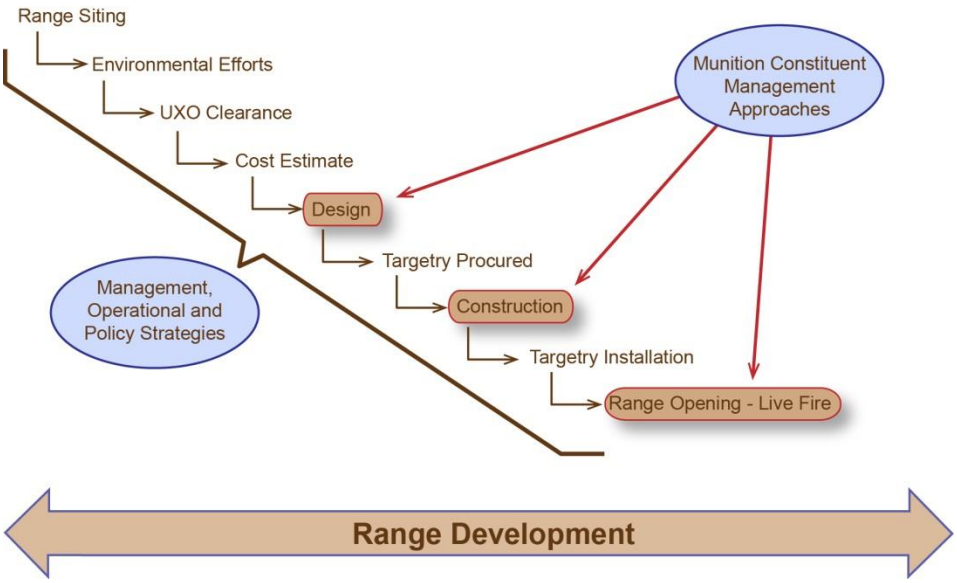

Figure 2-1. Steps in the range development process (adapted from USACE, 2004). ***Note that UXO clearance would not be required in situations where a new range is being developed on virgin land (i.e., land not previously used as a range).***

Energetic residues are deposited in and near impact areas and firing points from live-fire training and from activities at demolition ranges (see Sections 3.3 and 3.4). Some ranges are much more susceptible to the dissolution and migration of residues to groundwater or surface water than others. The rationale for implementing any of the management technologies discussed in this document should be based on the site-specific hydrogeologic, geographic, and climatological conditions at these ranges. Generally, sites with substantial concentrations of energetic residues deposited (in the case of existing operational ranges), continued future residue loading, moderate to high precipitation, shallow to moderate depth to groundwater, and permeable soils will be more vulnerable to the energetic compounds reaching groundwater/surface water. The management technologies discussed in this document can be incorporated into the siting, design and construction of new ranges or implemented at existing operational ranges to reduce the risks from energetic compounds reaching groundwater/surface water and migrating off-range.

Management, operational, and policy strategies appropriate to reduce the risk from the deposition, dissolution, and migration of energetic compounds to groundwater should be

considered during all stages of range siting, development, expansion, or upgrading. Although these types of strategies are not discussed in this document, following are a few examples.

- The high explosive in 155-millimeter (mm) rounds can either be 2,4,6-trinitrotoluene (TNT) or Composition B (hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX]/TNT). RDX does not sorb strongly to soil surfaces and, hence, once dissolved is more mobile in the environment than other explosives such as TNT. A strategy could be developed where TNT-containing rounds are used at the ranges where migration to groundwater is of greater concern and the Composition B rounds (containing RDX) elsewhere.
- The increased use of simulated rounds rather than explosive-filled rounds would reduce the amount of energetic residue deposited.
- Modify current policies to allow explosive ordnance disposal personnel or unexploded ordnance technicians to collect and destroy energetic residue during operational range clearance activities.

2.2 Determining Risk of Munitions Constituents Reaching Groundwater or Surface Water

The purpose of this document is to present technology options to reduce the risk of dissolution and migration of munitions constituents (MCs) to groundwater or surface water once they are deposited on the soil surface. That said, there are some ranges where the technical rationale for investing in these technologies will be more evident than at others due to site-specific hydrogeologic, geographic, and climatological conditions. For example, ranges located over critical aquifers, in areas with high to moderate precipitation, permeable aquifer material, shallow to moderate water table or adjacent to sensitive surface water bodies, and slow to moderate moving groundwater, would be candidates for the MC management technologies discussed in this document as opposed to ranges located in arid environments with deep groundwater having a low risk of MCs migrating to groundwater or surface water.

Each Service has developed and implemented an Operational Range Assessment Program (ORAP) to assess the potential environmental impacts to off-range receptors from military munitions used on operational ranges and range complexes (USAEC, 2007; HQ USMC, 2009; USN, 2006; USAF, 2006). The objectives of the ORAPs are to (1) determine whether there has been a release or a substantial threat of a release of MCs of concern from an operational range to an off-range area, and (2) whether the release (or substantial threat of release) of MCs of concern to an off-range area creates an unacceptable risk to human health or the environment (DoD, 2005). The goal of the ORAPs is to ensure that the operational range natural resource infrastructure is capable and will continue to be available to support the U.S. Department of Defense's test and training missions.

Data collected in support of the ORAPs can be useful in qualitatively prioritizing ranges in terms of the risk that energetic compounds will migrate to groundwater or surface water. Examples of data include:

- Description of MC source areas
  - Location of potential sources (e.g., impact areas, firing points, storage, and waste disposal areas)
  - Historical and current munition expenditure data
  - Frequency of clearance activities

- Topographic features/vegetative features
- Surface water features/drainage pathways
- Surface/subsurface geology (soil type/properties)
- Meteorological data related to precipitation, temperature, wind, evapotranspiration rate, and other data bearing on transport
- Geophysical data
- Hydrogeological data including depth to groundwater, groundwater flow rate (if available), aquifer characteristics, monitoring well logs (if available), and historical sampling and analytical results (if available)
- Site features that have a bearing on transport of MCs

Ranges identified with a higher risk of MCs reaching groundwater or surface water may warrant a more aggressive approach to manage MC dissolution and migration. These sites will require further characterization to better assess the risk and to determine which management technologies would be most appropriate.

2.2.1 Risk and Vulnerability Mapping

Land management tools are one approach to provide the decision making information needed to implement MC management approaches and operational changes on ranges. One tool developed by Canadian researchers for use on Canadian Army ranges involves the development of three maps. The first map, called a Vulnerability Map, assesses the vulnerability of various portions of a range to impacts to the underlying aquifer (e.g., the relative ease of dissolved MCs migrating from the ground surface to the upper boundary of the aquifer). The second map, called the Hazard Map, describes the pattern of deposition of MCs on the range due to the placement of firing points, impact areas, and demolition areas. The Vulnerability and Hazard Maps are overlain to produce a Risk Map, which identifies the critical areas of the range complex most susceptible to MC migration to groundwater or surface water.

An example of a Vulnerability Map for Canadian Forces Base (CFB) Wainwright, Alberta, Canada is shown in Figure 2-2. The methodology uses a three-dimensional (3-D) geologic model to relate vulnerability directly to a conservative estimate of the downward advective time for dissolved MCs to travel from the ground surface to the water table (Ross et al., 2004). The map is color-coded for ease in locating the most vulnerable areas of the range complex. This assessment can provide data useful in siting and planning new ranges to avoid high vulnerability areas or in relocating ranges on existing facilities.

The Hazard Map for CFB Wainwright is shown in Figure 2-3. A Hazard Index is estimated for each training area based on the frequency of use (number of rounds fired, estimate of low-order detonations, amount of residue deposited), environmental fate of the MCs (toxicity, solubility, degradation, and sorption), and the surface area of the training area.

Overlaying the Vulnerability Map with the Hazard Map produces a Risk Map (Figure 2-4) which assigns a level of risk (ranging from very high to very low/no data) that the MCs will reach groundwater or surface water to the different areas of the range complex. This information can be used to identify ranges where MC management approaches (or operational or policy approaches) should be implemented to reduce the risk.

Additional discussion on the approach taken by the Canadian Army to assess environmental risks at their operational ranges is provided in Appendix A.

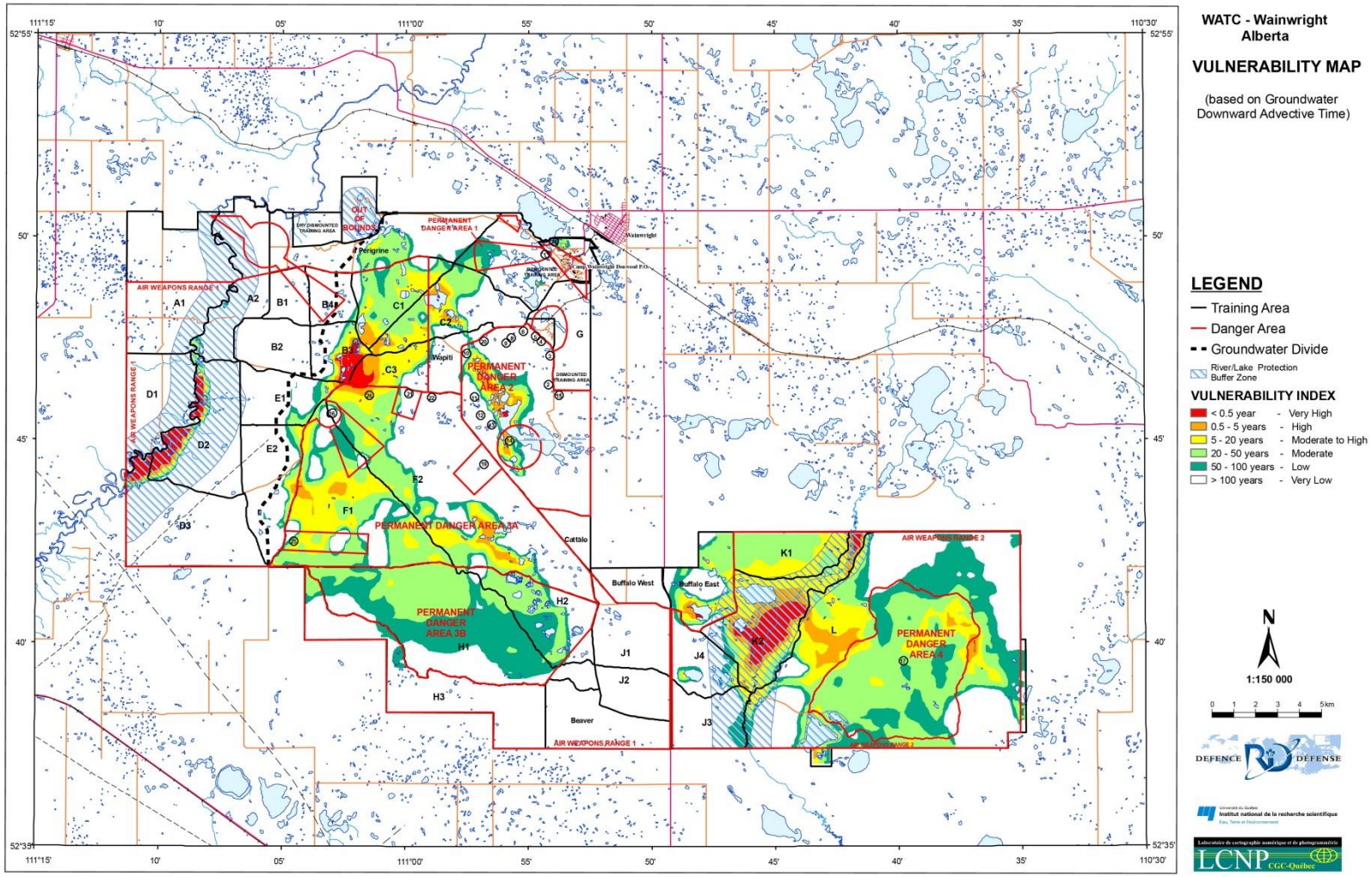

Figure 2-2. Vulnerability Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

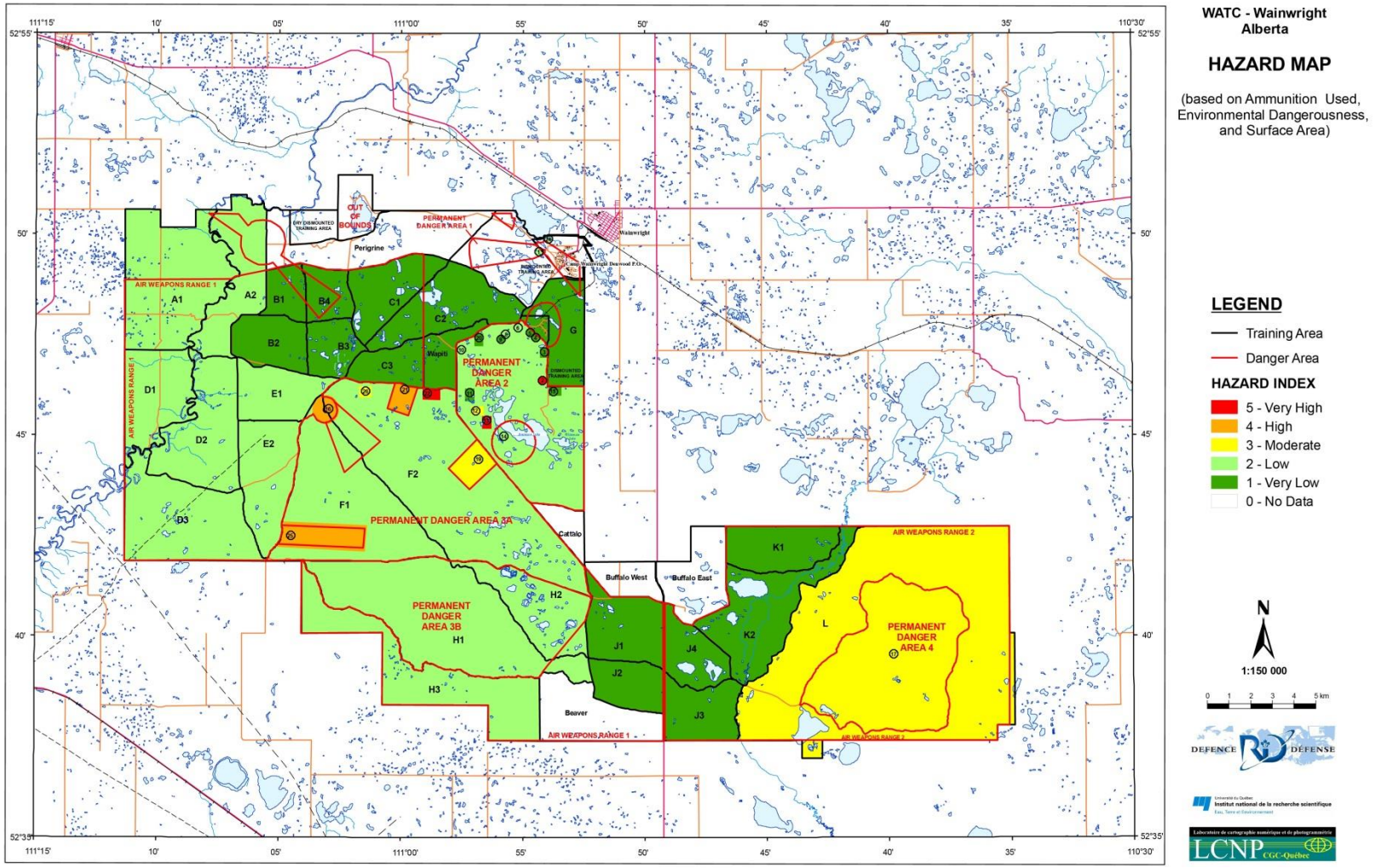

Figure 2-3. Hazard Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

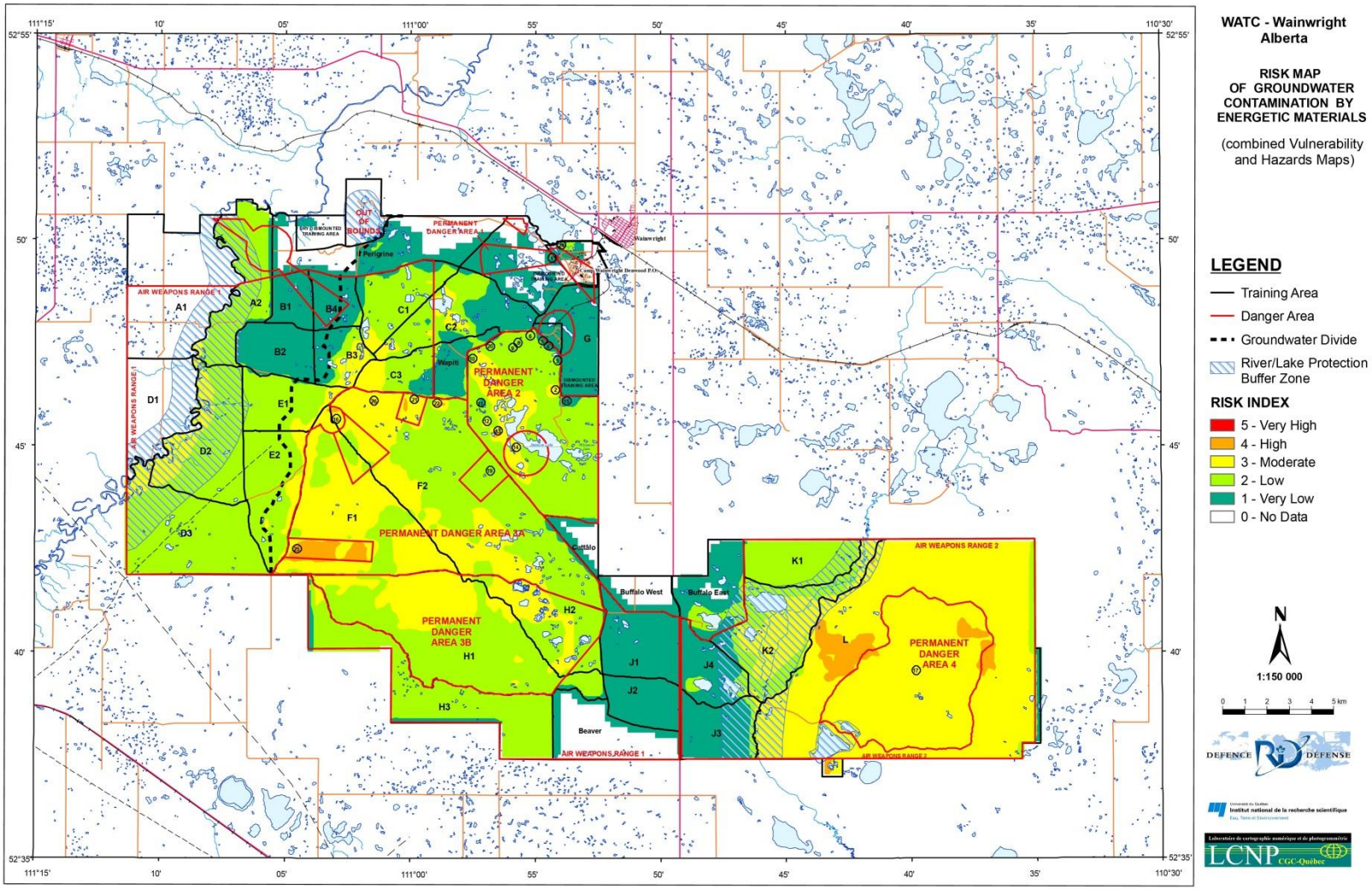

Figure 2-4. Risk Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

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3 Technical Background

Energetic compounds are those chemicals used by the U.S. Department of Defense (DoD) as propellants and explosives in military munitions and blasting agents. Energetic compounds are substances able to undergo exothermic reactions at extremely fast rates producing gaseous products at high pressure and temperature. Substances undergoing this type of behavior can initiate a propagating detonation or blast wave (U.S. Army, 1993). If the velocity of this wave is less than the speed of sound (subsonic) for a given substance, the substance is said to undergo *deflagration* (rapid burning).[5] If the velocity of this wave is greater than the speed of sound (supersonic), the substance is said to undergo a *detonation.*[6] Energetic compounds that undergo deflagration are used by the DoD as propellants to send munitions, projectiles, or warheads down range. Although significant engineering differences exist between ignition trains and explosive trains (a series of events resulting in an ignition or a detonation, respectively), in concept they are very similar. In both, a small electrical or mechanical stimulating impetus is magnified via a succession of intermediate charges to achieve optimum initiation of the propellant load or the main charge. The major difference between the two types of chains is in the component charge rates of reaction.

Because both propellants and explosives react at very high temperatures (approximately 3,000 Kelvin [K] or 2,700 degrees Celsius [°C] for 2,4,6-trinitrotoluene [TNT]), the reactions tend to go to completion forming mainly gaseous products. For TNT ($C_7H_5N_3O_6$), the reaction is shown in Equation 3.1:

$$4\ C_7H_5N_3O_6 \longrightarrow 7\ CO_2 + 21\ C + 6\ N_2 + 10\ H_2O \qquad \text{(Eq. 3.1)}$$

Because TNT has insufficient oxygen in the molecule relative to carbon, the detonation produces soot (solid carbon). For many years, it was thought that residues of energetic compounds from high-order detonations (detonations that function as designed) would be minimal because of the high temperature and pressures that occur during these processes, and this turns out to be true for detonations that go high order. Occasionally a low-order detonation takes place resulting in substantial deposition of unreacted energetic chemicals. This section will identify the energetic compounds most commonly used by the DoD, summarize their chemical and physical properties, and will discuss the deposition of these compounds on various types of DoD training ranges. Much of the following information was presented in USEPA, 2012.

[5] *Deflagration*: A rapid chemical reaction in which the output of heat is enough to enable the reaction to proceed and be accelerated without input of heat from another source. Deflagration is a surface phenomenon with the reaction products flowing away from the un-reacted material along the surface at subsonic velocity. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, rate of reaction and temperature, and may cause transition into a detonation. Reference: DoD Ammunition and Explosives Safety Standards, DoD 6055.9-STD, July 1999.

[6] *Detonation*: A violent chemical reaction within a chemical compound or mechanical mixture evolving heat and pressure. A detonation is a reaction that proceeds through the reacted material toward the un-reacted material at a supersonic velocity. The result of the chemical reaction is exertion of extremely high pressure on the surrounding medium, forming a propagating shock wave that originally is of supersonic velocity. When the material is located on or near the surface of the ground, a crater normally characterizes a detonation. Reference: DoD Ammunition and Explosives Safety Standards, DoD 6055.9-STD, July 1999.

3.1 Energetic Chemicals

Most energetic chemicals used by the DoD fall into one of three groups—nitroaromatics, nitramines, or nitrate esters (Figure 3-1). The three groups differ in chemical structure. All three groups contain nitro-functional groups ($-NO_2$). However, the nitro-functional group is bonded to a carbon molecule in nitroaromatic compounds, to a nitrogen molecule in nitramine compounds, and to an oxygen molecule in nitrate ester compounds. Among the nitroaromatics, TNT is widely used as an explosive, and 2,4-dinitrotoluene (2,4-DNT) as a component of many single-base propellants. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are nitramines used in various explosives, and nitroglycerin (NG) and nitrocellulose (NC) are nitrate esters used in gun and some rocket propellants (single-, double-, and triple-base propellants).

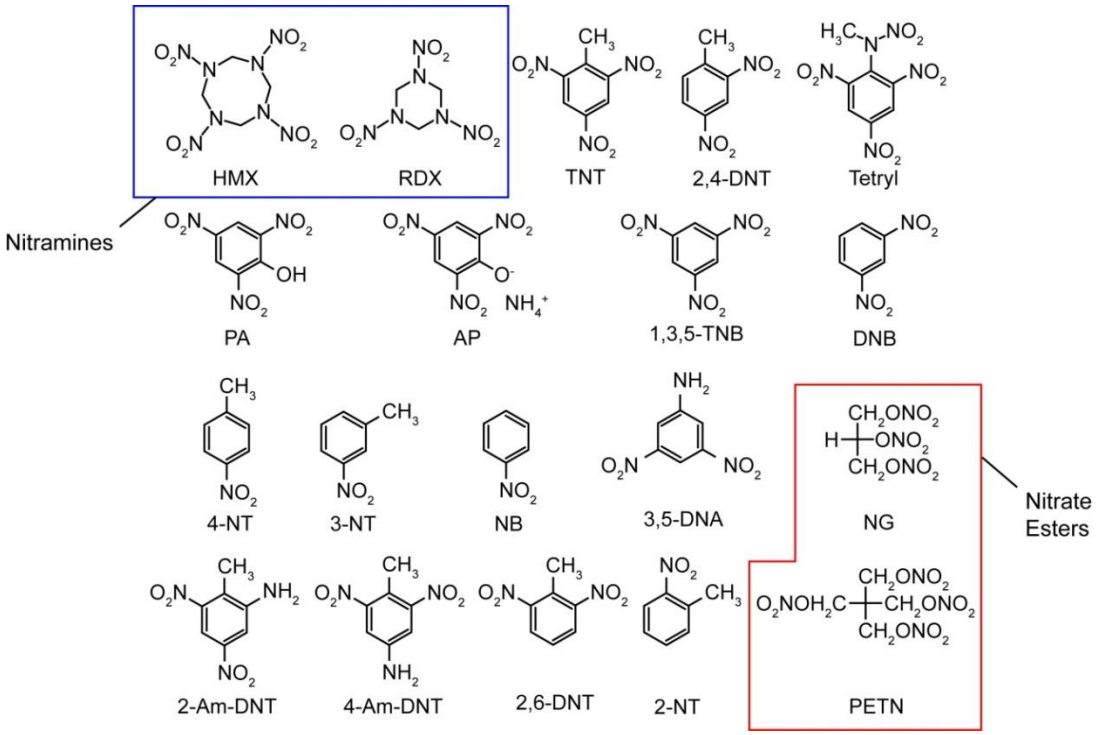

Figure 3-1. Structures of nitramines (upper left), nitrate esters (lower right), and nitroaromatic explosives (all others) of interest to the DoD (modified from Tomkins, 2000).

Note: 1,3,5-TNB – 1,3,5-trinitrobenzene; 2-Am-DNT – 2-amino-4,6-dinitrotoluene; 2-NT – 2-nitrotoluene; 2,6-DNT – 2,6-dinitrotoluene; 3-NT – 3-nitrotoluene; 3,5-DNA – 3,5-dinitroanaline; 4-Am-DNT – 4-amino-2,6-dinitrotoluene; 4-NT – 4-nitrotoluene; AP – ammonium picrate; DNB – dinitrobenzene; NB – nitrobenzene; PA – picric acid; PETN – pentaerythritol tetranitrate.

3.1.1 Explosive Formulations

Table 3-1 summarizes the energetic chemicals present in a variety of military explosive formulations, including those no longer in use. The discussions in this document concentrate on the major energetic components present in current munitions (Table 3-2). Other chemicals may be present in specific munitions but they have not been studied extensively and will not be discussed here.

The energetic compounds present in the most common DoD explosive formulations are presented in Table 3-1 and Figure 3-2. All of these formulations contain one or more of TNT, RDX, and/or HMX.

Information on the content of a specific munition may be found in Army manuals (e.g., U.S. Army, 1984; 1990; 1993) and from online sources such as:

- Munitions Items Disposition Action System (MIDAS). https://midas.dac.army.mil (requires logon and password)
- MVS Munitions Database. https://mvs-fs18-ecprr.mvs.ds.usace.army.mil/munitionsdb (link is only available from within the U.S. Army Corps of Engineers [USACE] firewall) (Compact disk [CD] available upon request from USACE Military Munitions Center of Expertise [EMCX])
- ORDATA. http://ordatamines.maic.jmu.edu/default.aspx

Table 3-1. Summary of Explosive Chemicals Present in Various Military Formulations (from M.E. Walsh et al., 1993 [sources: U.S. Army, 1990; U.S. Army Materiel Command, 1971]).

Composition	Use	Explosives Present (%)				
		TNT	RDX	HMX	DNT	Others
Anatols	a,b	20–50				Ammonium nitrate
Comp A	c,d,e,f		91–98			
Comp B	b,e,f,j	40	55–60			
Comp C	k		88			
Comp C2	k	5	79		12	m-Nitrotoluene, Nitrocellulose
Comp C3	h,k	4	77		10	m-Nitrotoluene, Nitrocellulose, Tetryl
Comp C4	g		91			
Cyclotol	b,e,f,i	25	75			
HBX–3	m	29	31			
H–6	a,m	30	45			Aluminum
HTA–3	a,b	29		49		
Minol–2	a,l	40				Ammonium nitrate
Torpex	a,f,l	40	42			
DBX	l	40	21			Ammonium nitrate
PBX			0–95	0–95		Trinitrobenzene
Baratol	a	33				Barium nitrate
Baranal	a	35				Barium nitrate
Black powder	n,o					Potassium nitrate
Explosive D	a,b					Ammonium picrate
PTX–1	g,p	20	30			Tetryl
PTX–2	f,i		28–33	41–44		PETN
Comp CH6	d		98			
Ednatols	a,c,i	40–50				Ethylene dinitramine
LX–14				96		
Octols	a,b,f,i	25–35		65–75		
Pentolite	f,g,i	25–90				PETN

Composition	Use	Explosives Present (%)				
		TNT	RDX	HMX	DNT	Others
Picratol	h					Ammonium picrate
Tetrytols	i,k	65–80				Tetryl
Tritonal	a	80				Aluminum
Amatex 20	c	40	40			Ammonium nitrate
HBX–1	m	40	38			

a – Bombs
b – High energy projectiles
c – Projectile filler
d – Boosters
e – Grenades
f – Shaped charges
g – Demolition explosives
h – Ammunition
i – Bursting charges
j – Fragmentation charge
k – Former used demolition explosive
l – Depth charges
m – High energy charge
n – Igniter powder
o – Time fuses
p – Land mines

Table 3-2. Energetic Chemicals Present in Current Military Explosive Formulations (USEPA, 2012).

Composition	Uses	Energetic Chemical Ingredients
Composition B	Artillery; mortar	60% Military-grade RDX (contains ≈ 10% HMX) 39% Military-grade TNT (contains ≈ 1% other TNT isomers and DNTs); 1% wax
Composition C4	Demolition explosive	91% Military-grade RDX
Tritonal	Air Force bombs	80% Military-grade TNT, aluminum
Composition A4	40-millimeter (mm) grenades	Military-grade RDX
TNT	Artillery	Military-grade TNT
Composition H6	Navy and Marine bombs	Military-grade RDX (45%) and TNT (30%), aluminum
Octol	Antitank rockets	Military-grade HMX (65-75%) and TNT (25-35%)

Note: Information presented in not comprehensive.

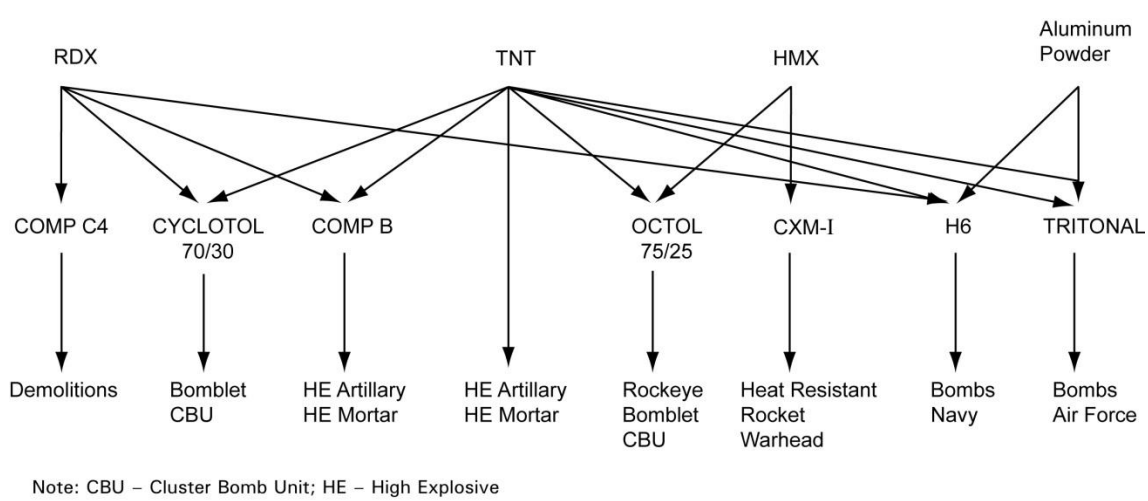

Figure 3-2. Energetic compounds present in the most common DoD explosive formulations (data presented is not comprehensive) (from Boudeau, 1993 [adapted from AEHA, 1985]).

3.1.2 Propellant Formulations

Solid propellants for small arms, artillery, and mortars are low-explosive materials[7] designed to burn at a controlled rate and rapidly produce gases, creating the pressure to accelerate projectiles from guns or propel rockets toward targets (U.S. Army, 1993; Folly and Mäder, 2004). The propellants used in large missile motors are often composite or composite modified double base (CMDB) propellants. The rapid but controlled burning of low explosives such as propellants is known as *deflagration*.

Propellant formulations contain several components, with the primary being an energetic material, commonly a nitro-containing organic chemical such as NC, often combined with other energetic compounds such as DNT, NG, NQ (nitroguanidine), and HMX. Also included are compounds that modify burn rate—binders or plasticizers (both energetic and inert) that enable loading and packing the propellant into the projectile. In addition, stabilizer compounds are used to absorb nitrogen oxides—the breakdown products of NC—to increase propellant stability during storage. Solid propellants used for rocket fuel (termed "composite" or CMDB) include a fuel such as powdered aluminum, an oxidizing solid (such as ammonium perchlorate, or barium nitrate), along with an inert binder (e.g., hydroxy-terminated polybutadiene [HTPB]). Composite propellants, also known as 'fuel-oxidizer type propellants,' consists of a finely-ground oxidizer (such as an inorganic perchlorate or nitrate) in a matrix of plastic, resinous, or elastomeric material that serves as a fuel (DoD, 1998). Often, other additives are included to assist in grain fabrication or curing, or as burning rate modifiers.

Solid propellants with NC are divided into three classes based on the presence of additional energetic compounds. A summary of the major ingredients in some of these propellants is given in Table 3-3. Additional information is available in the Propellant Management Guide published by the U.S. Army Defense Ammunition Center (1998). Single-base propellants contain NC alone as the principal energetic material. Double-base propellants contain NC infused with a liquid organic nitrate, such as NG, which can gelatinize the NC. Triple-base propellants include the two double-base compounds, NC and NG, along with NQ. NQ adds to the energy content of the formulation without raising the flame temperature, which reduces erosion in the gun barrel and also reduces flash. NQ tends to be found in the more powerful (higher charge number) artillery and tank propellants.

Table 3-3. Summary of Solid Propellant Classes with Common Examples (Jenkins et al., 2007; Chapter 1).

Type	Uses	Examples	Grain Type*	Principal Ingredients
Single base	Small arms to cannons	M1	Single- or multi-perforated cylinder	NC, 2,4-DNT
		M6	Multi-perforated cylinder	NC, 2,4-DNT
		M10	Flake; Single- or multi-perforated cylinder	NC, Diphenylamine
Double base	Multiple applications	M2	Single- or multi-perforated cylinder	NC, NG, Ethyl centralite
		M5	Single-perforated cylinder or flake	NC, NG, Ethyl centralite

[7] Explosives can be categorized by the speed at which they undergo combustion. Low explosives expand at rates from a few centimeters per minute up to 400 meters per second. High explosives are characterized by the extreme rapidity with which decomposition occurs, known as detonation. U.S. Army, 1993.

Type	Uses	Examples	Grain Type*	Principal Ingredients
	including small arms	M8	Perforated increment sheet	NC, NG, Diethyl phthalate
Triple base	Large caliber guns	M30	Multi-perforated cylinder or hexagonal	NC, NG, NQ, Ethyl centralite
		M31	Multi-perforated cylinder; Single-perforated cylinder or stick	NC, NG, NQ, Ethyl centralite
Composite	Rockets and missiles	Class 1.3	Single grain	Ammonium perchlorate, Aluminum, HTPB
CMDB	Rockets and missiles	Class 1.1	Single grain	NC, NG, Ammonium perchlorate, Aluminum, HMX, HTPB

* Particle shapes are shown in Jenkins et al., 2007 (Chapter 1, Figure 3).

Three of the stabilizers utilized in propellant formulations are DPA (diphenylamine), ethyl centralite (diethyl diphenyl urea), and akardites (methyl diphenyl urea). DPA is used only in single-base propellants because it is incompatible with the gelatinizing agent NG. NDPA (N-nitrosodiphenylamine) is the first transformation product of DPA and serves as a stabilizer itself (Jenkins et al., 2007). Double- and triple-base propellant formulations with NG use either ethyl centralite (diethyl-1,3-diphenylurea) or 2-nitrodiphenylamine as a stabilizer. Some double- and triple-base compositions that employ diethylene glycol dinitrate (DEGDN) rather than NG as the gelatinizer use a form of akardite (1-methyl-3,3-diphenylurea) for stabilization.

Deterrents or burn rate modifiers are added to propellants used in small arms and large caliber artillery rounds. Deterrents are impregnated into the propellant surface, forming a coating that slows the initial burning rate. Commonly used deterrents include 2,4-DNT, 2,6-DNT, and ethyl centralite. A variety of alkali metal salts are also added to some propellants to help reduce secondary flash and smoke. Other non-energetic binders and plasticizers are included in some propellant compositions to make the grains less brittle; examples include the two esters of 1,2-benzenedicarboxylic (or phthalic) acids—dibutyl phthalate and diethyl phthalate. The propellant grains are also often coated with graphite, a lubricant that prevents the grains from sticking together and dissipates static electricity, avoiding undesired ignitions. Other additives, such as wax, talc, and titanium dioxide, can be included to lower wear of the gun barrel liners. Tin and lead strips are often added to artillery and tank propellants as decoppering agents. Copper is the primary ingredient of rotating bands on projectiles. Copper residue is generated from the friction between the gun barrel and the projectile rotating band.

Table 3-4 summarizes the significant ingredients that compose the propellant portion of propelling charges. The greatest mass consists of the oxidizers and energetic binders, ranging between 60% and 90% by weight (MIDAS, 2007). Plasticizers and inert binders account for approximately 5–25% by weight. Stabilizers and other compounds (flash reducers, primers, and igniters) account for the remainder, occurring at <5% by weight each.

Table 3-4. Significant Compounds in Propellant Formulations.

Category	Compound
Energetic Compounds	Diethylene glycol dinitrate
	Nitroglycerin
	Nitroguanidine
	Nitrocellulose
Oxidizers	Ammonium perchlorate
	Potassium perchlorate
Inert Binders and Plasticizers	Dibutyl phthalate
	Diethyl phthalate
	HTPB *
	Talc
	Titanium oxide
	Triacetin
	Wax
Stabilizers	Diphenylamine
	Diethyl-1,3-diphenylurea (ethyl centralite)
	1-Methyl-3,3-diphenylurea (akardite)
	2-Nitrodiphenylamine
Burn Rate Modifiers	2,4-Dinitrotoluene
	2,6-Dinitrotoluene
	Ethyl centralite
Flash Reducers	Potassium nitrate
	Potassium sulfate

* Although HTPB is used primarily in tactical missiles, it may be found on operational ranges where demolition of missile motors takes place.

3.1.3 Secondary (High) Explosives

The most commonly used chemicals in military high explosives by the United States today are TNT, RDX, and HMX (Figure 3-2). In the past, tetryl and ammonium picrate (Explosive D) were also used, but they are not generally found in modern munitions though they may be present on ranges that have been used for decades. New compounds, such as China Lake-20 (CL-20), are being considered for future use, but these compounds are not currently being used at military training ranges and are not addressed by this document.

3.2 Properties of Energetic Compounds

This section presents information on physical and chemical properties that directly affect fate and transport of energetic compounds in the environment. With the exception of NG, the major energetic compounds used by the DoD are solids at ambient temperatures (Table 3-5) and are deposited on ranges as particles of the solid material (Taylor et al., 2004; 2006). Although NG is a liquid at ambient temperatures, it is deposited as a solid when used as a component of double- and triple-base propellants associated with the solid NC.

Table 3-5. Most Commonly Used Physicochemical Properties of Some Energetic Compounds (from Sunahara et al., 2009; Sheremata and Hawari, 2000; M.E. Walsh et al., 1993).

Common Name	Molecular Weight (g mol $^{-1}$)	Melting Point (°C)	Water Solubility at 25°C (mg L $^{-1}$)	Octanol/Water Partition Coefficient (log K_{ow})	Henry's Law Constant at 25°C (atm m ^{3} mol $^{-1}$)	Vapor Pressure at 25°C (mm Hg)
TNT	227.13	80.1	130	1.6	4.57×10^{-7} [a]	1.99×10^{-6} [a]
2,4-DNT	182.15	71	270	1.98	1.86×10^{-7}	1.47×10^{-4}
2,6-DNT	182.15	64-66	206	2.02		5.7×10^{-4}
2-Am-DNT	197.17	176	42	1.94		4.0×10^{-5}
4-Am-DNT	197.17	171	42	1.91		2.0×10^{-5}
Tetryl	287.17	129.5	75	2.04	2.69×10^{-11}	5.69×10^{-9}
TATB	258.15	ND	32	0.7	5.8×10^{-12}	1.34×10^{-11}
Picric Acid	229.10	121.8	12,800	1.33	1.7×10^{-8}	7.5×10^{-7}
NC	10^{5}–10^{6}	206[b]	Insoluble	ND[c]	ND	ND
PETN	316.17	143.3	43*	3.71	1.7×10^{-9}	5.38×10^{-9}
NG	227.11	13.5	1,800	1.62	3.4×10^{-6} [a]	2×10^{-4}
EGDN	152.08	-22.3	5,200	1.16	2.52×10^{-6}	7.2×10^{-2}
RDX	222.26	205	56.3	0.90	1.96×10^{-11}	4.0×10^{-9}
HMX	296.16	286	4.5	0.17	2.60×10^{-15}	3.3×10^{-14}
CL-20	438.19	260[b]	3.7	1.92	ND	ND
NQ	104.07	239	4,400	-0.89	4.67×10^{-16}	1.43×10^{-11}

[a] At 20°C; [b] With decomposition; [c] ND – Not determined.
Note: °C – degrees Celsius; atm – atmosphere; EGDN – ethylene glycol dinitrate; g – gram; Hg – mercury; L – liter; m – meter; mol – mole; TATB – 2,4,6-triamino-1,3,5-trinitrobenzene.
* This value is uncertain; range of cited values from 2.1 to 43 mg L^{-1}

The solubility of these compounds in water varies tremendously from a low of about 4.5 milligrams per liter (mg/L) for HMX to about 4,400 mg/L for NQ. Because these compounds usually are deposited as small particles of the energetic compound, the solubility and the rate of dissolution are important in determining the initial fate of the compounds in the environment. At some arid sites, chunks of energetic compounds (produced when a low-order or partial detonation occurs) persist on the soil surface for many decades.

Once dissolved or leached from NC matrices, the tendency of energetic compounds to sorb to soil substrates varies substantially. Physico-chemical properties of the energetic chemicals and the sorbent and environmental factors will affect sorption reactions (see Section 3.5.3). The octanol/water partition coefficients (K_{OW}) (see Table 3-5) are often correlated with soil/water partition coefficients for organic compounds. Soil/water partition coefficients vary widely for different soils. Lower soil/water partition coefficients for compounds such as NQ, HMX, and RDX indicate these substances will not be sorbed strongly to soil surfaces and, hence once dissolved, will be more mobile in the environment than others with higher soil/water partition coefficients, such as TNT or especially PETN. The low soil/water partition coefficients and limited water solubility make sampling soils in the subsurface problematic. Even when contamination has

reached groundwater, the concentrations of RDX in the subsurface soil, in particular, may be below analytical detection limits. The reason for this is because RDX is present mostly within the soil pore water (the water found in the pores between soil particles), which is small compared to the mass of the soil. More thorough lists of these physical properties with references for each value are given in McGrath (1995) and Clausen et al. (2006).

Energetic compounds are classified as semi-volatile organics, but because several of them are thermally unstable, they are generally not analyzed using gas chromatography (GC) or GC/mass spectrometry (MS). This has been a particular problem for analysis of HMX. Most analyses of energetic compounds in soil and water are conducted using high-performance liquid chromatography (HPLC) (USEPA, 2006). Because these compounds are not volatile (vapor pressures at 25°C vary from about 10^{-4} to 10^{-15} mm Hg), soil sample increments containing these chemicals can be combined and processed at atmospheric pressure without loss due to volatilization. This property has been exploited when collecting, preparing, and subsampling representative samples.

3.3 Energetic Residue Deposition

Numerous experiments have been conducted to estimate the mass of energetic residue deposition at firing points, impact areas, and from blow-in-place (BIP) detonations. Snow-covered surfaces have often been used for these studies to prevent cross-contamination with past activities and provide a visual footprint where residues are deposited (Jenkins et al., 2002).

3.3.1 Firing and Propellant Burning Points

The mass of propellant residues deposited was measured for artillery and mortar firing (M.R. Walsh et al., 2005a; 2005b; 2006; Hewitt et al., 2003; M.E. Walsh et al., 2004), for several different shoulder-fired rockets (M.R. Walsh et al., 2009; Jenkins et al., 2008, Chapter 4), one type of tank cannon (Jenkins et al., 2008, Chapter 6), and for common military small arms (M.R. Walsh et al., 2007a; Jenkins et al., 2008, Chapter 5). Measurements focused on the mass of NG or 2,4-DNT associated with the particles of NC deposited, and not NC itself.

The total mass of NG or 2,4-DNT deposited on a per-round-fired basis is presented in Table 3-6 along with an estimate of the maximum down range distance of deposition. The very small amount of residue produced from firing the 155-mm Howitzer is consistent with the very low concentrations found for soil samples collected at 155-mm firing points (Jenkins et al., 2007, Chapter 3). The much larger mass of residue deposited for shoulder-fired antitank rockets (M.R. Walsh et al., 2009) is also consistent with the high concentrations of NG observed for surface soil samples at these ranges (Jenkins et al., 2004).

Table 3-6. Mass of NG or 2,4-DNT Deposited at Firing Points per Round Fired for Various Weapon Systems.

Weapon System	Propellant	Constituent	Rounds Fired	Average Mass of Residues (mg/Round)	Maximum Downrange Distance for Deposition (m)	Reference
Howitzers						
105-mm	M1-I & II	DNT	71	34	ND [a]	M.R. Walsh et al., 2009
105-mm	M1	DNT	22	6.4	ND	Jenkins et al., 2007 (Chapter 4)
155-mm	M1	DNT	60	1.2	ND	M.R. Walsh et al., 2005a
Mortars						
60-mm	Ignition cartridge [c]	NG	40	0.09	12 m	M.R. Walsh et al., 2006
81-mm	M9 (illuminator)	NG	61	1,000	50 m	M.R. Walsh et al., 2006
120-mm	M45	NG	40	350	ND	M.R. Walsh et al., 2005b
Shoulder-Fired Rocket						
84-mm Carl Gustav	AKB 204/0	NG	39	1055	30 m [b]	Jenkins et al., 2008 (Chapter 4)
84-mm AT4	AKB204	NG	5	20,000	50 m [b]	M.R. Walsh et al., 2009
Tank (Leopard)						
105-mm	M1	DNT	90	6.7	ND	Ampleman et al., 2009
Grenade						
40-mm (HEDP)	M2	NG	144	76	5 m	M.R. Walsh et al., 2010b
40-mm (TP) [d]	F15080	NG	127	2.2	5 m	
Small Arms						
5.56-mm Rifle	WC844	NG	100	1.8	10 m	M.R. Walsh et al., 2007a
5.56-mm MG	WC844	NG	200	1.3	30 m	
7.62-mm MG	WC846	NG	100	1.5	15 m	
9-mm Pistol	WPR289	NG	100	2.1	10 m	
12.7-mm MG (.50 cal)	WC860 & WC857	NG	195	11	40 m	

Note: MG—machine gun.
[a] ND Downrange distance for deposition was not determined.
[b] Major deposition is behind the firing line for shoulder-fired rockets, but downrange for other types of munitions.
[c] No NG is present in the propellant used for this mortar round. The only NG present is in the ignition cartridge.
[d] Practice munition – does not contain a warhead.

Residue deposition from small arms is proportionally very large compared to the initial mass of propellant in the cartridge, but not surprising based on the short length of the barrel and forensics, i.e., powder burns on hands and clothing (M.R. Walsh et al., 2007a). In most cases, the residue is deposited close to the firing position. For small arms, M.R. Walsh et al. (2007a) estimated that 99% of the residue is deposited within 5 m of the firing line for pistols, 10 m for rifles and small machine guns, and 20 m for 127 mm (.50 caliber [cal]) machine guns. Deposition extends out to 50 m behind where shoulder-launched rockets are fired (Jenkins et al., 2007,

Chapter 3), and 10–20 m in front. By far, the greatest residue deposition is to the rear at these firing positions for antitank rockets. Downrange deposition is somewhat greater for 105-mm artillery and tanks than for 155-mm artillery.

For propellant residues, it is possible to estimate the mass of either NG or 2,4-DNT that would be deposited at firing points if the total number of rounds of a given type fired is known. In the past, detailed firing records needed to make this type of estimate were seldom maintained, but current record-keeping may allow this type of estimation in the future. Thus, the downrange distance for establishing sampling areas can be determined based on the measured depositional distances obtained in these studies.

After training with various large caliber weapon systems like mortars and artillery, there is often some quantity of unused propellant in various forms (e.g., propellant rings, bags) remaining after live-fire training is completed. The general practice, as would be anticipated in deployment, has been to destroy this unused material in the field by piling up the material or laying it in a line on top of the soil and igniting it. Several studies have been conducted to assess the residue remaining from these practices under different environmental conditions (M.R. Walsh et al., 2010a). The mass of propellant residues recovered in burn areas was large compared with the mass deposited from firing activities with the same propellant and was deposited over a smaller surface area resulting in higher point-source concentrations in the soil. At some ranges, excess propellant is now destroyed in a controlled setting using burning pans (Section 5.1.7).

The deposition of CMDB propellant residues will not be a problem at most DoD ranges because it is only used in missile motors, but it has been an issue at the Thermal Treatment Area at Hill Air Force Base (AFB), Utah. At this range, the second stage of old Trident missile motors were destroyed, and the residues deposited over a fairly large area because of the size of these detonations. Studies have found that both HMX and perchlorate were detectable in surface soil at concentrations ranging up to 4 milligrams per kilogram (mg/kg) and 86 mg/kg, respectively (personal communication, Karl C. Nieman, Select Engineering Services, Hill AFB, Utah, January 14, 2010).

3.3.2 Impact Areas

When projectiles reach the impact area and the explosive reaction goes to completion as designed, the round is said to have detonated at “high order.” When a malfunction occurs in some way so that the reaction is only partially completed, the round is said to have detonated “low order” or has undergone a “partial detonation.” Munitions that fail to function as intended or as designed are termed “duds.” They can be armed or not armed, or at some stage in between. The total explosive mass present in a given munition is referred to as the net explosive weight (NEW).

The mass of explosive residues deposited when a round detonates high order was estimated for a variety of munitions including: mortars (Hewitt et al., 2005b; M.R. Walsh et al., 2005b), artillery rounds (M.E. Walsh et al., 2004; M.R. Walsh et al., 2005a), and hand grenades (Hewitt et al., 2005b). The estimates for mortars and artillery were obtained from live-fire tests and those from the hand grenades were from grenades thrown in the normal manner. Table 3-7 is a summary of the estimated mass deposited per round that detonated at high order. Overall, the consumption of the high explosives present in the warheads of these rounds was always greater than 99.99% for all the munitions tested when the rounds functioned properly; thus, the mass

of residues deposited is quite small when rounds detonate as designed and result in a high-order detonation.

Table 3-7. Mass of Explosives Residue Deposited from High-Order Live-Fire Detonations of Composition B-Filled Rounds.

Weapon System	Analyte	Net Explosive Weight (g)	Average Mass Deposited (micrograms [µg])	Plumes Sampled	Percent of Explosive Deposited	Reference
Mortars						
60-mm	RDX	215	94	11	3×10^{-5}	Hewitt et al., 2005b
	TNT	140	14	11	1×10^{-5}	
81-mm	RDX	570	8,500	5	2×10^{-3}	Hewitt et al., 2005b
	TNT	370	1,100	5	3×10^{-4}	
120-mm	RDX	1,794	4,200	7	2×10^{-4}	M.R. Walsh et al., 2005b
	TNT	1,166	320	7	2×10^{-5}	
Hand Grenade						
M67	RDX	110	25	7	2×10^{-5}	Hewitt et al., 2005b
	TNT	72	ND*	7	$< 10^{-5}$	
Howitzer						
105-mm	RDX	1,274	95	9	7×10^{-6}	Hewitt et al., 2003
	TNT	812	170	9	2×10^{-5}	
155-mm	RDX	4,190	300	7	5×10^{-6}	M.R. Walsh et al., 2005a
	TNT	2,730	ND	7	$< 10^{-5}$	

*ND – Not Detected

Tests were also conducted to simulate the BIP detonations used to destroy unexploded ordnance (UXO) on the surface on many ranges (Pennington et al., 2006a; M.R. Walsh et al., 2007b). These items are detonated on active ranges by military explosive ordnance disposal (EOD) teams using C4 (Composition C4, 91% RDX) demolition explosive. On closed ranges, FUDS (Formerly Used Defense Sites), and Military Munitions Response Program (MMRP) sites, the destruction of UXO is usually conducted by private UXO technicians using other types of detonation explosives because they do not have access to military C4 (Pennington et al., 2006a). These contractors use a variety of initiators including oil well perforators that contain a small amount of either RDX or PETN. Unlike live-fire rounds that detonate from the inside out, BIP detonations take place from the outside in and do not use the detonation train built into the munition. Table 3-8 summarizes the results obtained for C4-initiated BIP detonations of a variety of munitions. The results are for high-order detonations. Overall, the mass of deposition from high-order detonations during BIP of duds is higher than from similar rounds that detonate as designed, but still much lower than from low-order detonations as described below. RDX predominates in the residue from detonations of items containing Composition B and from detonations using C4 (Thomas Jenkins, general observation).

Table 3-8. RDX Deposition from BIP of Military Munitions Using C4 Demolition Explosive (Pennington et al., 2006a; 2006b).

Detonation Type	Number of Trials	Mean RDX Deposition	
		(mg)	(%)
C4 (alone)			
	11	12	3.5×10^{-3}
Mortars			
60-mm	7	2.71	2.3×10^{-2}
81-mm	11	95	7.4×10^{-3}
Artillery			
105-mm	7	41	1.9×10^{-3}
155-mm	28	13	2.6×10^{-4}

Note: With the exception of the 60-mm mortar data, the data presented comes from tests conducted in the winter. The round and C4 were placed on a block of ice and detonated so that the residue was deposited on the surrounding undisturbed snow field. The 60-mm mortar data comes from tests conducted on sand.

A percentage of fired rounds will undergo low-order detonations. The frequency of occurrence has been estimated by Dauphin and Doyle (2000; 2001) and varies substantially from one munition type to another. To estimate the mass of energetic compounds remaining from low-order artillery rounds, detonation tests were conducted at Blossom Point, Maryland, on a raised table. Test rounds were configured to detonate at low order and then initiated. The mass of compounds deposited was obtained after sweeping the residue from tarps covering the surrounding area and weighing the residue (Pennington et al., 2006a). Five types of munitions were studied: 60-mm, 81-mm, and 120-mm mortars (all containing Composition B); 105-mm Howitzer projectiles containing Composition B; and 155-mm Howitzer projectiles containing either TNT or Composition B. The percent of original mass of explosives deposited ranged from 27% to 49% (Table 3-9). This is an enormous mass of residue compared with that deposited from high-order detonations (Table 3-7). For a rule of thumb, it takes about 10,000–100,000 high-order detonations to deposit the same mass of residue as that from one low-order detonation of the same type of munition. Clearly, from a management perspective, these low-order detonations constitute the main source of explosive residues at impact areas.

Table 3-9. Mass of Explosives Residue Deposited From Low-Order Detonation Tests (from Pennington et al., 2006a, Table 9-1).

Ordnance Item	Explosive Fill	Mass of Explosive in Round (g)	Percent Deposited (%)
Mortars			
60-mm	Composition B	191	35
81-mm	Composition B	726	42
120-mm	Composition B	2,989	49
Howitzer			
105-mm projectile	Composition B	2,304	27
155-mm projectile	TNT	6,985	29

Observations from on-range investigations indicate that low-order detonations are not uncommon events for many munitions. Low-order detonations are the major source of residues at impact areas and the frequency of their occurrence is hard to predict. Therefore, the

cumulative mass of residues deposited at impact areas over time is difficult to estimate with any degree of accuracy. Based on numerous observations of live-fire training exercises, published low-order rates from range records are not a reliable source of frequency, and the rates vary substantially from exercise to exercise (Thomas Jenkins, personal observation). For example, of 160 120-mm mortar rounds fired, eight (5%) did not detonate (duds) and four (2.5%) produced low-order detonations (M.E. Walsh et al., 2010). The dud and low-order rates for this ordnance were reported to be 4.7% and 0.1%, respectively (Stewart et al., 2006).

From observation at artillery ranges, these dud and low-order events often are not recorded and relayed to range managers. Thus, tabulated range record rates for some types of ranges underestimate malfunctions, confounding efforts to predict the mass of residue deposition on live-fire impact areas.[8] The surface area over which low-order detonations of the various types of munitions deposit residues is still uncertain, i.e., it is uncertain if they are co-located with high densities of craters, UXO, and metallic debris, or more random in distribution. Some research to address this topic is underway. The resulting distribution or energetic residues at impact areas can be described as distributed point sources, complicating both site sampling efforts as well as implementation of technologies to destroy residues onsite.

3.4 Energetic Compounds Found on Training Ranges

A series of field studies have been conducted to investigate the types of energetics residues that have accumulated in surface soils at a variety of ranges operated by the DoD and the Canadian Department of National Defense. A number of different types of live-fire and demolition ranges were studied at the U.S. and Canadian military bases shown in Figure 3-3. Included were hand grenade, rifle grenade, antitank rocket, demolition, tank firing, mortar, artillery, C-130 gunship, and bombing ranges. Training at these ranges is conducted with different types of munitions that contain a variety of energetic formulations.

Studies were performed to (1) characterize the distribution of explosives in surface soils at impact areas, target areas, and firing points associated with specific types of live-fire training; (2) characterize the distribution of explosives in surface water, groundwater, and sediments from all the Canadian ranges and from some of the artillery, antitank, and demolition ranges in the United States; and (3) determine the mass and distribution of energetic residues resulting from BIP of UXO using testing procedures conducted on snow at Canadian Forces Base (CFB) Valcartier, Quebec, Canada; Fort Richardson, Alaska; Fort Drum, New York; and Camp Ethan Allen, Vermont (Pennington et al., 2006a, and references contained therein). A summary of the most commonly encountered chemical residues at the different types of ranges tested is shown in Table 3-10.

[8] Navy safety policies in place require the documentation and notification of duds. If multiple duds occur in one exercise, the exercise is halted. The range managers keep track of these closely as the duds will need to be blown in place during operational range clearance (ORC) activities. On the East Coast, range managers supply the coordinates where the duds landed and provide the coordinate to the ORC team (R. Harrell, N45 CNO, personal communication, September 2011).

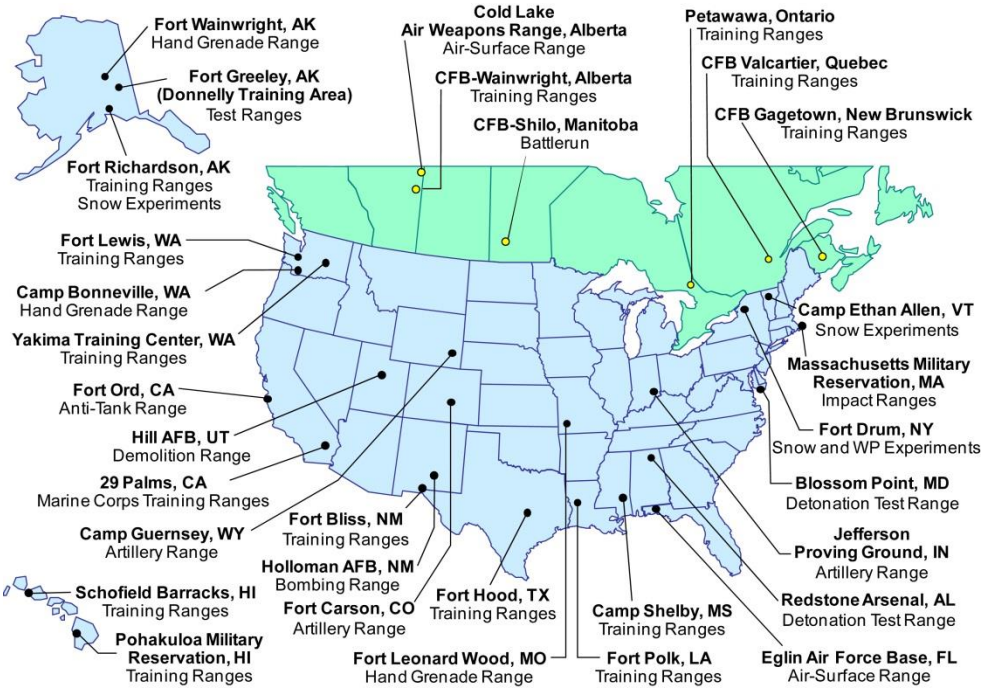

Figure 3-3. Field experiment sites at various U.S. and Canadian test and training ranges.

Table 3-10. Most Abundant Energetic Chemical Residues Found at Various DoD and Canadian Training Ranges, On and In Surface Soils.

Range Type		Energetic Related Chemical
Artillery/mortar/tank range	Impact area	TNT, 2-AmDNT, 4-AmDNT, RDX
	155-mm firing point	NG
	105-mm firing point	2,4-DNT, 2,6-DNT
	Tanks firing point	NG, 2,4-DNT
Hand grenade range (HGR)		TNT, 2-AmDNT, 4-AmDNT, RDX, HMX
Antitank rocket range	Impact area	HMX, TNT, 2-AmDNT,4-AmDNT, NG, RDX
	Firing point	NG
Small arms firing point		NG, 2,4-DNT
Demolition range		RDX, TNT, 2-AmDNT, 4-AmDNT, NG, 2,4-DNT
Bombing ranges	Air Force	TNT, 2-AmDNT, 4-AmDNT
	Marine	RDX, TNT, 2-AmDNT, 4-AmDNT

The following subsections summarize our understanding of the deposition and distribution of energetic compounds on the most common range types operated by the DoD.

3.4.1 Artillery/Mortar/Tank Impact Areas

The concentrations of chemical residues vary tremendously from place to place on ranges. For artillery/mortar/tank range impact areas, concentrations can range from non-detect in the soil (less than one part per billion) to areas with pieces of the pure explosive on the surface. The highest soil concentrations and the presence of pieces of undetonated explosive occur at and near areas where low-order detonations have occurred. The concentrations of energetic residues can be quite low in surface soil, even near heavily impacted targets, if no low-order detonations have occurred nearby (Hewitt et al., 2005a). When TNT is found, the environmental transformation products 2-AmDNT and 4-AmDNT are always found as well (Jenkins et al., 2006).

Because the major residue deposition at artillery ranges is from low-order detonations or breached duds, the distribution of energetic residues in soil is very heterogeneous. Concentrations can vary over several orders of magnitude over distances of just a few meters. This complicates sample collection for source estimation and is discussed in Section 4. The major portion of the residue source is deposited at the surface and remains on or in surface soil with only the portion that dissolves penetrating below the top few centimeters in the soil profile.

Most of the artillery ranges in the DoD inventory have been used for many decades with a wide variety of ordnance to include items in the current inventory such as 155- and 105-mm Howitzers, 120-mm main tank guns, 81-, 60-, and 120-mm mortars, 40-mm grenades, 2.75-inch (in) rockets, and tow missiles. Older munitions, such as 90-mm recoilless rifle rounds, 4.2-in mortar rounds, 8-in artillery rounds, bombs of various sizes, 106-mm high-explosive plastic (HEP) rounds, as well as some foreign ordnance may have been used as well, and duds of these ordnance items are sometimes visible on the surface.

3.4.2 Artillery/Mortar/Tank Range Firing Points

Concentrations of propellant chemicals in soils at firing points on artillery/mortar/tank ranges are generally very low, particularly for 155-mm Howitzer and mortar firing points. Concentrations can be somewhat higher for 2,4-DNT at 105-mm firing points. When 2,4-DNT was detected, 2,6-DNT was often detected as well, but at much lower concentrations (Jenkins et al., 2001). Propellant compounds have been found as far as 75 m from the firing line at tank firing points (Pennington et al., 2002).

Because residues of propellant are deposited via air deposition, the highest concentrations are located at the soil surface. Residues of NG and 2,4-DNT are associated with NC and slowly leach from this material in precipitation. Only small concentrations of NG and 2,4-DNT were found below the top few centimeters of soil (Jenkins et al., 2001; Pennington et al., 2002).

3.4.3 Hand Grenade Ranges (HGRs)

Concentrations of RDX and TNT in soils at HGRs have been found to range from <0.1 mg/kg to as high as 50 mg/kg (Jenkins et al., 2006). Evidence of the presence of either a low-order detonation or a grenade that had been detonated with C4 was always found when higher soil concentrations were encountered. The environmental transformation products of TNT (2-Am-DNT and 4-Am-DNT) were always found when TNT was detected at these ranges.

Because many hundreds of detonations occur over the course of a year at small HGRs, detonation craters form and deposition can occur into these craters resulting in a deeper penetration of the residue source than at many other ranges. Range maintenance at HGRs appears to be site-specific with craters filled in frequently in some places and allowed to remain

in others (Thomas Jenkins, personal observation). Thus, at some ranges, the residue will be found in the shallow subsurface, as opposed to on the soil surface.

3.4.4 Antitank Rocket Range Impact Areas

The explosive in the warheads of antitank rockets is Octol (HMX/TNT). Concentration of HMX in surface soils at antitank rocket range impact areas was often found to be quite high, sometimes in the thousands of mg/kg (Jenkins et al., 2006). The concentration of HMX has been found to be about 100 times higher than TNT in soils at these ranges even though the percentage of TNT in Octol is 30% or greater. It appears that some of the rockets fired at these ranges shear open rather than detonate, spreading undetonated Octol near targets. Because TNT is much more soluble in water than HMX, the TNT dissolves more readily leaving a disproportionate amount of HMX at the surface.

The major source of residues at antitank rocket range impact areas is in the top few centimeters of soil. The TNT that dissolves from the surface is apparently subject to environmental transformation and binding to soil humic constituents. The HMX that slowly dissolves leaches more readily into the subsurface than TNT, and at some sites, eventually into groundwater aquifers.

3.4.5 Antitank Rocket Range Firing Points

At antitank range firing points, NG is often found at concentrations in the hundreds to thousands of mg/kg a few meters behind the firing line (Jenkins et al., 2004). Detectable concentrations of NG can be found as far as 50 m behind the firing line at these ranges. Much lower concentrations of NG are found between the firing line and the targets. The higher concentrations of NG predominate in the surface few centimeters of soil. However, there is often a gravel parking area just behind these ranges and penetration of NG as deep as 60 centimeters (cm) in the soil profile has been detected in these areas.

3.4.6 Small Arms Firing Points

Soil sampling studies were conducted at several small arms ranges (SARs) in the United States and Canada (Jenkins et al., 2007; 2008). NG was found at concentrations ranging from 8.6 to 413 mg/kg in the top 5 cm of soil within 5 m of the firing line. In some cases, 2,4-DNT was also detected but concentrations were generally two orders of magnitude lower than NG. Most of the propellant residues are deposited within 10 m forward of the firing line at these ranges, but some small accumulation of NG was found as far as 30 m from the firing line. About 90% of the total accumulation of NG was in the top 5 cm of the soil profile.

3.4.7 Bombing Ranges

Only a few bombing ranges have been sampled for energetic chemical residues. At an Air Force bombing range, small pieces of tritonal and concentrations of TNT in the hundreds of mg/kg were found in surface soil. Away from this area that was influenced by a low-order detonation, TNT concentrations were much lower (Jenkins et al., 2006).

Similarly, at a mixed use U.S. Marine Corps bombing range, concentrations of RDX, TNT, and HMX were found at 9.4, 1.4, and 1.3 mg/kg, respectively, in surface soils near an area where chunks of Composition H6 explosive were found on the surface (Hewitt et al., 2005a). The Marines trained as they would fight at this range; multiple types of weapons and munitions are

used as the Marines traverse through the training area. The presence of these surface chunks of Composition H6 suggests that a low-order bomb detonation had probably occurred nearby.

3.4.8 Open Burn/Open Detonation (OB/OD) Ranges

For some of the Services, military EOD technicians use OB/OD ranges at DoD operational ranges to destroy duds of various munitions that are considered acceptable to move. Navy operational training ranges do not include designated OB/OD ranges. Rather, OB/OD is conducted in designated areas as part of range clearance work. Sometimes chunks of high explosives or unused propellants are also destroyed at these ranges either by detonation or burning. At active installations, C4 is placed on the item and detonated using a blasting cap, eliminating any detonation hazards from these items. At some U.S. Air Force and Navy demolition ranges, C4 is used to blow a hole in practice bombs for inspection to ensure they contain no high explosives before they can be removed from the range for metal recycling.

Several OB/OD areas have been sampled. RDX and HMX were generally found in surface soils at the ranges sampled, presumably from the use of C4. Small pieces of C4 are often observed on the surface at these ranges; unlike other ranges, residues are present in the subsurface soil as well due to resulting craters and grading of the soils back to a smooth surface. RDX concentrations in the groundwater near the OB/OD range at the Massachusetts Military Reservation (MMR) were the highest found at the installation (Clausen et al., 2004). Other energetic compounds such as TNT, NG, and 2,4-DNT are also often detected in soils at OB/OD ranges, but generally at lower concentrations than RDX.

3.5 Fate and Transport Issues

This section is not intended to provide an exhaustive discussion of the research associated with fate and transport of energetic chemicals in the environment; rather, it will introduce the important factors that affect their behavior in this regard. The major source of energetic chemicals in the environment at ranges are particles of the chemicals released from low-order detonations and leaking UXO at impact areas, and particles of propellant dispersed at firing points. The following provides some insight on what happens to these residues once they are deposited on ranges.

The key processes that influence the environmental fate and transport of energetic chemicals are shown in Figure 3-4 and are discussed in the following sections. Volatilization of the energetic chemicals is typically insignificant due to low vapor pressures and Henry's Law constants and is therefore not discussed. For additional information, the reader is referred to Clausen et al. (2006) for a detailed discussion of fate and transport issues and energetic chemical physiochemical properties. Halasz and Hawari (2011), Rylott et al. (2011), and Kalderis et al. (2011) provide recent reviews of the transformation and biodegradation of energetic chemicals.

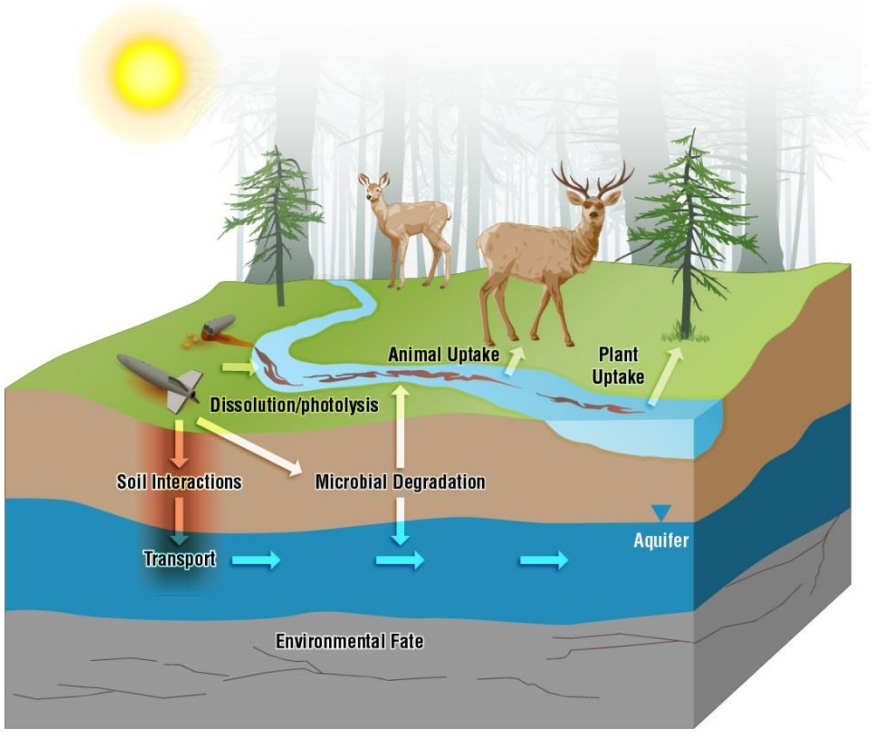

Figure 3-4. Environmental fate and transport mechanisms for energetic chemicals (modified from graphic provided courtesy of Judith Pennington, U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, Mississippi).

3.5.1 Photolysis

The surfaces of particles deposited on the soil surface are subject to reactions with sunlight (photodegradation or photolysis) (Taylor et al., 2010). Photolytic transformation of energetic chemicals may be direct (via direct adsorption of light energy) or indirect (via energy transfer from photosensitized compounds such as peroxide, ozone, or humic compounds) (Kalderis et al., 2011).

TNT is particularly subject to photodegradation leading to a complex array of products that vary in their environmental stability, some of which are highly colored (Figure 3-5). 1,3,5-TNB is the primary stable photodegradation product of TNT in environmental systems. For the solid explosives, photodegradation reactions occur only on the explosive's surface, but these products can be washed off by precipitation often producing a halo of reddish brown residue on the soil surface surrounding the TNT-containing particles. In laboratory experiments using aqueous systems, Spanggord et al. (1980) showed that TNT photolysis products and natural materials (such as humic or fulvic acids) can promote TNT photolysis. Similar results were observed for 2,4-DNT.

Figure 3-5. Reddish-colored, water-filled crater from the photodegradation of residual TNT from a low-order detonation.

RDX and HMX are susceptible to more complete photolytic degradation than TNT (Lewis et al., 2004), but the rates are generally slower than observed for TNT (Kalderis et al., 2011). Degradation products observed in laboratory studies include formaldehyde, nitrite, nitrate, and ammonia (Lewis et al., 2004). The indirect photolysis of RDX due to natural substances was found to be not important in aqueous systems (Spanggord et al., 1980).

The photolysis of picric acid results in the generation of its monoamino derivative, picramic acid (Lewis et al., 2004). Kayser et al. (1984) reported picrate ion, N-methylpicramide, methylnitramine, nitrate, and nitrite as photolytic degradation products of tetryl in aqueous solution.

3.5.2 Dissolution

Although it is possible that small particles of energetic compounds can be transported in surface runoff, there is little evidence that this is a major mechanism for transport of these residues beyond the source zone at ranges. A more significant mechanism is thought to be dissolution by precipitation and downward transport into the soil profile, and in some cases to underlying groundwater aquifers.

Information on the dissolution and transport of energetic compounds in unsaturated soil can be found in Taylor et al. (2009; 2010) and Jenkins et al. (2007, Chapter 5; 2008, Chapter 12). Taylor and co-workers conducted rainfall simulation experiments with TNT, Composition B, Tritonal, and Octol, both in the laboratory and in outdoor experiments, to determine the dissolution rate of centimeter-sized chunks of these compounds exposed to weather and dissolved under natural conditions. This work demonstrated that rainfall and solubility data can be used to calculate the dissolution rate and expected lifespan of chunks of explosives. Dontsova et al. report (in Jenkins et al., 2007, Chapter 5; 2008, Chapter 12) on column experiments evaluating the mobility of propellant-related compounds in soil columns. Results from these studies illustrate the importance of the dissolution rate of the various energetic compounds on their downward flux into the vadose zone.

Once dissolved, RDX and HMX in particular can migrate through the vadose zone and impact underlying groundwater aquifers, especially on ranges that have permeable soils, a shallow groundwater table, and abundant rainfall (Clausen et al., 2004; Jenkins et al., 2001; Martel et al., 2009; Pennington et al., 2006a, Chapter 3). TNT and its environmental transformation products have been found in groundwater aquifers below ammunition plants and depots but not thus far at training ranges, with the exception of one well in the impact area at MMR (Clausen et al., 2004).

Another energetic chemical thought to be mobile in the environment is ammonium picrate (Explosive D). It was used during the first half of the 20th Century primarily in naval bombs, rockets, and armor-piercing shells. Picric acid (2,4,6-trinitrophenol) was also used during this period for grenades and mines. Both picric acid and ammonium picrate dissociate into picrate anion in aqueous solution at pH values normally encountered in the environment (pH 4–10). Picrate is a bright yellow color, is highly water soluble (solubility is ~10 g/L), and because it is an anion, it is very mobile in the soil. Much less research has been conducted on these chemicals because they are no longer in use by the DoD. Kayser and Burlinson (1988) found that picrate migrated rapidly through four test soils in lysimeters, and picrate was observed in a groundwater sampling well at the Louisiana Army Ammunition Plant (AAP) (Thomas Jenkins, personal observation). U.S. Army and Naval munitions containing ammonium picrate and picric acid were known to have been used at MMR. Extensive groundwater sampling conducted at MMR did not identify the presence of these compounds (Clausen, 2005). The relevance of this observation to other military installations is unknown since groundwater sampling has not been conducted in impact areas elsewhere.

NG and NQ are components of various propellant formulations, in association with NC. NG and NQ leach from these NC particles via precipitation. Using saturated columns, Dontsova et al. (Jenkins et al., 2008, Chapter 12) found that in the absence of degradation, NG was mobile in soil columns, but was more retarded in its movement than NQ. However, NG is released in greatest concentrations from propellants, and in combination with its toxicity may present a greater environmental challenge. Studies thus far have not identified either NG or NQ in groundwater at training ranges, although except for MMR, very few groundwater samples have been analyzed for NQ. Analysis of water or soil for NQ requires a totally different analytical method that the other energetic compounds (M.E. Walsh, 1989).

3.5.3 Adsorption

Following dissolution, energetic chemicals and their transformation products may interact with and adsorb onto a variety of sorbent particles (e.g., colloidal and humic material, mineral components) (Kalderis et al., 2011). Physico-chemical properties of the energetic chemical and the sorbent and environmental factors will affect sorption reactions.

In experiments using topsoil, Sheremata et al. (1999) showed that sorption of TNT and its reduction products, 4-Am-DNT and 2,4-diamino-6-nitrotoluene (2,4-DANT), increased with an increase in the number of amino groups (i.e., 2,4-DANT > 4-Am-DNT > TNT). Slight to nonexistent sorption of these compounds was observed in experiments using Borden sand. Haderlein et al. (1996) observed that the type of clay and the exchangeable cation composition in the clay impacted the sorption of nitroaromatic compounds. The adsorption capacity of clays for nitroaraomatic compounds increased in the order of kaolinite < illite < montmorillonite. High adsorption was observed in clays with K^+ or NH_4^+ but low in clays with Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}.

RDX exhibited very low adsorption to clay compared to the nitroaromatic compounds tested by Haderlein et al. (1996).

The organic carbon content in soil also affects the adsorption of energetic compounds. Yamamoto et al. (2004) observed that the sorption of TNT, 2,4-DNT, and RDX was dependent on the organic carbon fraction of the soil tested. TNT and 2,4-DNT were more strongly sorbed compared to RDX. This and its low adsorption to clays are the major reason RDX is so mobile in the environment compared with the nitroaromatic compounds. Soil organic carbon content did not significantly affect HMX sorption either (Monteil-Rivera et al., 2003).

3.5.4 Hydrolysis

Most energetic compounds can be transformed by hydrolysis; however, elevated pH conditions are required for most of the compounds of interest (e.g., TNT [Davis et al., 2007]; RDX, HMX [Balakrishnan et al., 2003]). The pH conditions necessary for hydrolysis to occur for most of these compounds are not typically found naturally in the environment.

Tetryl hydrolyzes in aqueous solution (pH = 6.8) and the products are pH-dependent. Under acidic conditions, the major organic byproducts are picric acid and N-methylpicramide; under basic conditions the products were methylnitramine and the picrate anion (Kayser et al., 1984). Harvey et al. (1992) studied the biotransformation of tetryl in soil and concluded that the rate was very rapid and the product was N-methylpicramide.

3.5.5 Biodegradation

Detailed information on the microbial degradation of nitro-compounds can be found in several review articles (Halasz and Hawari, 2011; Kalderis et al., 2011; Rylott et al., 2011; Kulkarni and Chaudhari, 2007; Lewis et al., 2004).

TNT is a highly oxidized molecule and the microbial reduction of the nitro groups on the molecule is well documented (Rylott et al., 2011). The microorganisms responsible for the reduction processes typically require an organic electron donor and highly reducing conditions. The predominant biotransformation products are 2-Am-DNT, 4-Am-DNT, 2,4-DANT, and 2,6-diamino-4-nitrotoluene (2,6-DANT), although triaminotoluene may be formed under anaerobic conditions (Kalderis et al., 2011). Unlike TNT, these reduction products can chemically bind to natural organic matter in soils and become irreversibly immobilized (Thorn et al., 2002; Kalderis et al., 2011). The mineralization of TNT (e.g., the complete degradation of a compound to its inorganic components by a microorganism) has not yet been proven (Rylott et al., 2011; Kalderis et al., 2011). Picric acid and tetryl are susceptible to the same types of transformations as TNT, producing the corresponding amino derivatives under anaerobic conditions (Lewis et al., 2004). Biodegradation of picric acid under aerobic conditions is well established (Lenke et al., 2000), but natural attenuation in the environment has not been studied extensively.

Both isomers of DNT (2,4-DNT and 2,6-DNT) are biodegradable under aerobic conditions (Nishino et al., 2000). Although microorganisms capable of degrading DNT are commonly found at contaminated sites, degradation may be inhibited by a variety of factors: (1) high DNT concentrations that are toxic to the bacteria or inhibit degradation of one of the DNT isomers, (2) low pH from nitrite production, (3) nitrite accumulation, (4) insufficient nutrients, and (5) lack of moisture (Fortner et al., 2003). Induction of the 2,6-DNT degradation pathway is inhibited above 18 mg 2,6-DNT/L and by relatively high 2,4-DNT concentrations (Nishino et al., 2000). In some bacterial strains, concentrations of 2,6-DNT $\geq$18 mg/L will inhibit degradation of

2,4-DNT. Also, nitrite concentrations as low as 0.5 g/L have been shown to be toxic to DNT degraders.

Degradation of DNT in the groundwater and in the vadose zone has been studied at Badger AAP, Wisconsin. The natural attenuation of DNT has been demonstrated in a contaminated groundwater plume (Nishino et al., 2000). Using vadose zone soils from Badger AAP, the degradation of 2,4-DNT (but not 2,6-DNT) was stimulated through the addition of nutrients in laboratory scale column studies (Fortner et al., 2003).

RDX can be biologically transformed under both aerobic and anaerobic conditions (Kalderis et al., 2011). The transformation products depend on the redox conditions under which the degradation is initiated (Halasz and Hawari, 2011). Under highly reducing conditions (e.g., in anaerobic sludge, marine sediments), RDX is transformed into the nitroso products, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), which are reportedly more toxic than RDX. Degradation of RDX can also follow a denitration route, producing one of two key ring cleavage products, NDAB and MEDINA, depending on the oxygen concentration. NDAB is also biodegradable (Fournier et al., 2004; 2005). Because MEDINA is unstable in water and decomposes to nitrous oxide and formaldehyde, it is not often observed in groundwater samples.

As with RDX, HMX can be biotransformed via reduction of the nitro groups to form nitroso intermediates (1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocene, 1,3-dinitroso-5,7-dinitro-1,3,5,7-tetrazocene, 1,5-dinitroso-3,7-dinitro-1,3,5,7-tetrazocene) or through ring oxidation to produce the transient products, methylenedinitramine and bis(hydroxyl-methyl)nitramine (Kalderis et al., 2011).

The biodegradability of the nitrate esters, NG and PETN, has been demonstrated. Wendt et al., (1978) demonstrated the microbial degradation of NG in laboratory experiments inoculated with fresh activated sludge from a domestic sewage treatment plant. Breakdown occurred stepwise resulting first in the dinitrate isomers followed by the mononitrate isomers. The two dinitrate isomers have been observed in soils from a small arms firing range (Jenkins et al. 2008, Chapter 8). The rate of degradation is rapid in most soils (Jenkins et al., 2003). More recently, mineralization of NG has been shown in NG-contaminated soil and by isolated bacteria (Husserl et al., 2010). The bacteria use NG as the sole source of carbon, nitrogen, and energy by a pathway involving 1,2-dinitroglycerin and 1-mononitroglycerin. NG concentrations above 0.5 millimolar (mM) (0.11 g/L) were inhibitory, but degradation was still observed at 1.2 mM (0.27 g/L). This is well below the solubility of NG. NG degradation rates were optimal at pH 7.2, but were still substantial at values as low as 5.1.

Aerobic degradation of PETN has been demonstrated using a bacterium isolated from an explosives-contaminated soil (Binks et al., 1996). The culture used PETN as a sole source of nitrogen for growth. Although PETN was not mineralized, it was extensively transformed and denitrated to produce pentaerythritol dinitrate, 3-hydroxy-2,2-*bis*-[(nitrooxy)methyl]propanal, and 2,2-*bis*-[(nitrooxy)methyl]-propanedial.

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4 Supporting Technologies

This section summarizes information on site sampling technologies and mass loading estimation techniques used to support the selection and implementation of munitions constituent (MC) management technologies (e.g., Best Management Practices [BMPs]). Access to operational ranges to conduct sampling must be coordinated and approved in advance with the installation range control officer and UXO avoidance activities must be completed (see Section 4.1).

In order to determine if and how energetic residues need to be managed, the mass loading for the specific area (e.g., impact area, areas behind firing points) should be estimated. The best means of doing so is to conduct a soil sampling effort and calculate the mass loading from the soil concentration estimates. Section 4.2 describes the *MULTI INCREMENT®*[9] sampling (MIS) approach to collecting representative near-surface soil samples within a given area of interest. Section 4.3 describes how to estimate the mass loading by calculating the mean soil concentration and estimate of uncertainty for each energetic chemical analyzed. Information is also provided on estimating the mass loading for large areas for which no sampling data exists and when it is impracticable to do so (Section 4.3.2.2). Installation of groundwater monitoring wells near an impact area and groundwater sample collection techniques are discussed in Section 4.4. Analytical methods for determining concentrations of energetic chemicals in soil and groundwater samples are presented in Sections 4.4 and 4.5.

4.1 UXO Avoidance

Before any intrusive investigations are conducted within an area that could have buried UXO present, UXO avoidance activities must have been completed. Initially, qualified personnel (explosive ordnance disposal [EOD] or UXO technicians) will clear pathways to proposed sampling locations. This is usually done using magnetometers. The pathways must be wide enough for safe passage of personnel and equipment; generally a distance of twice the width of the widest vehicle to be used. The route must be clearly marked. Should a potential UXO anomaly be detected, the location will be clearly identified, and the route and potential drilling location will be moved appropriately. Specific details on clearance requirements and UXO avoidance regulations can be obtained by contacting the U.S. Army Corps of Engineers (USACE), Military Munitions Center of Expertise (Huntsville, Alabama). DoD Manual 6055.09-M, Volume 7 (DoD, 2008) provides the requirement to perform construction support and ordnance avoidance. Army Pamphlet EP 75-1-2 (U.S. Army, 2004) provides procedural guidance for munitions and explosives of concern (MEC) support during hazardous, toxic, and radioactive waste (HTRW) and construction activities.

For groundwater sampling, a sufficiently large area will be cleared at the sampling location to allow the drilling equipment to maneuver properly. At minimum, an area with a 25-foot (ft) radius from the bore hole location will be cleared and clearly marked. At all drilling locations, downhole avoidance techniques are required. Each 2-ft advancement of the drilling will be cleared using a magnetometer prior to further advancement of the drilling equipment. Upon reaching a 10-ft depth, or a depth predetermined for the specific site, it may be decided that the

[9] *MULTI INCREMENT®* is a registered trademark of EnviroStat, Inc. of Fort Collins, Colorado. (http://www.envirostat.org/, accessed March 13, 2014).

UXO avoidance may be terminated and drill advancement can proceed as normal. This is a site-specific judgment.

4.2 Surface Soil Sampling

The best way to estimate the mass of energetic residues present within a given area is to collect and analyze representative soil samples. Because deposition of residues is at the soil surface—both at the firing points and the impact areas—at most ranges, the mass of residues in the source zone can be estimated from near-surface soil samples.

Soil sampling studies for environmental assessments have often used what is commonly referred to as the *grid-node* sampling approach. Using this strategy, the area of interest is divided into a number of individual sampling units (grids), the size of each being a function of the total area to be assessed and the future land use envisioned. In this document, the term *sampling unit* will refer to the area that the sample is intended to represent. This area has sometimes been referred to elsewhere as the *decision unit* or the *sampling grid*. In the past, one (or sometimes several) discrete (grab) sample(s) were collected from a sampling unit and shipped to an offsite contractor laboratory where samples were processed and analyzed. The results of these analyses were assumed to be representative of concentrations within the sampling unit, and the concentrations of the individual samples were generally assumed to be normally distributed. The assumption that these discrete samples were "representative" of analyte concentrations within the sampling unit was generally not tested, although the concentrations determined for discrete samples collected from within the same unit often did not agree. The results from these discrete samples were then used to calculate the mean concentration for that sampling unit and the mass of residues present.

Because research indicated that the concentrations of energetic residues in discrete samples can vary substantially even over short distances (Jenkins et al., 1997a; 1997b; 1999), and because energetic residues are deposited at training ranges as discrete particles (Taylor et al., 2004; 2006), there was concern about using discrete samples to represent the mean concentrations in surface soils at firing points and impact areas. To test just how diverse individual discrete samples might be from within these sampling units, experiments were conducted at firing points and impact areas at several different military training ranges. In most cases, a 10-meter (m) × 10-m sampling unit was established and subdivided into 100 1-m × 1-m cells. A discrete sample was collected from each of the 100 cells and analyzed for energetic compounds according to established protocols (SW846 Method 8330 [USEPA, 1994] or 8330B [USEPA, 2006]).

The major analyte detected in eight different sampling units at six different installations varied from 2,4-dinitrotoluene (2,4-DNT) and nitroglycerin (NG) at firing point areas to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) at impact areas (Table 4-1). Maximum to minimum concentration ratios varied from over two orders of magnitude to almost five orders of magnitude for these sets of 100 discrete samples, indicating individual or small numbers of discrete samples cannot yield reliable estimates of mean concentrations within sampling units as small as 10 m × 10 m.

Table 4-1. Variability of Concentrations of Energetic Residues in Soils among 100 Discrete Samples Collected Within 10-m x 10-m Sampling Units at Various Training Range Impact Areas.

Installation	Area*	Range Type	Analyte	Concentration (mg/kg)				
				Max	Min	Median	Mean	Std. Dev.
Donnelly Training Area, AK[1]	FP	Artillery	2,4-DNT	6.38	0.0007	0.65	1.06	1.17
CFB-Valcartier, QC, Canada[2]	FP	Antitank rocket	NG	2.94	0.02	0.281	0.451	0.494
CFB-Valcartier, QC, Canada[2]	IA	Antitank rocket	HMX	1,150	5.8	197	292	290
Holloman AFB, NM[3]	IA	Bombing	TNT	778	0.15	6.36	31.8	87.0
Fort Polk, LA[4]	IA	Mortar	RDX	2,390	0.037	1.7	71.5	315
Cold Lake, AB, Canada[5]	IA	Bombing	TNT	289	0.38	6.57	16.2	32.3
Fort Richardson, AK[6]	IA	Artillery	RDX	172	<0.04	<0.04	5.46	24.8
Fort Richardson, AK[7]	IA	Mortar	RDX	4,450	<0.04	<0.04	—**	—**

* Firing point (FP) or Impact Area (IA).
** Not computed.
Note: mg/kg – milligram(s) per kilogram.
[1]M.E. Walsh et al., 2004; [2]Jenkins et al., 2004b; [3]Jenkins et al., 2006b; [4]Jenkins et al., 2004a; [5]Ampleman et al., 2004; [6]M.E. Walsh et al., 2007; [7]Hewitt et al., 2009 (results from 200 discrete samples).

In fact, the maximum and minimum concentrations among nine discrete samples collected within a single 1-m × 1-m cell in a bombing range at Holloman Air Force Base (AFB), New Mexico, varied by two orders of magnitude, demonstrating the extreme heterogeneous distribution of energetic residues in these areas (Jenkins et al., 2006b). This heterogeneity is due to the presence of particles of energetic residues. Median (middle) values for the 100 discrete samples within each data set were always less than the mean (arithmetic average), indicating most discrete samples underestimated the mean, although a few grossly overestimated the mean. The standard deviations for these sets of 100 discrete samples were always equal to or greater than the means, indicating that in no case were the concentration estimates from discrete samples normally distributed. In general, estimating the mean concentration and mass of residues present from one or a few discrete samples is discouraged because there is very little confidence that the resulting values are representative of the average site conditions within the sampling unit.

Another approach investigated to estimate mean concentrations within a sampling unit was the use of *MULTI INCREMENT* samples (MIS). Here, instead of collecting and analyzing single point samples and integrating the results for an area or assuming a single point is representative of the entire area, samples are built by combining a number of increments of soil from within the sampling unit to obtain a ~1-kilogram (kg) sample. The increments can be collected in a totally random fashion or more systematically. In the systematic-random pattern, a random starting point is selected and increments are gathered on an even spacing as the sampler walks back and forth from one corner of the sampling unit to the opposite corner (Figure 4-1). In this way, increments of soil from all areas of the sampling unit are included and no area is oversampled.

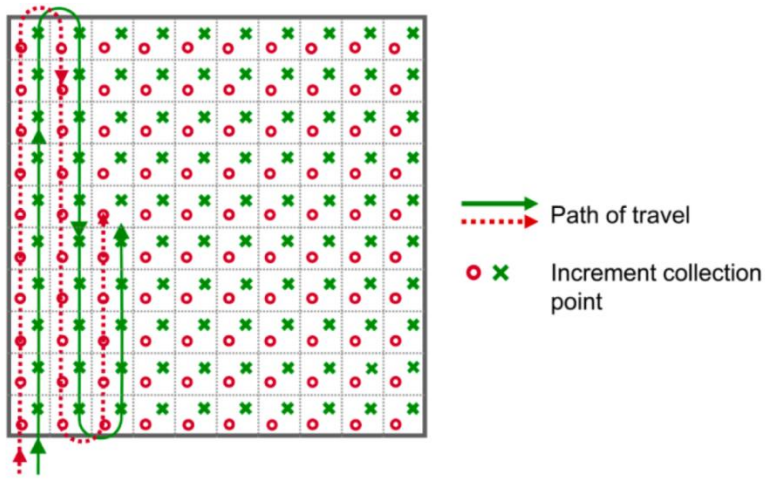

Figure 4-1. Illustration of MIS using a systematic-random sampling design for collecting two separate 100-increment samples.

In several comparative sampling studies, the variability among replicate MIS was much lower than for discrete samples taken within the same sampling units (Table 4-2). For example, 2,4-DNT concentrations in discrete samples collected within a 10-m × 10-m firing point sampling unit at the Donnelly Training Area ranged over almost four orders of magnitude (Table 4-1), whereas concentrations among the ten replicate MIS from this sampling unit varied by less than a factor of three (Table 4-2). Similarly, the range in RDX concentrations for discrete samples from a 10-m × 10-m sampling unit at a Fort Polk impact area varied by nearly five orders of magnitude; the range for MIS was reduced to less than two orders of magnitude. The study at Fort Polk employed a totally random collection scheme for the MIS; subsequent research indicated that more reliable results were obtained using a systematic-random design where increments are collected across the entire sampling unit and no areas are ignored or over-sampled (Figure 4-1). If that method had been used at Fort Polk, replicate samples would most certainly have more closely matched.

Table 4-2. Variability of Concentrations of Energetic Residues in Soil among Replicate MIS Collected Within Sampling Units at Various Ranges.

Installation	Area*	Range Type	Increments per Sample	Replicate Samples	Sampling Unit Size	Analyte	Concentration (mg/kg)				
							Max	Min	Mean	Std. Dev.	Median
Donnelly Training Area, AK[1]	FP	Artillery	30	10	10 x 10 m	2,4-DNT	1.35	0.60	0.94	0.24	0.92
Holloman AFB, NM[2]	IA	Bombing	100	3	10 x 10 m	TNT	17.2	12.5	14.4	2.45	13.5
Fort Polk, LA[3]	IA	Mortar	25**	10	10 x 10 m	RDX	290	4.6	54	86	25
29 Palms, CA[4]	IA	Artillery/ Bombing	100	6	100 m x 100 m	RDX	9.4	3.9	5.6	2.1	4.8
Hill AFB, UT[5]	TTA	Thermal Treatment	100	3	100 m x 100 m	HMX	4.26	3.96	4.13	0.15	4.16

* Firing point (FP), Impact Area (IA), or Thermal Treatment Area (TTA).
** A totally random sampling pattern used, all others collected using a systematic-random pattern.
[1]M.E. Walsh et al., 2004; [2]Jenkins et al., 2006b; [3]Jenkins et al., 2004a; [4]Hewitt et al., 2005a; [5]Nieman, 2007.

Sampling units up to 100 m × 100 m have been sampled using the MIS approach. The number of increments in each MIS varied from 30 to 100, depending on the grid size being characterized and the amount of chunks of pure energetic compound observed on the surface (Jenkins et al., 2006b). Triplicate samples varied from 3.9 to 9.4 mg/kg for RDX for soil samples from an impact area at 29 Palms, California (Hewitt et al., 2005a) and from 3.96 to 4.26 mg/kg for HMX for samples from a thermal treatment area at Hill AFB, Utah (Nieman, 2007). MIS provided much more reproducible estimates of mean concentrations within sampling units at firing point and impact areas than one or a few discrete samples. MIS should be collected using a systematic-random pattern rather than a totally random pattern that sometimes over- or under-represents various areas of the sampling unit (Table 4-2). In addition, when sufficient replicates were obtained, replicate MIS were often found to be normally distributed whereas the data distribution of discrete samples was always non-normal. This is a direct result of the central limit theorem of statistics that can be rewritten for MIS: as the number of individual increments in each MIS gets "large enough," the distribution of replicate MIS can be approximated by a normal distribution, regardless of the shape of the distribution of individual increments. Thus, the more increments collected, the more representative the sample will be. It should be noted, however, that for areas where large numbers of solid pieces of the energetic compound are present within the sampling unit, soil sampling by any technique will underestimate the mass of residues present. To get a good estimate of the total mass present in the sampling unit for these cases, an estimate of the mass of solid energetic present must be included.

Although thus far we have talked about sampling units as a two-dimensional area, in fact, the sampling depth is also important, and sampling units should best be thought of in three dimensions. Specifically, it is the sampling unit volume that is used to convert average concentration to mass of residues present (see Section 4.3).

As discussed above, accumulation of energetic residues at ranges occurs as particles on the soil surface of either pure or mixtures of explosive compounds and as fibers and particles of propellants and rocket fuels. Locations where high concentrations of these energetic particles are typically found include: firing points for certain types of munitions, sites where munitions have low-ordered (undergone a partial detonation) or ruptured (breached upon impact or by proximate detonations), sites where disposal activities occur frequently, and sometimes where unexploded ordnance (UXO) is blown-in-place on impact ranges. Figure 4-2 shows concentration profiles of energetic residues obtained directly beneath chunks (>2 centimeters [cm] diameter) of explosives found on the surface, normalized to the surface concentration. Concentrations of energetic compounds in the surface soil immediately beneath the chunks were a consequence of small (<1 millimeter [mm]) particles that had washed off or abraded from the surface. With increasing depth, the concentration results from the migration of dissolved energetic compounds. The lower concentrations of energetic chemicals in the subsurface result from a combination of limited solubility, limited volumetric soil moisture content, and low soil/water partition coefficients. A large decrease in energetic residue concentrations with profile depth is also characteristic of firing point locations. Therefore, with the exception of ranges where the surface is physically moved and particles become buried, the highest concentrations are present at the ground surface on active ranges (Jenkins et al., 2006a; Hewitt et al., 2005a). Generally, most of the energetic residues are within the top 10 cm; in many cases, the vast majority are in the top 2.5 cm. The exception would be where buried UXO items have corroded and are leaking energetic compounds. In this case, concentrations of TNT/RDX could be higher at depth, but at present no methods have been developed to collect samples and estimate the source strength of these items.

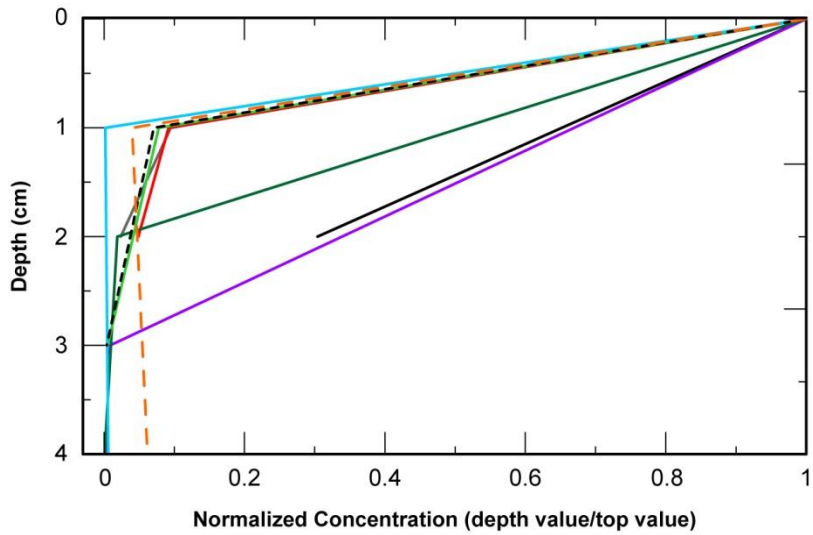

Figure 4-2. Normalized concentration profiles for TNT (solid lines) and RDX (broken lines). Profiles show a decreasing trend of these two energetic residues with depth directly beneath chunks (>2 cm) of explosives found on the soil surface (Hewitt et al., 2007b).

Thus, in general, soil sampling need not be conducted below 10 cm for the majority of cases. Collection of deeper samples increases sample sizes and makes sample processing and analysis more difficult. Because most energetic particles are near the ground surface, the surface vegetation (short grasses and mosses) should not be removed prior to sampling on active ranges. Use of a specially designed coring tool makes sampling at vegetated sites much easier (Figure 4-3).

Figure 4-3. Coring tool designed specifically for collecting cohesive multi-increment soil samples (M.R. Walsh, 2004).

The sampling unit size needs to vary depending on the manner in which the deposition has occurred. For example, the residue at an artillery range firing point is dispersed over a fairly large (e.g., 10,000 square meter [m^2]) area from a single training exercise. Near a low-order detonation, the size of the impacted surface area can be rather small (e.g., 25 m^2). In some

cases, the sampling unit can cover the entire area where it is thought that the most energetic residues are present. Situations where a single sampling unit might be utilized include firing points, blow-in-place (BIP) detonations, direct line-of-fire impact areas (e.g., antitank ranges), and observed individual low order detonations (Hewitt et al., 2005b; M.R. Walsh et al., 2005a, 2005b, 2005c, 2006). Multiple sampling units may be needed at indirect fire impact areas. However, research is continuing on the appropriate sizes of sampling units for various activities.

Factors to consider when choosing sampling unit size include the total size of the area influenced by the activity and what constitutes a manageable sample for field and laboratory operations without compromising data quality. These parameters coupled with range use records, range function and design, surface conditions, and the data quality objectives should all be considered when deciding where to sample and the size of the sampling unit. In some cases the area impacted by an activity is so large that it must be divided into multiple sampling units. Specific recommendations for sampling unit sizes for various types of military training ranges and the number of increments per sample are available in USEPA, 2012. A practical guide for setting up and sampling these areas are presented in Appendix C of USEPA, 2012.

Soil samples should be immediately placed on ice after collection and shipped via overnight carrier to the laboratory. No chunks of energetic compounds or soil samples containing TNT or RDX in excess of 10% can be shipped offsite. Onsite methods can be used to ensure that soil samples are below the 10% level (EPA SW846 Methods 8510 [USEPA, 2007] and 8515 [USEPA, 1996]).

4.3 Mass Loading Estimation Techniques

In order to determine if energetic residues for a given area need to be managed, the mass loading for the area must be estimated in some fashion. When possible, the best means of doing so is to conduct a soil sampling campaign, and compute the mass from concentration estimates in decision/sampling units configured for that purpose (refer to Section 4.2). For small ranges, the entire range can sometimes be sampled and the mean value and uncertainty obtained. For larger ranges, it is not possible to characterize the entire range area. In this case, it is necessary to understand how the range has been used and stratify the range into various use categories. This is discussed in greater detail below.

4.3.1 Small Ranges

For small ranges, such as hand grenade ranges (HGRs) and antitank range firing points, representative samples can be obtained using the MIS approach detailed in Section 4.2. Using this approach, a mean concentration and an estimate of uncertainty is obtained for each chemical measured for that area. In general, RDX, HMX, and TNT are the most important residues in impact areas, and NG and 2,4-DNT at firing point areas.

The mean concentration will most often be expressed as milligrams (mg) of the specific chemical c (mg_c) per mass of soil (kg_s) or mg_c/kg_s. The number of kilograms (kg) of soil is the surface area (SA) of the decision unit where the sample was collected in square meters (m^2) multiplied by the depth of soil (d) sampled in that area in meters (m), times an estimate of the bulk density of the air dried soil (BD) in kg_s/cubic meters (m^3) (Equation 4.1). Generally, the largest mass of residue is concentrated in the top few centimeters of soil and any mass of chemicals that has leached below this area can be ignored for the purpose of estimating the mass of chemical in the source zone.

$$\text{mass of soil } (kg_s) = SA\ (m^2) \times D\ (m) \times BD\ (kg_s/m^3) \qquad \text{(Eq. 4.1)}$$

The mass of chemical *c* in that area in kg (kg_c) is then the concentration of *c* (mg_c/kg_s) multiplied by the mass of soil (kg_s) (Equation 4.2):

$$mass_c\ (kg_c) = conc_c\ (mg/kg_s) \times \text{mass of soil } (kg_s) \qquad \text{(Eq. 4.2)}$$

The mass computed is then compared with acceptable levels or used in predictive models designed to estimate either surface water or groundwater concentrations resulting from this mass of chemical in the soil.

4.3.2 Larger Ranges

4.3.2.1 Ranges with Characterization Data

Artillery and some bombing ranges are often too large to conduct a thorough site characterization to estimate mass loading. In fact, research conducted by U.S. Army Engineer Research and Development Center (ERDC) and U.S. Army Environmental Command (AEC)/U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) (now the U.S. Army Public Health Command [USAPHC]) has demonstrated that residues are concentrated in a relatively small portion of these ranges where targets, crater fields, and firing points are located. Thus, it is not acceptable to simply divide the entire range into a large number of sampling units and randomly select a small number for sampling. This was tried by AEC/USACHPPM and no residues were generally found (USACHPPM, 2004; 2005) even when visual residues were apparent elsewhere, and residues were detected at the same time by the ERDC team at target areas within the range (Pennington et al., 2003; Jenkins et al., 2004a).

Instead, the range area needs to be stratified—that is, divided into various categories such as target areas, crater fields, firing points, and everywhere else. For the most part, sampling away from targets, crater fields, and firing points can be ignored when trying to estimate mass loading because these areas will contribute very little to the total energetic residues present.

It would be best to sample all the important potential areas where residues are likely present, but for very large ranges, even sampling all of the impact areas, crater fields, and firing points may still require an impractical number of sampling units. Thus, these areas should be identified and a random number of the various types of these areas selected and sampled. The number of potential sampling units that are selected for sampling of each type depends on the confidence that is desired in the resulting concentration estimate (and mass loading) for the entire area. A statistician should be consulted when setting up this sampling strategy.

The mass load for each important chemical is then obtained by multiplying the mean concentration for a given type of range area by the mass of soil present in these types of areas. The mass of soil is estimated as described in Equation 4.1 above.

Very little information has been published on the cost of range characterization using MIS. However, Nieman and Downs (2012) published the cost for range characterization using MIS and the proper laboratory analytical procedures (SW846 Method 8330B) for the Thermal Treatment Area, Hill AFB, Utah. The total cost of characterization of 780,000 m^2 (192 acres) was estimated to be $263,000. This effort consisted of sampling 95 100-m x 100-m grid cells, yearly, over a five-year period.

4.3.2.2 Ranges with No Characterization Data Available

It may be necessary to estimate the loading rate for ranges where no characterization data has been obtained and it is impractical to do so. If so, an estimate of the loading rate can be calculated based on the military expenditure rates for the munitions used at the range and the tabulated dud and low-order rates. One example of an approach that can be used to make this calculation is the MC Loading Rate Calculator contained in the Marine Corps Range Environmental Vulnerability Assessment (REVA) Users Guide (U.S. Marine Corps, 2006). The calculator uses an estimation of military expenditure rates for the munitions used at the range and tabulated dud and low-order rates provided by the U.S. Army Defense Ammunition Center (Dauphin and Doyle, 2000; 2001) to estimate the mass of residues in the various loading areas within ranges. The calculator was developed as one component of a conservative modeling approach used to determine the likelihood of MCs reading the boundary of an operational range at detectable levels. However, the MC Loading Rate Calculator (or similar approaches) can be used to estimate the loading rate for ranges where no characterization data has been obtained.

The assumptions used in this approach are enumerated in the REVA Guide. A few of the most important ones are provided here. The total energetic residues on the range are the sum of the residues from low-order detonations, high-order detonations, and the leachate from duds. The low-order and dud rates are taken from Dauphin and Doyle (2000; 2001). If no rates are provided for specific munitions, dud rates of 3.45% and low-order rates of 0.028% are used. For the REVA, the amount of residues deposited from low-order and high-order detonations are assumed to be 50% and 0.1% of the specific chemical present in the round, respectively. So the mass loading is computed for each indicator compound (TNT, RDX, HMX, perchlorate and lead) as follows:

Mass loading for a specific munition type a = mass low order (a) + mass high order (a) + mass from UXO (a)

Mass low order (a) = (# of military munitions expended) × (low order rate) × (amount remaining from a low order) × (% available to environment)

Mass high order (a) = (# of military munitions expended) × (high order rate) × (amount remaining from a high order) × (% available to environment)

Mass UXO (a) = (# of military munitions expended) × (dud rate) × (amount of residue exposed as a result of damage to UXO casings)

Then, the total mass load for a given chemical would be the sum from all the munitions used on the range.

This is a logical approach; however, parameter uncertainty will impact the calculated total mass load. The reader should consider the uncertainty introduced in the calculation from the following factors:

- Expenditures of various munitions have only recently been recorded and thus the total number of munitions fired into ranges over the life of the range cannot be estimated with accuracy. This is particularly true for individual loading areas within a range.
- The low-order and dud rates for a given munition are overall estimates, but actual rates are probably lot specific and difficult to estimate.
- The percentage of residue deposited for low-order detonations is conservative and probably overestimates actual deposition.

- The percentage of residue deposited from high-order detonations is very conservative based on results from a series of experiments conducted at ERDC. Instead of the 0.1% value, a value an order of magnitude lower seems more appropriate and would still be conservative.
- The mass of residues leaching from compromised UXO is very difficult to estimate at present, and any value chosen would suffer from a high degree of uncertainty.

If no other data is available, this approach is the best method for estimating the mass of residues present within the total range.

4.4 Installation of Groundwater Monitoring Wells

In some cases, it may be advantageous to install groundwater monitoring wells within the confines of an impact area. The advantage is that the question of whether energetic compounds are impacting groundwater can be addressed directly and not be the subject of speculation. The major concern for the installation of these wells is the possibility of encountering buried UXO during well installation. A secondary concern that has often been voiced is that the wells could be damaged or destroyed during training operations; either accidentally or deliberately if the well is viewed as a 'target.' The installation of flush mounted wells has greatly reduced this issue, and these types of wells have been installed within impact ranges across Canada (Bordeleau et al., 2008; Martel et al., 2009) (Figure 4-4).

Figure 4-4. Installation of groundwater monitoring well at Canadian Forces Base (CFB) Shilo, Manitoba, Canada (provided courtesy of Sonia Thiboutot, Defence Research and Development Canada – Valcartier, Québec, Canada).

General information about well construction can be found at ASTM D5092-04(2010)e1 (ASTM, 2010a). After wells are constructed, they must be properly developed before reliable samples can be collected. Recommendations regarding well development are provided in ASTM D5521-05 (ASTM, 2005).

4.4.1 Well Installation

Mailloux et al. (2008) used a hollow stem auger to drill wells at the Arnhem antitank rocket range at CFB Valcartier in Canada. A 1.5-m well screen was installed at a depth of 1 m below the groundwater table. In a few wells, a well screen at 3-m below the water table was installed to investigate the depth of the plume of energetic compounds. In a few boreholes, a split spoon was used to sample the soil at depth to determine the stratigraphy of the formation. The stratigraphy refers to the layering of the soil strata, and it is important when trying to understand the hydraulic properties of the soil profile. It is critical that wells be installed within the proper aquifer to assess questions of offsite migration.

Direct push wells can sometimes be used for groundwater monitoring, depending on the geology and stratigraphy of a given location. Information on direct push wells can be found in ASTM D6725-04 (ASTM, 2010b) and ITRC (2006).

It is important to locate the screened interval in the well properly no matter what technique is used to install the well. The screened interval is the vertical location where the water enters the well. Often the screened interval is near the top of the water table, but not always depending on the distance of the well from the suspected source location (Clausen et al., 2004).

4.4.2 Groundwater Sampling and Analysis

An important consideration in the collection of any environmental sample is that it is representative of the conditions at the site. For groundwater, samples are collected to investigate the water in the aquifer that is migrating through the formation. The act of installing a well can modify the aquifer's structure and environment near the well screen and this can sometimes affect stability of various chemicals in the well and in the vicinity of the well point. To minimize this effect, common practice is to purge the well prior to collection of a groundwater sample from the well. This removes the stagnant water that is present in the casing above and below the well screen and water near the screen that might have been affected by the conditions within the well. Purging of the well is generally accomplished using bailers or pumps, prior to the collection of the sample.

There are several sample collection methods that are commonly used for groundwater sampling. These include the use of bailers, low-flow pumping, passive diffusion samplers, and the HydraSleeve™. There are advantages and disadvantages of each approach depending on the specific set of target chemicals of concern for a given location.

A *bailer* is a hollow tube that is lowered into a well using a wire or rope and used to collect water that can then be retrieved from the well. Bailers are generally equipped with a simple ball check valve that seals at the bottom to retain the water as it is lifted to the surface. Bailers and tubing can be made of stainless steel, Teflon®, or polyvinyl chloride (PVC) (Parker et al., 1990) and can be dedicated to a given well, or a disposable bailer can be used. Bailers have not proven the best option for collection of samples where volatile organics are the major concern, but are acceptable for collection of water for analysis of energetic compounds.

Bailers have the advantage of being inexpensive and do not require expensive equipment for water collection. Bailers can be used to collect water from any well, independent of depth. Purging of a well and subsequent water sampling with a bailer can be time consuming but may often be completed in less time than some other technologies, such as low-flow sampling. Use of bailers does increase the turbidity of the water removed from the wells and this can be a problem for certain types of analytes, but is not generally thought to be a major issue for

energetic chemicals; if they have passed through the formation to get to the well site, they tend to stay in solution as opposed to being sorbed by the suspended material.

For low-flow sampling, a pump is positioned in the middle or towards the top of the screened length of the well. Water is then purged from the well in a manner to minimize drawdown of the water in the well (generally a drawdown of <10 cm is desired at flow rates that are 0.1–0.5 liters/minute [L/min]) (Puls and Barcelona, 1996). Usually, the water is passed through a continuous monitor cell using a multiparameter probe equipped with several water quality probes including dissolved oxygen, conductivity, oxidation-reduction potential, pH, and temperature. Samples are collected after stabilization has occurred; usually stabilization is said to have been achieved when electrical conductivity, dissolved oxygen, and oxydo-reduction potential maintain within 10%, pH stays within 0.1 unit, and the water temperature remains within 0.1 degrees Celsius (°C). The tubings used with the peristaltic pump are made of Teflon in the well and Viton in the pump. If a bladder pump is used, it is made of Viton and stainless steel or Teflon if the watertable is deeper than 8 m. Low flow is an excellent sampling procedure, but it can be time consuming to achieve adequate stabilization.

Another type of groundwater sampler is the *passive diffusion sampler*. The device is placed in the screened portion of the well and diffusion of the analytes into a semipermeable chamber within the sampler continues until equilibrium is reached. The time required to reach equilibration depends upon the rate of exchange within the well, water temperature, analyte(s) present, and type of membrane material. These samplers integrate analyte concentrations over time because equilibration is not instantaneous and they are often used to profile discrete intervals in the screened portion of the well. Because no water is drawn into the well via pumping, water is not pulled from other parts of the formation. Therefore, concentrations of contaminants in the sampler are considered to be equivalent to those in the groundwater immediately adjacent to the screened interval where the sampler is placed. Unfortunately, Parker and Clark (2002) found that equilibrium for several energetic compounds was not reached even after 18 days, thus this type of sampler is not recommended for this application.

The *HydraSleeve™* sampler is a flexible polyethylene (PE) sleeve with a PE check ball at the top, that is suspended from a line and has a weight attached to the bottom. To use, the device is lowered to sampling depth (in the well screen) and left for 24 hours to allow the well to re-equilibrate and the materials in the device and contaminants to equilibrate. When the device is lowered through the water column, the check valve remains closed, thereby preventing water from entering the device. To collect a sample, the device is raised and lowered approximately 6 in, 20 times, and then retrieved. During the upstroke the check valve opens and water fills the bag, during the down stroke the check ball seals. In addition, this device is designed to be used without purging, therefore it is well suited for collecting samples from low-yield wells. Parker and Clarke (2002) found that this device was able to recover representative concentrations of explosives.

Another sampler that can be used for collection of water from within a well casing is the Snap Sampler® (ProHydro, Inc.; http://www.snapsampler.com/). This sampler consists of four components: sample bottles with openings at both ends and spring loaded end caps, a sampler body that holds one or more sample bottles, a trigger mechanism to allow closure of the bottles, and a docking station (Parker and Mulherin, 2007).

To use the Snap Sampler®, the unit is lowered into the well casing with the bottles in the open position and positioned in the well at the depths of interest. After a suitable period of time, the bottles are closed using the trigger mechanisms thereby collecting water from specified depths

with the casing. One advantage of this approach is that the samples are not exposed to overlying water in the casing as the sampler is retrieved from the well. This sampler can be used to sample well water from casings that are 2 inches in diameter or greater.

Sample bottles available from the manufacturer for the Snap Sampler® are 40 mL glass volatile organic analysis (VOA) vials or 125 mL polypropylene bottles. For analysis of energetic compounds, a series of sample bottles would be required to obtain volume sufficient for current analytical methods.

A study conducted by ERDC evaluated the use of the Snap Sampler® for the collection of samples for energetics analysis (Parker and Mulherin, 2007). Both laboratory and field studies were conducted comparing the results from the analysis of water from the Snap Samper® versus water collected using low-flow sampling. The results for the field study for five wells at the former Louisiana Army Ammunition Plant indicated that the water contained measurable concentrations of RDX, TNT, HMX, TNB, tetryl, 1,3-DNB, and 2,4-DNT and no significant difference was found between samples analyzed from the Snap Sampler® versus those from low-flow sampling.

One consideration when sampling groundwater for explosives is possible loss due to sorption by sampling and storage materials. Several studies (Parker et al., 1990; Parker and Ranney, 1994; 1997; 1998) have shown that explosives are not as readily sorbed by the materials used to sample them as volatile organic compounds (VOCs) are. Sorption of explosives is minimal for less-porous materials such as stainless steel, rigid PVC well casing, and several fluoropolymers (polytetrafluoroethylene [PTFE], perfluoroalkoxy polymer resin [PFA], fluorinated ethylene propylene [FEP]). However, other rigid plastics such as PE, polypropylene (PP), and polyamide (Nylon), and flexible tubing materials such as flexible PVC, polyurethane, and plasticized PP, can sorb relatively large quantities of even these analytes. Therefore, glass sample bottles are recommended. If more sorptive materials are used, such as PE tubing, water should be pumped through the tubing to allow for equilibration before samples are collected. For tubing, some equilibration occurs during the purging process; the time required for equilibration will depend upon the analyte, tubing material, length of tubing, and flow rate (Parker and Ranney, 1998).

Groundwater samples are collected in a 1-L amber glass bottle to prevent photodegradation. Samples are cooled to 4°C and shipped by overnight carrier. Generally no preservative is added if the water can be cooled rapidly after collection and will be analyzed within the standard holding times (USEPA, 2006). If samples are collected in a remote location and cannot be cooled immediately, stability of energetic compounds can be extended if the water is acidified to pH 2 with sodium bisulfate after collection (Jenkins et al., 1995; Douglas et al., 2009). For surface water samples, preservation is probably more important than for groundwater samples because of the higher numbers of microorganisms present.

Sample analysis is conducted as described in SW846 Method 8330B (USEPA, 2006). Groundwater samples are generally pre-concentrated using solid phase extraction to provide adequate detection capability. Most analyses have been conducted using reversed phase high performance liquid chromatography using an ultraviolet (UV) detector. In some cases, a liquid chromatography–mass spectrometry (LC/MS) method could be preferable.

4.5 Analytical Methods for Soil Samples

After soil samples are collected, they are generally sent to a commercial analytical laboratory to determine the concentrations of energetic compounds present. Analytical labs use solvent

(acetonitrile) to extract the energetic residues from the soil sample, and a small portion of the acetonitrile extract is analyzed by high performance liquid chromatography, usually using SW-846 Method 8330 (USEPA, 1994) or SW-846 Method 8330B (USEPA, 2006).

Because of the expense associated with the purchase and eventual disposal of acetonitrile, the minimum volume of acetonitrile is used for soil extraction. Consequently, only a small subsample is extracted rather than the entire soil sample. Unfortunately, the common practice at commercial laboratories has been to remove a small portion of the soil sample from the top of the jar, air dry it, and extract it with solvent. The remainder of the sample (often >90%) was never processed or even removed from the jar. Any replicate analysis for this sample also came from the same small portion of soil that was removed and air dried. The question of how well this small subsample represents the total soil sample was generally not evaluated.

In most cases, MIS from training ranges will contain very few energetic particles or propellant fibers compared to the total mass of soil. For example, if the MIS contains one energetic particle in each 100 grams (g) of soil, a typical analytical subsample (a few grams from an un-ground sample) will likely not contain the particle and result in a non-detect value. On the other hand, if the subsample contains the particle, the concentration that is determined will be very high—at a much higher concentration than actually exists in the MIS (Hewitt et al., 2009).

Hewitt et al. (2009) conducted a study to assess the variability of energetic compound determinations for replicate composite subsamples. They studied samples collected at five different training ranges including two impact areas, two firing points, and a demolition range. After briefly stirring the contents of the jar, independently collected replicate subsamples from each MIS soil sample were obtained in a fashion similar to that often used at commercial laboratories, i.e., a single scoop off the top. There were 37 possible comparisons (sum of samples × analytes detected), but in six cases, analysis of at least one of the subsamples of a given sample failed to result in a measurable concentration of an analyte above analytical detections limits. In the worst case, TNT concentrations among three replicates varied from <0.035 to 262 mg/kg. Among the 31 triplicates without non-detect results, the relative standard deviation (RSD) ranged from 8.4% to 155%, with a mean RSD of 70.1% and a median of 61.7%. The entire sample was also analyzed in each case and compared to the individual subsamples. In 67% of the cases, the mean of the subsamples was biased low, compared to the bulk sample. In over half of these, the mean was less than 50% of the concentration in the bulk sample. Clearly, subsampling by taking a scoop off the top of a sample does not yield an accurate average concentration of the analyte in the soil sample.

M.E. Walsh et al. (2002) studied the variability among subsamples after bulk samples had been air dried and ground with a mortar and pestle as specified in SW846 Methods 8330 and 8095 (USEPA, 1999). Twelve 50-g subsamples were taken from three explosives-contaminated soils and analyzed; the RSDs varied from 47% to 264% for TNT and RDX. Most of this variability came from a few subsamples with substantially higher concentrations than the rest, probably due to the inclusion of a larger particle of energetic material. It is clear that grinding in a mortar and pestle does not sufficiently homogenize the soil, even when large subsamples (50 g) are used. However, when two of these samples were mechanically ground with a ring mill, the RSDs for similarly sized subsamples ranged from 1.3% to 3.5%, a huge improvement in repeatability. A ring mill is a mechanical grinder used for pulverizing rocks, soil, coal, cement, glass, limestone, bricks, concrete, etc., in order to obtain a representative sample for subsequent analysis. Subsequent research by M.E. Walsh and co-workers found that grinding for 60–90 seconds (sec) on a ring mill reduced particle size of samples from impact areas containing crystalline

explosives adequately to produce a homogeneous sample (M.E. Walsh et al., 2002). However, for soil samples from firing points and open burn/open detonation (OB/OD) ranges containing fibers of propellant, five 60-sec grinding periods were necessary to adequately reduce the particle size (M.E. Walsh et al., 2002; Hewitt et al., 2007a). In both cases, a 10-g subsample built from 30 increments of the ground material was extracted with 20 milliliter (mL) of acetonitrile. Samples must be air dried and sieved prior to grinding to ensure that pieces of explosive above the critical diameter are not mechanically ground.

These changes to the way samples are collected and processed have been described in SW846 Method 8330B (USEPA, 2006). In addition to those discussed above, several other method modifications were needed to measure average concentrations of energetic residues in soils from training ranges and demolition ranges. Hewitt et al. (2007a) demonstrated the energetic compounds in samples that had been air dried and ground in a ring mill were stable for up to 53 days, and likely much longer. Walsh and Lambert (2006) found acetonitrile extraction on a shaker table was equivalent to using acetonitrile in an ultrasonic bath. M.E. Walsh et al. (2002) found the sieve size for removal of oversized material after air drying and before machine grinding needed to be increased to 2 mm (#10 sieve) because a large portion of the energetic particles was in the size fraction between 0.6 and 2 mm. This fraction would not have been included in the analysis of the material passing through the 0.6-mm sieve, as was specified in the earlier Method 8330. Method 8330 (USEPA, 1994) specifies using high-performance liquid chromatography (HPLC)-UV (HPLC with an UV detector), and this has been the most widely used analytical approach for detecting energetic compounds in soil samples from military sites. Another method used is Method 8095 (USEPA, 1999) that employs the same sample processing steps as Method 8330, but uses gas chromatography (GC) with an electron capture detector for determination. There is no reason that this method of determination could not be used with the sample processing steps specified in Method 8330B.

Two other methods that have been used for determination of energetic compounds in soil are SW846 Method 8321 and a method developed by Army Environmental Hygiene Agency that is now used by the USAPHC and laboratories working for them (Bishop et al., 2003). The Bishop method appears to be reliable, but it has not been subjected to the rigorous interlaboratory testing requited for U.S. Environmental Protection Agency (USEPA) methods. Method 8321 is an HPLC-MS method and energetic analytes are not target analytes of this method. In addition, the sample processing steps outlined in this method are not appropriate for use with energetic compounds. Most of the time when Method 8321 has been specified, samples were processed according to Method 8330 and the extracts were determined by HPLC-MS. Use of HPLC-MS for determination of energetic compounds is attractive because the MS can provide more unequivocal identification of analytes than those obtained via retention time matching using HPLC-UV techniques. However, the instrumentation is more expensive, and thus it is a more costly approach than HPLC-UV. As a part of the study conducted by Roote et al. (2010), a direct comparison of determinations for the same extracts from soil samples from two training ranges were analyzed by HPLC-UV and HPLC with tandem MS (MS/MS). This included samples from an Air Force bombing range where TNT was the major analyte detected and from an antitank rocket firing point where NG was the major analyte detected. In both cases, the reproducibility for the HPLC-UV was slightly better than for the HPLC-MS/MS, but overall, both methods provided similar detection for the target analytes. HPLC-UV and HPLC-MS/MS techniques are both included within SW846 Method 8330B. Only laboratories that have demonstrated proficiency with Method 8330 or 8330B should be used for analysis of soil samples for energetic

compounds. Hewitt et al. (2009) estimated the cost for collection and analysis of soil samples using Method 8330B at $300/sample.

4.6 Analytical Methods for Water Samples

Groundwater and surface water samples are generally analyzed using SW846 Method 8330B (USEPA, 2006). The target analytes for the water portion of this method are the same as those discussed for the soil portion of the method in Section 4.5 and include nitroaromatics (TNT, 2,4-DNT, 2,6-DNT, trinitrobenzene [TNB], dinitrobenzene [DNB], 2-nitrotoluene [2-NT], 3-NT, 4-NT, nitrobenzene [NB], tetryl), nitramines (RDX, HMX), nitrate esters (NG, pentaerythritol tetranitrate [PETN]), and amino nitrotoluene transformation products (2-amino-4,6-dinitrotoluene [2-Am-DNT], 4-amino-2,6-dinitrotoluene [4-Am-DNT], dinitroanaline [DNA]).

Water samples are preconcentrated by passing a 500 mL portion through a solid phase extraction cartridge and eluting the target analytes using acetonitrile. The acetonitrile extracts are analyzed using either RP-HPLC-UV or LC-MS.

Sometimes other energetics-related analytes may also need to be determined. For example, it may be necessary to analyze for the transformation product of NG. If so, a method modified from Method 8330B and developed by Martel et al. (2010) may be used. Occasionally, the three nitroso degradation products of RDX must be analyzed for. This is usually accomplished using a modified Method 8330B that uses gradient elution rather than an isocratic separation. Picric acid/picrate can also be added to the target analyte list if a pH buffered eluant is used.

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5 Best Management Practices (BMPs) – Energetic Residue Mitigation Technologies

5.1 Technologies to Mitigate Transport of Energetic Residue from Surface Soil

One approach to mitigate the dissolution and transport of energetic residues is to apply surface amendments to soils that contain the energetic residues. The amendments destroy the various residue chemicals, modify them to less mobile chemicals, bind them to soil components, or enhance the biota thereby increasing their rate of degradation. The most developed of these technologies is alkaline hydrolysis using hydrated lime (Section 5.1.1). Approaches to stimulate the biodegradation of energetic chemicals in shallow soils are discussed in Section 5.1.2.

Much work has been done to exploit the ability of plants to uptake and degrade energetic compounds in surface soils. The use of plant-based mitigation approaches to manage energetic residues on ranges is discussed in Section 5.1.3.

Several *ex situ* technologies have been developed for use at ammunition plants to address high concentrations of energetic compounds in soil. These include composting, bioslurry reactors, biopiles, and landfarming. Although these technologies are best suited for high-concentration, low-volume applications, there may be limited instances of applicability to energetic residues on operational ranges (Section 5.1.4).

Fire ecology—the use of fire to manage vegetation in ecosystems—continues to be studied to determine its ability to destroy energetic residues in surface soils. Results from past laboratory and field efforts are presented in Section 5.1.5. Section 5.1.6 discusses onsite residue collection and destruction—the practice of picking up chunks and particles of energetic residue and destroying them in some manner to prevent the dissolution and migration of the chemicals. Field portable burn pans, which provide for the controlled field disposal of excess propellant, are presented in Section 5.1.7.

5.1.1 Alkaline Hydrolysis (Liming)

Using an all-terrain vehicle and a drop spreader to apply lime to soil surface at a HGR (Larson et al., 2007).

Description: Alkaline hydrolysis (e.g., liming) involves the application of hydrated lime to surface soils containing energetic residues. The increased alkalinity, caused by the lime addition to the soil, results in the transformation of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), reducing the potential for migration in the soil.

Where It Can Be Used: This approach has been shown to be successful in several field demonstrations for managing energetic residues in soil at hand grenade ranges (HGRs) and demolition ranges. The lime and energetic residues must be in solution for the transformation reactions to occur. Thus, ranges located in arid environments are not suited for this approach due to lack of precipitation.

Advantages: This is an inexpensive, easy to implement approach for managing energetic residues at small ranges. For ranges not accessible for troop maneuvers, there seems no occupational health issues associated with this technology.

Disadvantages: The addition of hydrated lime and modification of the surface soil pH must be compatible with National Environmental Policy Act (NEPA) requirements and not pose other environmental concerns (e.g., endangered species). Hydrated lime is much less effective for the management of residues of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4-dinitrotoluene (2,4-DNT) than for RDX and TNT and would be less effective at antitank rocket range impact areas where HMX is the predominant residue present. Additionally, caution should be used if implementing alkaline hydrolysis for aluminum-containing explosives, such as tritonal or Composition H6, due to the potential to generate hydrogen gas, which could become a safety concern. The use of hydrated lime in areas where troops maneuver, as in some Marine Corps ranges, may not be appropriate due to potential health risks.

Application Frequency: Generally, it is recommended that hydrated lime be applied twice per year at HGRs, and that the lime should be tilled into the soil to a depth of 6 inches. (*Note: Safety concerns must be paramount—lime application should only occur after an area has been cleared by Explosive Ordnance Disposal [EOD] personnel*). However, site-specific factors such as range usage, soil type, and amount of rainfall will influence the required application frequency.

Cost Information: The cost for implementation of the alkaline hydrolysis technology at an HGR is approximately $15,000/year/hand grenade bay. These costs were based on a conservative assumption of reapplication of lime being required on a quarterly basis. Factors such as presence of unexploded ordnance (UXO), whether application equipment is rented or purchased, and the amount of rainfall and soil type will impact this estimated cost. The cost of implementing alkaline hydrolysis at an open burn/open detonation (OB/OD) range is estimated to be $2400/acre with an additional cost of $1200 per detonation event treated.

Recommendation: **Recommended for the management of energetic residues at HGRs and demolition ranges.**

Key Resources:

ESTCP. 2008. Grenade Range Management Using Lime for Metals Immobilization and Explosives Transformation. ESTCP Cost and Performance Report for ER-0216. August.

ESTCP. 2012. Open Burn/Open Detonation (OBOD) Area Management Using Lime for Explosives Transformation and Metals Immobilization. ESTCP Cost and Performance Report for Project ER-200742. October.

Johnson JL, Felt DR, Martin WA, Britto R, Nestler CC, Larson SL. 2011. Management of Munitions Constituents in Soil Using Alkaline Hydrolysis: A Guide for Practitioners. ERDC/EL TR-11-6. U.S. Army ERDC, Vicksburg, MS. October.

Larson SL, Davis JL, Martin WA, Felt D, Nestler CC, Fabian G. 2007. Implementation Guidance Manual: Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation. ESTCP ER-0216. Performed by US Army ERDC, Vicksburg, MS for the ESTCP, Arlington, VA.

5.1.1.1 Technology Description

The concept of using strong base to destroy energetic compounds dates back to at least the 1950s (Epstein and Winkler, 1951). Considerable work was done for treatment of red/pink waters (wastewaters generated during the production of 2,4,6-trinitrotoluene [TNT]) using base hydrolysis at ammunition plants and depots by Hoffsommer and co-workers at the White Oak Laboratory, Silver Spring, Maryland, Naval Surface Weapons Center, among others. Emmrich (2001) reported some initial work on the use of base to react with TNT and other nitroaromatic compounds in soil at high pH using calcium hydroxide ($Ca[OH]_2$; also called hydrated lime).

A series of studies conducted at the U.S. Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL), Vicksburg, Mississippi, have indicated that TNT, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and some other energetic chemicals can be removed from soil by alkaline hydrolysis. Alkaline hydrolysis works by bringing together the energetic compound and hydroxide ion in soil pore water (Brooks et al., 2003; Hansen et al., 2003). The pH required to hydrolyze TNT and RDX at an adequate rate proved to be at least 10.5. Several possible alkaline amendments were considered (Table 5-1). Hydrated lime ($Ca[OH_2]$) was selected as the favored amendment for this application (Brooks et al., 2003). Hydrated lime is a very inexpensive amendment that is commonly used for various engineering applications to include wastewater and sludge treatment, soil stabilization, metals immobilization, and treatment of acid mine drainage.

Table 5-1. The Equilibrium pH for Various Alkaline Amendments in Water (from Brooks et al., 2003).

Amendment	Common Name	Solubility	pH	Applications
$CaCO_3$	Calcium carbonate, chalk, agricultural lime	<0.1%	8	Manufacturing, pharmaceuticals, agriculture, lawns
$CaO/Ca(OH)_2$	Calcium oxide, quicklime, hydrated lime	0.18 g/100 mL	12.5	Wastewater treatment, construction, manufacturing, fertilizers
$MgO/Mg(OH)_2$	Magnesium oxide, hydroxide, milk of magnesia	0.076 g/L	10.3	Medicines, water treatment,
NaOH	Sodium hydroxide, lye	111 g/100 mL	14	Chemical, industrial, construction
KOH	Potassium hydroxide, potash	110 g/100 mL	13.5	Soaps, fertilizers, electroplating
Fly ash	Boiler ash	<2%	9–12	Construction, concrete, pavements
K_2CO_3	Potassium carbonate	112 g/100 mL	11.6	Glass, ceramic, explosives, fertilizer

Note: g—gram(s); L – liter(s); mL—milliliter(s).

Alkaline hydrolysis of TNT results in a complex variety of transformation products to include some high molecular weight polymers depending on the pH at which the reaction occurs, and the length of time that the reaction takes place (Davis et al., 2007). In fact, the reaction of TNT

with a base was used as the basis for the most widely-used onsite analytical method for TNT in soil (Jenkins, 1990; commercially available from SDIX[10]). TNT is not mineralized by alkaline hydrolysis, but the reaction products are apparently immobilized in the soil thereby eliminating or reducing any leaching potential.

Alkaline hydrolysis of RDX is thought to result in complete transformation of RDX, leading to inorganic products (nitrate, nitrite) and formate, as well as some polar, water soluble, low molecular weight organic compounds (Davis et al., 2007). The pH must be higher for RDX transformation compared with TNT transformation and the rates of reaction for RDX at any given pH are slower than for TNT. Apparently, the hydrolysis rate for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4-dinitrotoluene (2,4-DNT) are much slower than for RDX and require a higher pH before the rates of reaction are adequate.

Native soil pH varies substantially as does the cation exchange capacity and buffering capacity for various soils. Thus, the amount of hydrated lime required to achieve a pH of 10.5 differs widely for various soils. For example, Larson et al. (2007a) provided a table of the required lime dose to achieve a pH of 11.5 for a number of soils from a variety of Army installations (Table 5-2). The dose to attain a pH of 10.5 would be a bit less, but this does demonstrate that the lime doses are not constant from soil to soil. The method to determine the lime dose requirements for a given soil is provided in Larson et al. (2007a).

Table 5-2. Examples of Soil Types and Lime Dose Required to Achieve pH 11.5 (from Larson et al. 2007a).

Site	Predominant Soil Type [a]	Initial Soil pH	Lime Dose to Achieve pH 11.5 (tons/acre-3 inch depth)
Waterways Experiment Station (WES) reference soil, MS	Loess	8.67	4.15
Fort Drum, NY	Clay silt	6.75	18.46
Fort Knox, KY	Silty loam	5.12	9.23
Fort Jackson, SC	Silty sand	5.48	4.62
Fort Lewis, WA	Silty sand	4.96	20.77
Fort Polk, LA	Silty sand	6.15	1.85
Iowa Army Ammunition Plant, IA	Silty clay	8.10	18.46
Volunteer Army Ammunition Plant, TN	Silty loam	8.14	3.92
Nebraska Ordnance Plant, NE	Loamy sand	5.70	6.92
Yakima Training Center, WA	Silty loam	7.20	3.51
Camp Guernsey, WY	Shallow sandy loam	7.43	1.15
Redstone Arsenal, AL	Silty clay, loam	7.42	5.31
Camp Edwards, MA	Loamy, coarse sand	4.90	0.55
Fort Hood, TX	Cobbley, silty clay	4.90	1.62
U.S. Military Academy, NY	Gravelly loam	7.70	1.92

[a] Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture. Web Soil Survey (available online at http://websoilsurvey.nrcs.usda.gov/, accessed March 14, 2014).

[10] http://www.sdix.com/, accessed March 14, 2014.

5.1.1.2 Technology Demonstrations

A number of laboratory studies have been conducted at ERDC to investigate the use of alkaline hydrolysis for the management of RDX and TNT and immobilization of heavy metals for hand grenade range (HGR) and demolition range soils (Hansen et al., 2003; Johnson et al., 2010). The HGR studies included a lysimeter study using HGR soils from the U.S. Military Academy at West Point, New York, and Fort Jackson, South Carolina (Larson et al., 2007b), and an initial field trial at the HGR at Fort Lewis, Washington (Thorne et al., 2004). The emphasis of these studies has been on the effect of alkaline amendments of the leachability of RDX and TNT from HGR soils as well as the effects on various heavy metals. It was found that incorporation of the lime into the soil profile was much more effective than just topical (surface) application. The results of these studies were quite favorable, and a full-scale demonstration was conducted at one hand grenade bay at Fort Jackson, from 2005 to 2007.

The goals of the Fort Jackson demonstration included the following (Larson et al., 2008):

1. Reduce RDX and TNT concentrations by >90% in the pore water leaching from the source area based on baseline and control area concentrations.
2. Reduce RDX and TNT concentrations by >90% in the surface water running from the source area based on baseline and control area concentrations.
3. Reduce metals (iron [Fe], zinc [Zn], manganese [Mn], chromium [Cr], lead [Pb] [if present], nickel [Ni], and vanadium [V]) concentrations in the pore water leaching from the source area and in the surface water running from the source area by >90%.
4. Assess the overall effectiveness and potential side effects of the lime amendment technology, including the following:
    a. Evaluate explosives reductions and metals (total and dissolved) soil stabilization or reductions in the surface water and pore water samples. Compare results from the treated (lime added) and control (no lime added) impact areas.
    b. Maintain or reduce explosives concentrations in soil at the source area. (Since continuous loading of explosives will occur, maintaining explosives concentrations in soil below baseline levels is an appropriate objective.)
    c. Determine ability to maintain pH above 10.5 in the source area and below 12.5 outside the source area.
    d. Evaluate ease of use. Identify problems, if any, with amendment application and maintenance of the lime-amended impact area. Determine the mixing efficiency required and estimate the frequency of lime reapplication. Identify factors other than range use that may affect the maintenance frequency.
    e. Evaluate the human health risks, including occupational risks associated with technology installation, range use, and range maintenance.
    f. Determine transport characteristics by using calcium (Ca) from the dissolution of lime as a tracer in pore water, surface water, soils, and air monitoring samples. Fort Jackson HGR soil has a naturally occurring low Ca concentration.

Several different lime application methods were also evaluated (example provided in Figure 5.1). These included: simply opening bags of lime on the range by hand and raking the material into the soil to give a uniform color distribution, use of a drop seed spreader, and use of a hydroseeder. Lime was incorporated into the soils to a 6-inch depth using a garden rototiller, a small disc, a cultivator, or a rake.

This study was not designed to determine the necessary frequency of lime application at the active HGR; however, the application frequency can be determined by observing the soil pH and explosive concentration trends in the field.

At the Fort Jackson demonstration, a variety of samples were collected to include: pore water from within the treatment and control areas, runoff water, air samples, soil samples within the treatment and control areas, and soil samples along the runoff pathway. The rainfall was 33 inches over the 12-month period from August 2006 to August 2007. The following is a summary of the results obtained (Larson et al., 2008):

1. There was a 77% reduction in the RDX concentration in pore water from the lime-treated area compared to an untreated control, even with continued use. No TNT was detected in pore water samples collected from the treated area and from the untreated control area.
2. There was a >96% reduction in the RDX concentration in the treated area runoff water compared to the control area. No TNT was detected in any of the surface water samples.
3. Most metals were reduced in the pore water relative to the control except for Zn and Ni, which remained unchanged. Zn was the most prominent metal in the surface water runoff and it was reduced by 98% relative to the control. Nickel was not prominent in the surface water runoff samples.
4. Overall effectiveness results:
    a. Decreased concentrations of RDX were detected leaving the range either in the pore water or the surface waters in the limed bay versus the control bay. Lime addition stabilized metals within the soil in the treated area (i.e., there was a decreased concentration of metals entering the pore water and the metals that did leach from the soil were detected at lower concentrations than the metals leaving the untreated soil).
    b. RDX concentrations in the source area were reduced when the pH was kept above 10.5.
    c. The pore water pH was maintained above 10.5 with quarterly lime application and there appeared to be no increase in pH outside the treated area.
    d. The application of lime and the incorporation into the soil was accomplished easily using commonly available equipment (Figure 5.1).
    e. Air monitoring indicated that no increase in lime ($Ca[OH]_2$) was detectable in the air leaving the site, application of lime only required the use of Level D personal protective equipment with the addition of a particulate respiratory mask and goggles.
    f. No increase in the concentration of Ca below 12 inches in the soil profile was observed in the treated area.

An implementation guidance manual was prepared for HGRs under Environmental Security Technology Certification Program (ESTCP) Project ER-0216 (Larson et al., 2007a). This manual utilizes hydrated lime for transformation of energetic compounds and immobilization of metals.

A second lime demonstration was conducted by ERDC-EL at Redstone Arsenal, Alabama, from October 2004 to April 2005 for management of soils where explosives residues were deposited from blow-in-place (BIP) detonations (Johnson et al., 2010). In this study, lime was topically

applied to an area where five 60-millimeter (mm) mortars containing Composition B were blown in place, each with a block of C4. The lime application rate was estimated at 2.52 tonne (metric ton)/hectare. Comparing RDX concentrations and mass estimates between the treated and untreated sites suggests that the topical addition of hydrated lime had little effect on the RDX deposited in the area, although the authors indicate that some initial RDX reduction occurred in the treated area. It should be mentioned that the median soil pH in the lime treated area was only 7.63, a pH much too low to hydrolyze either RDX or TNT.

A third demonstration of the use of hydrated lime was conducted by ERDC-EL at an OD portion of an open burn/open detonation (OB/OD) site at the Aberdeen Proving Ground (APG) (Maryland) (Martin et al., 2012; ESTCP, 2012). The goal was to evaluate the use of lime to destroy energetic compounds and immobilize heavy metals.

The site of this demonstration is in continuous use for the detonation of out-of-date munitions and explosives. A pit is dug and a variety of explosives and out-of-date munitions are placed in the pit with a 1:1 ratio of donor charge, generally C4. Craters as deep as 14 feet (ft) are sometimes formed from these detonations.

To conduct the test, lime was initially added to the surface of a 9-acre area with a drop spreader and disced into the soil. The lime application rate was 0.5% of the dry weight of the top 6 inches of soil. A detonation crater 3–4 ft in depth was then dug and lime was placed at the bottom of the crater along with the material to be detonated. The soil was mounded about 5 ft above surface. Seven additional amendment strategies were evaluated prior to the detonation. The most successful were placement of 50 bags of lime (1.25 ton) (or twice that) around the mound 2 ft from the toe of the mound prior to detonation. Following the detonation, 1,250 lbs of lime was placed in the hole prior to backfilling the crater.

Surface and subsurface soil samples were collected before and after detonations. Pore water was extracted using a suction lysimeter and few groundwater samples were collected. Air monitoring was done to determine if protective clothing was needed to be worn by site workers. Analyses were conducted for energetic compounds, metals, and calcium for air samples. Test data were compared to baseline measurements or to established regulatory guidance where available.

Within the soil profile, RDX, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), TNX, and HMX were detected but at concentrations <1 milligram per kilogram (mg/kg). In the soil ejected during the detonations, RDX was the only energetic detected. In general, nitroaromatics such as TNT were not detected at this site. The major metals detected were copper (Cu), Zn, and Ni along with Fe and Pb.

The authors report that the lime application at APG was effective at controlling off-range transport of energetic compounds and heavy metals without significantly modifying soil properties or the pH of water leaving the site. The initial cost of soil treatment was estimated at $2,400/acre with an additional cost of $1,200 per detonation event treated.

The Navy is conducting a lime demonstration project under the Navy's Environmental Sustainability Development to Integration (NESDI) Program. This demonstration is being conducted at a simulated demolition area at Pinecastle Range, Florida, where practice bombs would be “vented” using C4. Lime is being applied only to an area with no energetic residue. The purpose of the study is to determine the pH of the soil after lime addition (Joey Trotski, NFESC, Port Hueneme, California; personal communication, 2011).

Figure 5-1. Lime incorporation using a disc at Fort Jackson (from Larson et al., 2007a).

5.1.1.3 Cost and Ease of Implementation

The cost of hydrated lime application for a HGR has been estimated to range from $15,000 to $16,000/year/HGR bay, depending on whether the application equipment is rented or purchased by the installation. This cost assumes quarterly lime amendments and includes capital and operation and maintenance (O&M) costs (ESTCP, 2008). The frequency of adding lime to a site is dependent on the soil type and pH, and the amount of rainfall.

The application is both straightforward and simple to implement. The equipment required will often be available at the installation and the hydrated lime will generally be available locally.

5.1.1.4 Limitations and Recommendations

Base hydrolysis with calcium hydroxide (e.g., hydrated lime) seems best suited for use at HGRs, where it has been demonstrated, demolition ranges, and perhaps areas where low-order detonations have deposited large quantities of TNT/RDX in a small area within a large range, such as an artillery or bombing range, or in OB/OD areas. This last use would only be effective if the large pieces of explosives were removed. Wider application to larger ranges, such as artillery target areas, bombing ranges, or antitank rocket ranges seems impractical for logistical and safety reasons. Because hydrated lime works best when incorporated into the soil, there can be limitations with respect to the possible presence of unexploded ordnance (UXO). Certainly, safety concerns must be paramount, and thus application/soil incorporation can only be conducted after the area has been cleared by explosive ordnance disposal (EOD) personnel using magnetometers or other geophysical techniques. This is true even for HGRs where undetonated grenades can sometimes get buried within craters. The need to till the lime into the soil also may disturb and uproot vegetation, thus increasing potential erosion concerns.

Because the hydrolysis occurs in solution, the residue must first dissolve into pore water before the reaction can take place. This can be a limiting factor for some residues such as nitroglycerin (NG) and 2,4-DNT, which are largely present at firing points associated with small particles of nitrocellulose (NC), and HMX at antitank rocket ranges due to its low solubility. NC will not dissolve and hence the NG and 2,4-DNT present in the NC matrix must first leach from the NC

particles before it can react with the lime. Experiments conducted by Taylor et al. (2008) indicate that leaching of 2,4-DNT from NC particles is quite slow and NG a bit faster. As mentioned earlier, the hydrolysis rate for HMX and 2,4-DNT is much slower and requires a higher pH than for RDX or TNT. The slow rate of reaction with HMX indicates that use of this technology at antitank rocket range impact areas may not be effective. Similarly, the slow rate of reaction with 2,4-DNT may limit its effectiveness for use at firing points where single base propellant containing 2,4-DNT is fired (Jeffrey L. Davis, U.S. Army ERDC-EL, Vicksburg, MS; personal communication, June 2011).

The soil moisture must also be adequate to dissolve the lime and hence this technique might not be useful in arid environments where insufficient rainfall may limit the dissolution of both RDX and lime. In these arid areas, however, the leaching of RDX is unlikely to be a problem.

The application of large quantities of hydrated lime to soil over time, however, will affect the exchangeable cations on the soil, substituting Ca ions for Na, K, and NH_4 ions. As a result, the adsorptivity of the soil for TNT will be reduced significantly (Haderlein et al., 1996), but this should not markedly affect the sorptivity for RDX, which is low in any case. The continued application of $Ca(OH)_2$ will probably also sterilize the soil and reduce the organic carbon content as well, further reducing the sorptivity for TNT and for RDX . Thus, it may not be prudent to stop the lime treatment once it has been initiated, or leakage of TNT/RDX downward in the soil profile or in runoff might be enhanced. The use of hydrated lime may not always be acceptable depending on other site-specific factors such as the presence of endangered species or other National Environmental Policy Act (NEPA) concerns, and these factors should be considered before selecting base hydrolysis as a management option.

For ranges not accessible for troop maneuvers, there seems no occupational health issues associated with this technology. However, the use of hydrated lime in areas where troops maneuver, as in some Marine Corps ranges, may not be appropriate. A minor health risk to personnel applying the lime to the site was identified at the APG demonstration site and wearing the proper personnel protective equipment is recommended (Martin et al., 2012). At APG, personnel wore air-purifying respirators, disposable coverall suits and chemical resistant gloves.

One other potential concern is the use of lime with aluminum-containing explosives, such as tritonal or Composition H6. At basic pH, evolution of hydrogen gas is likely, which could become a safety concern (Marianne Walsh, U.S. Army Cold Regions Research and Engineering Laboratory [CRREL], Hanover, NH; personal communication, 2011).

Caution should be exercised when preparing soil samples collected from lime-treated areas for analysis. Analytical errors due to false degradation occurring post collection can occur if the soil samples are not neutralized properly prior to extraction and analysis. Larson et al. (2012) developed a neutralization approach that can be used for alkaline hydrolysis approaches. It is recommended that this document be consulted prior to developing site-specific sample collection and analytical protocols for alkaline hydrolysis applications.

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5.1.2 Passive *In Situ* Management Approach for Shallow Soil

Application of PMSO material to HGR Bay 1, Remagen Grenade Training Range, Fort Jackson, South Carolina (Fuller and Schafer, 2010).

Description: Applying biological amendments to surface soils has the potential to sorb, transform, and/or mineralize energetic contaminants at military ranges, thereby reducing the potential for residue migration to groundwater or surface water resources. 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) can be sorbed onto organic substrates, reducing their rate of migration. The presence of readily degradable organic material can stimulate microbial activity, thereby reducing the oxygen concentration and driving the environment anaerobic. Under this condition, TNT is reduced and can be irreversibly bound to the organic substrate, and RDX (and perhaps HMX) can be mineralized.

Where It Can Be Used: This approach is currently under development for use at ranges where energetic residues have been deposited over a small area (e.g., mortar and grenade ranges, tank target areas, and open burn/open detonation [OB/OD] areas).

Advantages: The major potential advantage of the amendments currently under development will be the ability to apply them via spraying them onto the soil surface without the need to till them into the profile. This would allow the use of this management option at ranges with unexploded ordnance (UXO) still present.

Disadvantages: The main disadvantages of the passive *in situ* shallow soil management approaches that have been tested to date are the potential need to apply amendments frequently, the flammability of some amendments, and a possible increase in dust emissions, although a new approach being evaluated may significantly reduce these disadvantages.

Cost Information: Costs for the implementation and maintenance of a buried peat moss/soybean oil (PMSO) layer 2 feet (ft) below ground surface (bgs) at a hand grenade range (HGR) have been estimated (ESTCP, 2010; Fuller and Schafer, 2010). However, to the authors' knowledge, implementation of a shallow, buried layer of PMSO has not been field-tested to date; thus, operational and logistical challenges may hinder implementation of this approach at some sites. New amendments that can be applied directly to the soil surface (without grading or tilling) are currently under development (Borden, 2011). Cost and performance information will be posted to the Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) website (http://www.serdp.org/) when available.

Recommendation: **Although still in the demonstration/validation phase of development, passive *in situ* shallow soil management appears to have the potential to be a very useful approach for the control of energetic residues at both small and large ranges.**

Key Resources:

Borden R. 2011. Generation of Biodegradation-Sorption Barriers for Munitions Constituents. ESTCP Project No. ER-201123 Fact Sheet. Available at http://www.serdp.org/, accessed

March 14, 2014.
Fuller ME, Schafer CE. 2009. Treatment of Explosives Residues from Range Activities. ESTCP Project No. ER-0434 Final Report. September. 354 p.
Fuller ME, Schafer CE. 2010. In Place Soil Treatments for Prevention of Explosives Contamination. ESTCP Project No. ER-0434 Grenade Range Final Report. January. 225 p.
ESTCP. 2010. Treatment of Explosives Residues from Range Activities. ESTCP Project No. ER-0434 Cost and Performance Report. January. 73 p.

5.1.2.1 Technology Description

Applying biological amendments to surface soils is a management technology that is designed to stimulate native soil microorganisms to transform and/or mineralize chemicals in near surface soils, thereby reducing the potential for migration of the chemicals deeper into the soil profile or the underlying aquifer. Native microorganisms are not capable of mineralizing 2,4,6-trinitrotoluene (TNT), but they can sequentially reduce the nitro groups in the aromatic ring to amino functions if the conditions within the soil are favorable. Once initially transformed, these amine functions can covalently bind irreversibly to soil organic matter, thereby immobilizing the reduced form of TNT. The larger the number of amine functions on the molecule, the more tightly the molecule is bound.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) can be mineralized by some native microorganisms under certain soil environmental conditions via several different mechanisms. The resulting products are inorganic chemicals and small organic chemicals that can be further destroyed *in situ* (McCormick et al., 1981; Hawari, 2000). Because RDX is very mobile in the surface soil, destroying it utilizing this type of approach is a desirable management strategy if the technology can be implemented at military training ranges of various types.

5.1.2.2 Transformation Processes

TNT Immobilization

TNT can be transformed to either 2-amino-4,6-dinitrotoluene (2-ADNT) or 4-amino-2,6-dinitrotoluene (4-ADNT) under either aerobic or anoxic conditions (see Figure 5-2 for anaerobic TNT degradation pathway).

Both 2-ADNT and 4-ADNT can then bind to natural organic matter and become irreversibly bound via covalent bonds. Many different management approaches utilize this reaction to immobilize TNT. Under anoxic conditions, both 2-ADNT and 4-ADNT can be further reduced to the diamino compounds, 2,4-diamino-6-nitrotoluene (2,4-DAT) or 2,6-diamino-4-nitrotoluene (2,6-DAT) and ultimately to triaminotoluene (TAT). These compounds can also bind irreversibly to soil organic matter thereby eliminating the possible migration of TNT.

RDX Mineralization

RDX is not extensively mineralized in the soil under aerobic conditions. Under anoxic conditions in soil, the three nitramine functions on the RDX ring are sequentially reduced to nitrosamine functions. Because the RDX ring is not aromatic like TNT, the ring can be cleaved and further reduced to inorganic substrates like ammonia, carbon dioxide (CO_2), and nitrous oxide (N_2O), and to small organic molecules like formaldehyde and methlenedinitramine that can be further reduced.

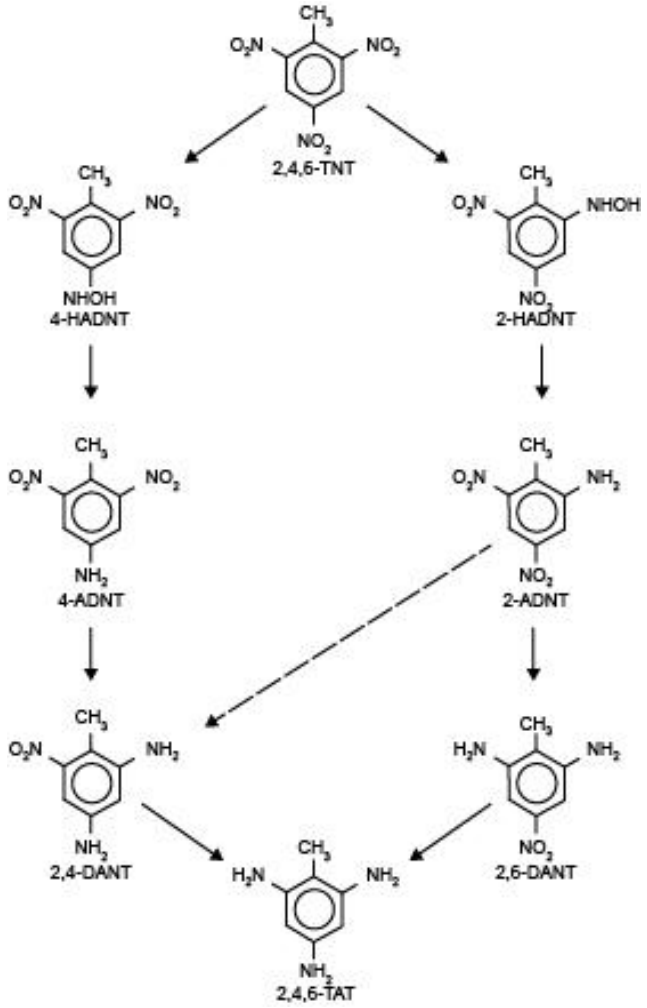

Figure 5-2. Pathway summarizing the biodegradation routes of TNT under anaerobic conditions (from Hawari and Halasz, 2003).

5.1.2.3 Surface Bioamendment Studies

Several studies have been conducted to try to engineer the type of soil environment that will mineralize or immobilize the major types of energetic residues present on military training ranges to protect groundwater resources from contamination. The intent has been to provide a readily degradable, inexpensive, organic substrate to surface or near surface soils that will create the anoxic conditions required to immobilize TNT and mineralize RDX.

Hatzinger et al. (2004) and Fuller et al. (2004) evaluated the addition of several adsorbents and carbon sources in various combinations to initially sorb TNT, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and then stimulate indigenous microorganisms to transform/mineralize the sorbed energetic compounds. Initial studies showed that *Sphagnum* peat moss was the most effective adsorbant for the three energetic compounds, although sawdust, wheat straw, rice hulls, and ground rubber tires also adsorbed appreciably more TNT and RDX than the native soils tested from Massachusetts Military Reservation (MMR). The energetic compounds were found to desorb from the peat moss more slowly than they adsorbed.

Microcosm studies were performed to determine if the biodegradation of energetic compounds that had been sorbed to peat moss and sawdust could be stimulated though the addition of various carbon substrates (Fuller et al., 2004). The addition of either crude soybean oil or molasses stimulated the mineralization of RDX and, to a lesser extent, HMX. Minimal TNT mineralization was observed; however, mass balance results indicated the formation of bound transformation products.

Fuller et al. (2005) continued research on this topic by conducting large-scale unsaturated soil column experiments using soil from MMR. Three columns were studied: a no treatment control, a column with peat moss alone placed on the surface, and a column with *Sphagnum* peat moss and crude soybean oil (PMSO) placed similarly. Soil spiked with 1,100 milligrams (mg) TNT/kilogram (kg), 900 mg RDX/kg, and 110 mg HMX/kg was placed on the soil surface in each column. Simulated rainfall initiated dissolution and leaching of the explosive compounds. Water samples were removed from the columns at various depths and analyzed for the energetic compounds. Overall, the soluble concentrations of TNT, RDX, and HMX detected at the 10 centimeters (cm) depth in the PMSO column were reduced by 100%, 60%, and 40%, respectively, compared to the control column. Peat moss alone reduced soluble TNT and HMX concentrations at the 10 cm depth, but not RDX concentrations. Very little mineralization was realized in any of the columns, however. This appears to be due to the lack of maintaining an anaerobic environment in the near surface soils.

Following the laboratory studies, Fuller and Schafer (2009; 2010) conducted two field studies to evaluate the effectiveness of PMSO to reduce the transport of dissolved energetic compounds on active training ranges. The first study was designed to determine the effectiveness of the PMSO technology with respect to reducing the flux of dissolved RDX, HMX, and TNT in soil. The second study evaluated the compatibility of the PMSO technology with U.S. Department of Defense (DoD) hand grenade training activities.

The first study was performed at the MMR using nine outdoor *ex situ* instrumented plastic tanks (e.g., soil plots) (Figure 5-3). The soil plots were filled with clean soil. Six of the plots received a layer of PMSO on the soil surface; the remaining three served as controls. Composition B detonation residue was applied to the surface of each soil plot. The PMSO material resulted in 25–100-fold reduction in the flux of RDX through the soil compared to flux of RDX in the untreated controls. Dissolved TNT and HMX were not detected with enough frequency to allow calculation of fluxes of these compounds. The PMSO material also reduced the residual concentrations of explosive compounds as a function of depth compared to the explosive compound concentration profile observed in the untreated controls.

The objectives of the second study conducted at the Ramegen hand grenade range (HGR) at Fort Jackson, South Carolina, were to (Fuller and Schafer, 2010):

1. Determine to what extent the PMSO material is redistributed by grenade detonations after being emplaced,
2. Determine any incompatibilities between hand grenade training activities and the PMSO technology, and
3. Perform an initial assessment of the effectiveness of the PMSO technology for preventing new near surface soil contamination.

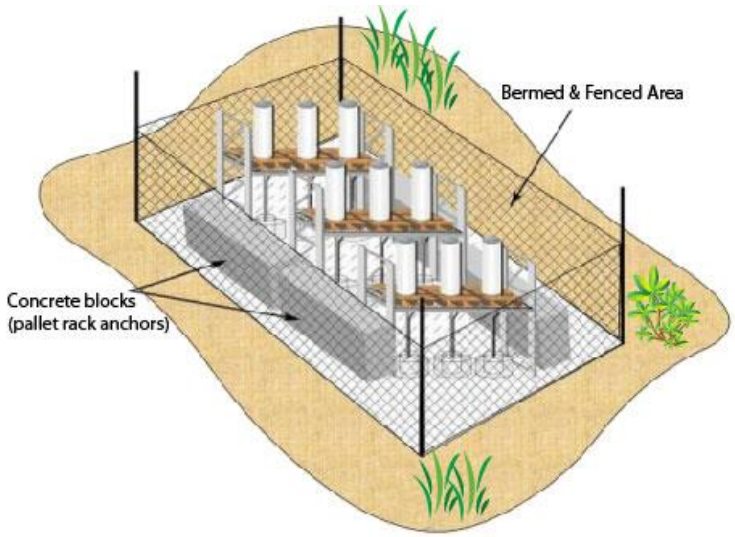

Figure 5-3. Conceptual layout of the soil plot demonstration at MMR (from Fuller and Schafer, 2009).

A 10-cm layer of PMSO (1:1 peat moss:crude soybean oil [weight:weight]) was applied across the surface of a 10-m X 10-m area in a single hand grenade bay. After the PMSO was applied, hand grenade training continued. After three days of training (128 grenade detonations), 88% of the original 1,000 square meter (m^2) area remained covered by some amount of the PMSO. Objectives 2 and 3 were not able to be accurately evaluated due to ignition of the PMSO layer from the use of Composition C4 (C4) explosives to detonate dud grenades. Water application was required to quench the smoldering PMSO. Additionally, nuisance dust was created from ash from the smoldering PMSO as well as the finer portions of the peat moss. The bay underwent regrading so as to not adversely impact training activities and the demonstration was terminated early.

Borden (2011) recently started an effort to address some of the challenges posed by the surface application of a bioamendment: the need to apply the amendment frequently because the amendment is in the near surface soil where oxygen can penetrate rapidly; an increase in the likelihood of range fires by surface application of flammable organic substrates; and the potential for increasing dust emissions. Borden proposes using a combination of waste glycerol and a humic material. The glycerol is soluble in water and would rapidly penetrate surface soils with precipitation carrying with it the humic substances. This would create an anaerobic zone for sorption and transformation/mineralization deeper in the soil profile where oxygen penetration would be much reduced resulting in a lower requirement for reapplication of the amendments. While no cost and performance data is available as this project is just underway, Borden speculates that the cost would be similar to lime application. Because it appears that the amendments can be applied via spraying, this technology may be useful in areas where unexploded ordnance (UXO) are still present and tilling would not be allowed, and on larger ranges where air dissemination might be possible.

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5.1.3 Plant-Based Mitigation

Wild type and transgenic plants expressing XplA growing on soil with and without RDX. The transgenic plants show minimal signs of toxicity and removed significant amounts of RDX from the soil (Bruce, 2012)

Description: Plant-based mitigation refers to the direct use of plants to detoxify munitions constituents in soil or groundwater by destruction or stabilization. Normal plants are capable of taking up large quantities of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), but do not destroy these chemicals and can release them at a later date. Incorporation of genes from microorganisms into plants that have the ability to destroy these chemicals might offer a long-term management approach to reducing the most mobile contaminants in soil at ranges.

Where It Can Be Used: Once fully developed, this technology would be applicable to large ranges, such as artillery or bombing ranges, and could provide a long-term strategy for reduction of energetic residues.

Advantages: The major advantage of this technology is the possible implementation at large ranges where engineered plants could be established to manage energetic residues and minimize leaching over an extended time periods.

Disadvantage: The major issue is the need to develop transgenic plants because native plants generally do not destroy energetic compounds that are taken up into the plant. The second disadvantage is the toxicity of 2,4,6-trinitrotoluene (TNT), which is generally co-resident in areas with RDX contamination, to plants.

Cost Information: No cost information is currently available for the full-scale application of this technology.

Recommendation: **Although not sufficiently developed at present for implementation, this technology has the potential for application at large military impact areas if suitable transgenic plants can be developed and a means of distribution demonstrated. Refer to the SERDP/ESTCP website for updates on currently funded plant-based mitigation projects.**

Key Resources:

Best EPH, Smith JC, Ringelberg DB. 2009. Phytoremediation of Composition-B Derived TNT and RDX in Herbaceous Plant-Vegetated and Bare Lysimeters. ERDC TR-09-10/SERDP Project ER-1500 Final Report. December. 102 p.

Bruce N. 2012. Sustainable Range Management of RDX and TNT by Phytoremediation with Engineered Plants. SERDP Project ER-1498 Fact Sheet.

Schnoor J. 2011. Phytoremediation for the Containment and Treatment of Energetic and Propellant Material Releases on Testing and Training Ranges. SERDP Project ER-1499 Final Report. June. 169 p.

Shanks JV. 2007. Genetic and Biochemical Basis for the Transformation of Energetic Materials (RDX, TNT, DNTs) by Plants. SERDP Project ER-1319 Final Report. April. 558 p.

Strand S, Bruce N. 2009. Engineering Transgenic Plants for the Sustained Containment and In Situ Treatment of Energetic Materials. SERDP Project ER-1318 Final Report. June. 103 p.

5.1.3.1 Technology Description

According to the U.S. Environmental Protection Agency (USEPA),[11] phytoremediation (e.g., plant-based mitigation) is:

> *"the direct use of green plants and their associated microorganisms to stabilize or reduce contamination in soils, sludges, sediments, surface water, or ground water. … Because it is a natural process, phytoremediation can be an effective remediation method at a variety of sites and on numerous contaminants. However, sites with low concentrations of contaminants over large cleanup areas and at shallow depths present especially favorable conditions for phytoremediation. Plant species are selected for use based on factors such as ability to extract or degrade the contaminants of concern, adaptation to local climates, high biomass, depth root structure, compatibility with soils, growth rate, ease of planting and maintenance, and ability to take up large quantities of water through the roots."*

Research on the uptake of energetic compounds by plants has been underway since the 1980s (Palazzo and Leggett, 1986). Initial concern was the possibility that energetic compounds might enter the food chain via plant uptake. More recently, research has centered on the use of plants to reduce energetic residues on sites where energetic residues are present in the soil, particularly at training ranges. Because energetic residues are mostly deposited at the surface as particles, if they are to leach to groundwater they must first dissolve and then pass through a plant's root zone. Thus, plants do have the potential to reduce the concentrations of energetic compounds that can migrate to underlying aquifers.

The Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) has invested resources to assess the possibility that plant-based mitigation might be useful in managing energetic residues at training ranges. Several types of studies have been conducted to include the uptake/toxicity reduction of energetic compounds by hybrid poplar trees (ER-1317),[12] development of transgenic (genetically modified) plants that are less phytotoxic to 2,4,6-trinitrotoluene (TNT) but can detoxify TNT and degrade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (ER-1318,[13] ER-1498[14]), and the ability of plants already present at training ranges with energetic residues to detoxify energetic compounds (ER-1499,[15] ER-1500[16]).

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[11] http://www.epa.gov/superfund/accomp/news/phyto.htm, accessed January 24, 2012.

[12] http://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1317 , accessed March 14, 2014.

[13] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1318/ER-1318, accessed March 14, 2014.

[14] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1498/ER-1498/(modified)/03Mar2011, accessed March 14, 2014.

[15] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Characterizing-Fate-and-Transport/ER-1499/ER-1499/(modified)/24Aug2010, accessed March 14, 2014.

[16] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-15002, accessed March 14, 2014.

5.1.3.2 Plant Uptake of Various Energetic Compounds

A number of studies have been conducted to understand the uptake of energetic compounds by various plants, the translocation of the various compounds, and their transformation products, to different portions of the plants, particularly the leaves. In general, it is thought that TNT is taken up by the roots, but that unaltered TNT is not translocated to other parts of the plant including the leaves. Most likely, TNT is initially taken up in the roots and transformed by reduction of one nitro group to the nitroso analog, and then to the relatively unstable hydroxylamino reduction products. They can be further reduced to the more stable 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) or react with themselves, the amino containing compounds, or plant organic matter to form dimers, higher conjugates, or plant associated material (Harvey et al., 1990; Rylott and Bruce, 2009). It is thought that a major portion of the initial TNT ends up associated with conjugates that are immobilized in cell walls of the plant (Rylott and Bruce, 2009).

TNT can also be transformed via an oxidative mechanism within plant roots leading to a different array of transformation products. These products also appear to react with plant material to form plant conjugates. Most of these conjugates of both reductive and oxidative transformation are not well extracted using organic solvents unless the plant material is extracted with a strongly acidic medium (Palazzo and Leggett, 1986). Over 95% of the plant-conjugated TNT-derived material appears to remain in the roots (Rylott and Bruce, 2009).

Unlike TNT, both RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are readily taken up by plants and translocated to the aerial portions of the plant, including the leaves, as the unaltered compounds (Harvey et al., 1991; Thomson et al., 1999; Vila et al., 2007; Rylott and Bruce, 2009). Recent evidence using radiolabeled compounds seems to show that RDX may also be transformed to a certain degree by reduction to form the nitroso-containing analogs. Further mineralization apparently requires light (Just and Schnoor, 2004) and results in production of formaldehyde and methanol. Although plants can take up large amounts of RDX and HMX, they have only a limited ability to transform or degrade the compounds leading to fairly large accumulated concentrations of HMX and RDX in aerial portions of the plants. From the use of radiolabeled compounds, it appears that a small portion of the RDX in plants can also be transformed to volatile compounds to a greater degree than HMX and some loss of the compounds containing the radiolabel occurs via volatilization. Because of the very low vapor pressure of RDX, the loss is probably due to some portion of the RDX that has been converted to a more volatile chemical.

5.1.3.3 Toxicity to Plants

TNT is toxic to plants at concentrations between 50 and 100 milligrams per kilogram (mg/kg) in soil (Rylott and Bruce, 2009; Hannink et al., 2002). The degree of toxicity appears to be species and soil dependent. The presence of organic matter in soil appears to reduce toxicity by sorbing TNT, thus reducing its concentration in pore water. The transformation and formation of plant conjugates appears to detoxify the TNT to a certain degree, but plants will not grow to any extent in areas with high concentrations of TNT in soil.

Although RDX and HMX are not very toxic to plants, they are almost always used with TNT in munitions and are co-resident in soil residues. The co-location with TNT limits the uptake of RDX and HMX by plants more so than any inherent toxicity due to RDX and HMX. It must be emphasized that the deposition of RDX and HMX at range impact areas results in a distributed point source, not a uniform low-level distribution across the range (Jenkins et al., 2006). Thus,

for plants to be successful at detoxifying ranges, with respect to RDX and HMX, they must be tolerant of fairly high concentrations of TNT. This is a major limitation of the use of natural plants as a management technique to reduce leaching or runoff of RDX from ranges.

5.1.3.4 Transgenic Plants

As discussed above, there are two major difficulties with the use of plant uptake to reduce RDX migration. First, RDX taken up in the aerial portions of plants can be re-released when the aerial portions of plants die off for winter (Thorne, 1999). Second, the distribution of residues is as distributed point sources containing TNT, along with either RDX or HMX. The inherent toxicity of TNT to plants appears to be fairly universal, although different species of plants are more or less tolerant of TNT in soil.

Certain microorganisms have shown the ability to degrade RDX and HMX to a much greater extent than plants. Similarly, other microorganisms have shown the ability to tolerate much higher concentrations of TNT than plant species. Research has been underway to incorporate these desirable characteristics into plant species that are adaptable for use at military training ranges (Rylott et al., 2011). These genetically modified plants are referred to as *transgenic plants* and research on their possible development and use for range management has been and is being sponsored by SERDP/ESTCP (ER-1318,[17] ER-1319,[18] ER-1498[19]).

Currently, an ESTCP-sponsored effort is underway to utilize transgenic analogs of three types of grasses that have been found to establish quickly, be resilient, show ability to spread to disturbed areas, and be fire tolerant (Palazzo et al., 2009; 2012). These species include two native species, first strike slender wheatgrass and recovery western wheatgrass, and an introduced species, Siberian wheatgrass. Grasses cover much of the impact areas at most training ranges and hence would be a good choice for range application. These species are currently being tested under laboratory conditions and should be field tested in 2012.

5.1.3.5 Potential Use of Plant-Based Mitigation for Management of Energetic Residues at Training Ranges

Thus far, it appears that grasses and trees, such as poplar, are the most useful species for potential use for management of energetic residues on ranges. One scenario would be to plant hybrid poplar trees in buffer zones around various training ranges. These trees have deep rooting networks that could remove RDX from shallow aquifers. Toxicity issues with TNT would not be a problem for poplar trees because TNT is generally immobilized in near surface soils at the source zones. A transgenic poplar, where an RDX degradative gene had been incorporated, would be particularly advantageous for situations where a shallow aquifer contaminated with RDX was present.

In contrast, transgenic grasses, such as the types being evaluated by Neil Bruce and co-workers (ER-1498), would have to be seeded across the range and operate within the distributed source

[17] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1318/ER-1318, accessed March 14, 2014.

[18] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1319, accessed March 14, 2014.

[19] http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminants-on-Ranges/Protecting-Groundwater-Resources/ER-1498/ER-1498/(modified)/03Mar2011, accessed March 14, 2014.

zones created by low-order detonations. Because these zones are also impacted by high-order detonations that create craters, the grasses would have to establish quickly after disturbance and tolerate high concentrations of TNT, which is nearly always present as a co-contaminant with RDX or HMX.

5.1.3.6 Limitations of Plant-Based Mitigation for Training Ranges

A major limitation for plant-based mitigation at training ranges is the common occurrence of wildfires. These fires would destroy any residues present in the aerial portion of the plants but would denude the site for a period of time after the fire. This would be a significant problem for the use of poplar trees if fires spread into buffer zones. Another issue is how to seed training range areas with transgenic grasses without the ability to use seeding equipment normally used for agronomic applications. Currently, the ranges where RDX leaching poses a problem are subject to moderate rainfall and will already be heavily vegetated (Clausen et al., 2004).

5.1.3.7 Status of Plant-based Mitigation Demonstrations at Training Ranges

At present, plant-based mitigation has not been subjected to large- or full-scale evaluation in the field at training ranges. Thus, there is no operational data to assess how well it would actually work at reducing the leaching or runoff from RDX-contaminated zones or detailed cost data.

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5.1.4 *Ex Situ* Soil Management

Compost windrow being turned by a windrow turner at Plum Brook Ordnance Works, Sandusky, Ohio (USACE, 2011).

Description: The practice of excavating soil containing energetic chemicals and mixing it with a degradable carbon source, microorganisms, and/or nutrients in an aboveground pile, windrow, or reactor. The technologies rely on biological processes to transform the contaminants, generally to break down the energetic chemicals to intermediates that can be mineralized or bound irreversibly to the organic material in the soil.

Where It Can Be Used: These *ex situ* technologies have primarily been used to manage small volumes of heavily-contaminated soil, such as those found at ammunition plants and explosive manufacturing sites. They might have utility in areas where small volumes of soil have been impacted by low-order detonations or where repeated detonations occur.

Advantages: By excavating the impacted soil and managing *ex situ*, the risk of dissolution and migration of the energetic chemicals is eliminated.

Disadvantage: These technologies have typically been applied to smaller volumes of heavily-impacted soil. To manage larger volumes of less contaminated soils would likely require process changes in some cases. Implementation of these *ex situ* approaches requires that the soil be excavated prior to management, something that may be dangerous when working in areas with unexploded ordnance (UXO). With the bioslurry technology, the slurry requires dewatering prior to disposal, which adds to the overall management cost.

Cost Information: Cost estimates for the *ex situ* technologies discussed in this section are as follows:

- Windrow composting – $206–$1,025/ton soil
- Bioslurry reactors – $309/ton soil
- Biopiles – $205/ton soil
- Landfarming – $90–$150/ton soil

Recommendation: **These technologies are recommended primarily for high-concentration, low-volume applications at sites where the soil can be excavated. These *ex situ* approaches may have application at demolition ranges where repeated use has resulted in fairly high concentrations of energetic chemicals in a fairly small volume of soil or at hand grenade ranges (HGRs).**

Key Resources:

Jerger DE, Woodhull PM. 2000. Applications and Costs for Biological Treatment of Explosives-Contaminated Soils in the US. In Spain JC, Hughes JB, Knackmuss H-J (eds) Biodegradation of Nitroaromatic Compounds and Explosives. Lewis Publishers, Boca Raton, FL, USA. Chap. 14.

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5.1.4.1 Composting

Composting was the first biological process approved for the treatment of soils contaminated with energetic compounds (Craig et al., 1995). It was investigated in the 1980s and 1990s as an alternative to incineration for the treatment of heavily-contaminated soils from ammunition plants and depots.

Composting is an *ex situ* process where contaminated soils are excavated and mixed with a bulking agent and a readily degradable organic amendment. It is a controlled biological process where organic contaminants are converted by microorganisms under both aerobic and anaerobic conditions to innocuous stabilized products. Generally, composting is a self-heating, thermophilic process that is maintained at temperatures between 54 degrees Celsius (°C) and 65°C for the destruction of organic contaminants.

The amendments used for composting have varied depending on the part of the country where the process is used. Some amendments that have been used include wood chips; sawdust; straw; both vegetative and animal wastes, such as various manures; and food processing wastes including corn, apple, and potato waste. Figure 5-4 shows the construction of compost windrows by creating consecutive layers of contaminated soil and straw amendment. The process requires either continuous or periodic aeration and processes have been engineered utilizing static piles with aeration or windrows where the compost is placed in long, trapezoidal piles and periodically turned.

Figure 5-4. Straw placement at Plum Brook Ordnance Works, Sandusky, Ohio (USACE, 2011).

The degradation of 2,4,6-trinitrotoluene (TNT) that occurs during composting has been studied extensively (Lewis et al., 2004). When radiolabeled TNT was studied, it was found that TNT is not mineralized by this process, but rather it was humified (Pennington et al., 1995). That is, TNT is partially transformed to a variety of amino-containing compounds that then bind to natural organic matter from the organic amendments (Thorn and Kennedy, 2002). Hexahydro-1,3,5-

trinitro-1,3,5-triazine (RDX) is also treated effectively by composting, as is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), but HMX degradation is slower, thus requiring longer treatment times.

One of the earliest uses of composting for treatment of energetic compounds in soil was at Umatilla Army Depot in Oregon. The largest use of composting for energetic compounds was at the Joliet Army Ammunition Plant (AAP) in Joliet, Illinois. Here, 200,000 dry tons of soil contaminated with TNT, dinitrotoluene (DNT), tetryl, and a small amount of RDX was composted starting in 1999 (Lewis et al., 2004). Composting has been used successfully at a number of other Army and Navy sites (USACE, 2011).

Composting has been effective at substantially reducing or eliminating energetic contaminants from soil. In a field demonstration, TNT concentrations were reduced from 11,840 milligrams per kilogram (mg/kg) to 3 mg/kg after the 153-day test at the Louisiana AAP, Louisiana (Williams et al., 1992). Similarly, nitrocellulose (NC) concentrations were reduced from 4,933 mg/kg and 3,039 mg/kg, to 133 mg/kg and 54 mg/kg in two batches after 100 days at Badger AAP, Wisconsin.

Costs of windrow composting have been estimated at $206–$766/ton of contaminated soil (Craig et al., 1995) and from $84 to $1,025/ton (USACE, 2011). These costs appear to be too high for routine use of composting at military training ranges. Composting is best used for small volumes of heavily-contaminated soils. At many ranges, much larger volumes of soil might need to be managed, and the concentrations will generally be much lower. Composting also requires that soils be excavated—something that may be dangerous when working in areas with unexploded ordnance (UXO)—and the volume of treated soil is about twice the initial volume due to use of large masses of amendments. There might be a few applications where composting could be used at ranges. One application might be at demolition ranges where repeated use has resulted in fairly high concentrations of a variety of energetic contaminants in a fairly small volume of soil. Depending upon what other contaminants are present, the treated soil can often be returned to the excavated site.

5.1.4.2 Bioslurry Reactors

Another biological process that has been used to destroy nitroaromatic and nitramine explosives in soil is the bioslurry reactor. Contaminated soil is mixed with water, a readily degradable source of organic carbon, and nutrients in a reactor, often a concrete basin. The microbes rapidly degrade the carbon source consuming the oxygen in the water and create an anaerobic environment that is conducive to the reduction of the nitro groups on TNT. The nitro groups are sequentially reduced to amino functions that rapidly bind irreversibly to soil organic matter. Sometimes the system is aerated at the end of the process and this presumably causes the bound material to become even more irreversibly bound (Lewis et al., 2004). RDX, HMX, and other nitroaromatics, such as 2,4-DNT, are also degraded or bound.

Several commercial processes utilizing this process have been developed. The first was a proprietary process called the SABRE™ process, developed by J.R. Simplot as a full-scale process to treat explosives-contaminated soils. In this process, waste from a potato manufacturing process is mixed with a phosphate buffering agent and nitrogen containing fertilizers in a slurry with contaminated soil. The system is initially mixed and then allowed to incubate to create anaerobic conditions, usually in a lined lagoon or a tank reactor. The process takes weeks to achieve adequate treatment, and because it is not self-heating like compost, the rate of treatment is reduced because it takes place at lower temperatures. The University of Idaho

Research Foundation now owns the license for this process and it has been renamed the FAST™ process.

Other similar non-propriety processes have been developed as well. The U.S. Army Environmental Command (AEC) developed an aerobic/anoxic bioslurry process that was demonstrated in the field at Joliet AAP (Jerger and Woodhull, 2000). The study revealed that the process is very temperature sensitive and the rate of reaction slows below 20°C. In addition, the process requires a readily degradable cosubstrate, such as molasses, and an aerobic-anoxic sequence.

The cost of the slurry reactor process using SABRE™ has been estimated at $309/ton of contaminated soil for treating 25,000 tons (Jerger and Woodhull, 2000). It is an *ex situ* process and shares some of the limitations discussed above for composting with regard to use for residue destruction at ranges. The slurry generally will require dewatering at the end of the process, which adds to the cost of the process. Like composting, it is best used for high-concentration, low-volume applications. Overall, bioslurry reactors have only a limited application to energetic residues on ranges.

5.1.4.3 Biopile

The biopile is a biologically-based technique that has often been used for treatment of petroleum-contaminated soils. In this technology, the contaminated soil is excavated and mixed with soil amendments and placed on an impermeable liner to prevent the risk of leachate contaminating uncontaminated soil.

A biopile technology that was developed to treat explosives-contaminated soil is based on the use of wood decay fungi, often called white rot fungus. In this process, the soil is excavated and mixed with the fungal inoculum, and a variety of amendments such as sawdust, straw, or cottonseed husks. The material is formulated into a pile instrumented with a forced-aeration system to provide adequate oxygen for the process (Jerger and Woodhull, 2000).

Treatability studies of this process were conducted by EarthFax Engineering (Midvale, Utah) for TNT-contaminated soils at Mead AAP, Nebraska, and for TNT- and tetryl-contaminated soils at Joliet AAP, Illinois. Differences in the extent of treatment were found at Mead AAP depending on the specific inoculum used. TNT and tetryl concentrations were reduced substantially at Joliet AAP. This treatment did not result in mineralization of the TNT or tetryl, and laboratory studies indicated that the rapid decrease in TNT and tetryl concentrations was due to reduction of one ring nitro group (Jerger and Woodhull, 2000) presumably followed by immobilization by chemisorption to organic matter in the pile. The cost of this technology was estimated at $20/ton of contaminated soil. As with composting and bioslurry, this technology appears to have limited application to energetic residues at training ranges except for small ranges, such as hand grenade ranges (HGRs).

5.1.4.4 Land Farming

Land farming is another biologically-based technology that is similar to composting in that the contaminated soil is mixed with bulking agents and nutrients. It has found successful use for the treatment of petroleum-contaminated soils.

Grace Bioremediation Technologies developed a land farming technology called the DARAMEND® process. This process can be used in an *in situ* or *ex situ* mode. The contaminated soil is mixed with a proprietary amendment containing an organic substrate, zero-valent iron

(ZVI), and water to produce anoxic conditions. The mixture is allowed to stand unaerated for about a week and then it is tilled to aerate the soil. This amounts to one cycle of the process and this anoxic-oxic process is repeated a number of times until the treatment goals are met.

Full-scale use of the DARAMEND® process has been applied for treatment of explosives-contaminated soil at several sites including Naval Weapons Station Yorktown, Virginia, and Iowa AAP, Iowa. The concentrations of TNT, RDX, 2,4-DNT, and HMX in the untreated soils at these two sites ranged from 96 to 15,359 mg/kg. The treatment process reduced the contaminant concentrations to 14 mg/kg TNT and 1.6 mg/kg RDX at Naval Weapons Station Yorktown and to 8 mg/kg TNT and 16.2 mg/kg RDX at Iowa AAP.[20] The treatment costs reported by the vendor ranged from $90 to $150/ton.

Here again, this technology seems to have limited application for management of energetic residues on ranges, except perhaps soils from HGRs.

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5.1.5 Use of Fire to Destroy Energetic Particles on Surface Soils

Description: The use of controlled burning to reduce the mass of energetic residues present on range surfaces. Explosives such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are unstable at high temperatures and it appears that temperatures at the soil surface during range fires may be hot enough to destroy explosives deposited on the surface as particles from low-order detonations.

Where It Can Be Used: The amount of energetic residue reduction achieved is a function of the maximum temperature achieved and the duration of that temperature. The levels of available fuel will determine these parameters. For most sites, the native mass of vegetation present will be insufficient to achieve these conditions and additional fuel will be needed.

Advantages: Energetic residues present at the surface can be destroyed using this technique as well as any energetic residue present in aboveground vegetation. Large pieces of residue that would be present just after the occurrence of a low-order detonation appear to be consumed by fire to a greater extent than small particles on the soil surface.

Challenges/Disadvantages: For most sites, additional fuel will have to be supplied to the site. How feasible this might be for a given location and range size is very site-specific. In general, subsurface residues will be minimally affected. If the temperature developed in the burn is insufficient to destroy the residues, melting and downward transport of TNT and perhaps other analytes associated with the TNT is possible. Obtaining regulatory approval for a controlled burn may present challenges due to air emission concerns.

Cost Information: Not available. Full-scale controlled burns have not been implemented for the purpose of destroying explosives residues at training ranges.

Recommendation: **This technology has the potential to reduce energetic residues at impact ranges and antitank rocket range firing points. This approach is one of the few technologies that could be implemented fairly easily over a large area, such as at an artillery or bombing range. It could be used in conjunction with some form of plant-based mitigation technology to destroy energetic compounds that have been taken up into plants.**

Key Resources:

Battelle, Integrated Science and Technology, Inc., University of Rhode Island. 2006. Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges. SERDP CP-1305 Final Report. Prepared for the SERDP, Arlington, VA, USA. Available at http://www.serdp.org/, accessed March 14, 2014.

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5.1.5.1 Technology Description

Fire ecology is the science of the use of fire to manage vegetation in ecosystems (Battelle et al., 2006). Wildfires at training range impact areas are a fairly common occurrence, being initiated by detonations of various types of ordnance in dry, vegetated areas. In addition, controlled burning has been used at training ranges for a variety of purposes to include safety clearance prior to destruction of unexploded ordnance (UXO), wildfire avoidance, and plant and wildlife management. Thus, it appears the implementation of this management technology is possible, even for large ranges. To avoid uncontrolled range fires, environmental conditions should be critically evaluated prior to initiating controlled burns.

Explosives such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are known to be unstable at high temperatures (Oxley et al., 1994; 1995), and it appears that temperatures at the soil surface during range fires may be hot enough to destroy explosives deposited on the surface as particles from low-order detonations, or in near-surface soils. Because of the frequent detonations that occur in areas where residues are deposited on ranges, the vegetation may be sparse in these areas. Additional fuel will often be required to sustain an effective burn across the areas with the highest amounts of explosives residues present.

Some of the important questions regarding the use of fire to destroy explosives residues include the following:

- What are the temperatures required to destroy the various energetic chemicals, such as TNT, RDX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), nitrocellulose (NC), and nitroglycerin (NG)?
- What are the oxidation products and are any undesirable organic transformation products produced from burning of explosives?
- Are sufficient temperatures achieved for a long enough time to achieve significant destruction at the surface and at depth?
- Does melting and downward transport of explosives occur during burning (melting points for TNT, RDX, and HMX are 80.1°C, 205°C, and 286°C, respectively)?
- Is the amount of additional fuel placed on the soil surface critical to achieve effective explosive destruction?

Certainly, fire will destroy any energetic compounds that have been taken up into the aboveground portion of vegetation that is subsequently consumed in a fire, but until recently, the impact of fires on the concentrations of energetic compounds on the surface or the shallow subsurface soil had not been investigated.

In order to destroy the energetic compounds, the temperature must be sufficiently high to ignite the various military formulations. Results from bench-scale pan studies show that Composition B began to melt at 93.3°C and combusted at 171°C (Price and Bourne, 2011). Battelle et al. (2006) conducted laboratory studies and found that the critical temperatures for the destruction of RDX and TNT were 175°C and 250°C, respectively. Thus, if the location where these compounds are present was maintained at or above these temperatures, rapid destruction of RDX and TNT would occur.

5.1.5.2 Technology Demonstrations

Destruction of Energetic Compounds Without Added Fuel

Price and Bourne (2011) report the results of a small-scale study using 1.2-meter (m) x 4.9-m test plots that had been seeded with *Schizachyrium scoparium* (little bluestem, a North American perennial prairie grass) and allowed to grow for one season. The study investigated whether energetic compounds would be destroyed if an area vegetated with dried grass was burned. They placed 0.5–2-gram (g) chunks of Composition B on the surface of the dried plot and placed a wind tunnel on the plot and the plot was burned. Samples collected before and after burning indicated a 72% net mass loss of Composition B from the soil surface, presumably by burning. Soil analysis indicated the parent compounds—RDX, TNT, and HMX—were present in soil where exposure of the Composition B particles to heat only resulted in slight melting of the particle. Where combustion of Composition B was complete, residual concentrations of RDX, TNT, HMX, and degradation products hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), and 2-amino-4,6-dinitrotoluene (2-ADNT) were present.

Following the pilot-scale tests, field tests of prescribed burning were conducted by the U.S. Army Engineer Research and Development Center (ERDC) at Fort McCoy, Wisconsin; Fort Pickett, Virginia; Fort Stewart, Georgia; and Camp Shelby, Mississippi. The tests included various vegetative cover types and variations in plant densities. Composition B particles were emplaced at the Fort McCoy field test location, while M10 propellant particles were used as a surrogate for Composition B at the remaining three field test locations. The percent of Composition B or M10 propellant lost to combustion was 79–96% (Fort McCoy), 88% (Camp Shelby), 88–100% (Fort Pickett), and 100% (Fort Stewart) (Price and Bourne, 2011). Concentrations of the parent compounds or degradation products in the soil were not reported for the field test studies.

At Fort Lewis, Washington, a wildfire burned the grass-covered area behind the live-fire and subcal firing points of an antitank firing range in June 2009. The concentration of NG in the live-fire and subcal areas had been characterized in June 2006, and the average concentration was 936 milligrams per kilogram (mg/kg) (relative standard deviation [RSD] = 15%) and 629 mg/kg, respectively (Jenkins et al., 2007). The areas were used for live-fire or subcal practice with light antitank weapon (LAW) and AT-4 rockets for the three years after characterization and before the burning took place. During training, small particles of unburned propellant containing NG are deposited on the surface behind the firing line. Before the wildfire took place in June 2009, Roote et al. (2010) sampled the area behind the firing area where subcal training had taken place and the concentration of NG had increased to 863 mg/kg, a 37% increase after three years of training. After the wildfire burned both areas, Roote et al. (2010) sampled the live-fire area in July 2009. The concentration of NG was estimated at 1,640 mg/kg, a 75% increase over 2006, even after the burn took place. *MULTI INCREMENT*® sampling (MIS) was conducted in both 2006 and 2009, with analysis using SW846 Method 8330B (USEPA, 2006). While it is not possible to estimate the percent destruction that occurred due to the fire, clearly the loss of NG had to be small. It does not appear that the wildfire consumed a great deal of the NG present in small particles of propellant on the surface at this range.

Destruction of Energetic Compounds with Added Fuel

The laboratory portion of a study conducted by Battelle (2005) and Battelle et al. (2006) found that rapid decomposition of RDX and TNT occurred at 175°C and 250°C, respectively. The gases produced were nitrogen (N_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrous oxide (N_2O),

and nitric oxide (NO) for both compounds. No organic transformation products from TNT were observed, but methanol, methyl formate, and dimethynitrosoamine were observed for RDX. In a subsequent experiment, however, Battelle et al. found that the dinitrotoluenes were observed when TNT in soil was heated to 250°C. It was also observed that TNT melted and moved downward into uncontaminated soil during this experiment.

In the field portion of the Battelle study, four different areas at Eglin Air Force Base (AFB), Florida, were studied. These included two target areas for air-to-ground practice, a washout area, and a blow hole used for demolition. Three different masses of fuel (pine straw), ranging from 2.3 to 7.6 tons/acre were placed by hand in these areas. Mechanical application was not used because of the presence of metallic debris and the possibility of encountering UXO. The sites were ignited by helicopter to minimize risks from UXO. The temperature at ground level during the burn was found to be above 175°C for 5.3, 6.5, and 5.3 minutes for the three levels of fuel, and above 250°C for 2.8, 5.6, and 3.5 minutes, respectively. The maximum temperature observed at 2.5 centimeters (cm) below ground surface (bgs) was only 96°C. Interestingly, the highest temperatures were obtained at the surface and in the subsurface for the medium level of fuel; apparently the additional fuel served to insulate the surface from the fire accruing above. Thus, the amount of fuel added appears to be critical to obtaining an effective burn.

The concentrations of TNT and RDX in the soil at the locations where the burning was conducted were insufficient to determine the level of destruction due to the burn. However, fortified soil ranging in depth from 1 to 3 cm was placed in glass dishes within the burn area before the burn was initiated, and pre- and post-burn analyses were conducted to determine the TNT and RDX removal. In general, little or no reduction in TNT and RDX was observed, but the authors postulated that oxygen limitations due to the glass sides and bottoms of the dishes prevented sufficient oxygen from being present during the burn (Battelle et al., 2006). Results obtained from soil columns placed within the same areas where the bottoms were open indicated that much higher reduction of TNT/RDX was obtained. No air monitoring data was reported for the field study.

Melting and downward movement of TNT was observed in migration columns. The percentage melted out of the 1.3 cm layer and transferred to below depth layers were 102%, 83%, and 25%, for the low, medium, and high fuel conditions, respectively. No similar melting and downward movement of RDX was observed. It should be emphasized, however, that the RDX in this experiment was pure and not a component of Composition B, as is most of the RDX residues at training ranges. It is unknown whether the TNT portion of Composition B would melt during burning and carry particles of RDX with it as it migrated downward.

Poulin et al. (2009) conducted a series of laboratory studies to investigate the destruction of NG in firing point soils behind an antitank rocket range firing point by burning using added fuel. First, laboratory studies were conducted using uncontaminated sand to determine the efficiency of penetration of heat during a controlled burn. A number of fuels were investigated including gelled ethanol, gelled methanol, wood shavings, ethanol soaked wood shavings, ethanol, methanol, and isopropanol. The highest burning temperature (191°C at 1 cm depth) was achieved using gelled ethanol (~1:1 percent by volume [v/v]). A temperature of 131°C (at 1 cm depth) was achieved using a 1.25-cm thick layer of gelled ethanol spread on top of the sand.

Next, laboratory studies were conducted with propellant-contaminated soil from an antitank rocket range firing point (Poulin et al., 2009). Trials included topically applied gelled ethanol and methanol, and ethanol gel that had been mixed into the top 1 cm of soil. Samples were collected before and after burning and the concentrations of NG obtained using SW846 Method 8330B. A

percent reduction of over 90% NG was achieved using the gelled ethanol that had been mixed into the top 1 cm of soil (~1:1 v/v), while a decrease of 53% and 76% in NG mass (two different trials) was observed when the gelled ethanol was placed directly on the soil surface, but not mixed into the top 1 cm of soil.

Poulin (2011) then conducted a small-scale field study of controlled burning using gelled ethanol at an antitank firing range firing point at the Wellington Range at Canadian Forces Base (CFB) Gagetown. This range has been used for target practice with 84-millimeter (mm) and 66-mm antitank rockets for 40 years (yrs).

A set of 1 m × 1 m plots located behind the antitank rocket firing point were designated and gelled ethanol was used for fuel. For some of the plots, the ethanol was poured directly on the undisturbed soil surface, and for others, the soil was tilled to a 5 cm depth. For some plots, the ethanol was mixed within this tilled layer and for others the ethanol was poured on top of the tilled soil. After burning, multi-increment samples were collected from each plot, then the soil samples were mixed, subsampled, and the subsamples analyzed by SW846 Method 8330B.

The results of this study are shown in Table 5-3. The percent destruction was much greater in the surface soil than soil from a 2-cm depth. Tilling the soil appeared to improve the destruction efficiency of NG for the surface soil, an increase from about 50% to the mid-80%s, but the results were so variable for the subsurface that a conclusion is not possible in this case. A larger scale field study is planned to complete this work.

Table 5-3. Removal of NG in Soil Samples after Application of Gelled Ethanol and Burning at Small Scale Field Study at CFB Gagetown Antitank Rocket Range (Poulin, 2011).

Experiment	Surface Soil (0–1 cm)			Subsurface Soil (2 cm depth)		
	% Reduction (Range)	% Reduction (Mean)	% Reduction (%RSD)	% Reduction (Range)	% Reduction (Mean)	% Reduction (%RSD)
Gel poured on surface	25–80	50	30	-14–56	20	30
Soil tilled to 5 cm and gel mixed in	85–89	87	3	31–51	40	10
Soil tilled to 5 cm and gel poured on top	83–86	84	2	21–25	23	3

Conclusions from the Burning Studies

These studies indicate that controlled burning can reduce the mass of energetic residues present on range surfaces. The amount of reduction is clearly a function of the maximum temperature achieved and the duration of that temperature. The levels of fuel available will determine these parameters. For most sites, the native mass of vegetation present will be insufficient to achieve optimum conditions and some additional fuel will have to be supplied. How feasible this might be for a given location and range size is very site-specific.

Residues present at the surface can be destroyed using burning techniques. Large pieces of residue that would be present just after the occurrence of a low-order detonation appear to be consumed in the fire to a greater extent than small particles on the surface. In general,

subsurface residues will be minimally affected. If the temperature developed in the burn is insufficient to destroy the residues, melting and downward transport of TNT and other analytes that are associated with the TNT is likely. For example, a subsurface layer of TNT was discovered during soil sampling at one location in the burning grounds at Ravenna Army Ammunition Plant (AAP), Ohio (T.F. Jenkins, personal communication). This TNT had melted during burning activities and recrystallized as a TNT layer in the subsurface.

To our knowledge, full-scale controlled burns have not been implemented for the purpose of destroying explosives residues at training ranges. Burning activities are conducted routinely for a variety of other reasons at many large ranges, but the impact on residue concentrations has not been studied. Planning and implementation of prescribed burns must be consistent with DoD and Component instructions and policy (DoD, 2011, and Component-specific instructions) and integrate applicable state and local permit and reporting requirements. Additionally, prescribed burns in areas likely to contain UXO will need to satisfy additional safety requirements.

The use of control burns in conjunction with plant-based mitigation is also an alternative. RDX and HMX have been shown to be taken up and translocated within plants to the leafy portions of the plant (see Section 5.1.3). Burning these areas would very likely destroy the explosives incorporated into these plants.

5.1.5.3 Cost Information

There appears to be no cost information available for the use of this technology for range maintenance.

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5.1.6 Onsite Residue Collection and Destruction

Ruptured 155-millimeter (mm) round at Fort Bliss, New Mexico; the red chunks in front of the round are 2,4,6-trinitrotoluene (TNT) (from Jenkins et al., 2005).

Description: The practice of collecting and destroying chunks of energetic chemicals at ranges by explosive ordnance disposal (EOD)/unexploded ordnance (UXO) personnel to reduce the mass of energetic residues in source zones thereby preventing their dissolution and migration.

Where It Can Be Used: Currently, the collection and destruction of chunks of energetic chemicals have not been implemented for environmental purposes. Some of the Military Services conduct routine range clearance activities to destroy UXO items present on the surface. Sometimes during clearance activities, large chunks of energetic compounds are collected and detonated to remove explosive hazards from these ranges. These activities are not designed to reduce energetic residues at ranges, but have that effect as a side benefit.

Advantages: The major advantage of this approach is its effectiveness in reducing the mass of energetic residues in source zones. Collecting large pieces of residue and destroying it using an explosive charge or in another manner is the least expensive means of preventing the dissolution and migration of the residues. A few large chunks of residue that contain 1 kilogram (kg) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), when dissolved, has the potential to contaminate 500 million liters (L) of water to 2 micrograms per liter (µg/L) (U.S. Environmental Protection Agency [USEPA] health advisory), assuming no natural attenuation occurs.

Disadvantage: Several U.S. Department of Defense (DoD) and Service Instructions currently prevent or limit the ability of EOD personnel to remove energetic residues from ranges during operational range clearance activities.

Cost Information: Not available.

Recommendation: **Recommended for the management of energetic residues at artillery, mortar, bombing, and antitank rocket range impact areas. Implementation would require modifications to current DoD and Service policy.**

Key Resources:

Brochu S, Thiboutot S, Lewis J, Ampleman G, Brousseau P. 2004. Estimation of the Quantity of Explosive Residues Resulting from the Detonation of Unconfined Explosives Charges. In Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 4. ERDC TR-04-4. U.S. Army ERDC, Vicksburg, MS, USA. Chapter 7.

Jenkins TF, Thiboutot S, Ampleman G, Hewitt AD, Walsh ME, Ranney TA, Ramsey CA, Grant CL, Collins CM, Brochu S, Bigl SR, Pennington JC. 2005. Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges. ERDC TR-05-10. U.S. Army Engineer Research and development Center, Vicksburg, MS, USA. November.

Thorne PG. 2004. On-Range Treatment of Ordnance Debris and Bulk Energetics Resulting from Low-Order Detonations. SERDP Final Report CP-1330. Prepared for SERDP, Arlington, VA, USA. Available at http://www.serdp.org/, accessed March 14, 2014.

5.1.6.1 Technology Description

When low-order detonations occur, residue is deposited as pure explosive over a relatively small area in particle sizes ranging from micrometers (µm) to centimeters (cm) (Taylor et al., 2010). The largest mass is initially contained in the larger particles and any residue remaining in the ruptured casing. Over time, sunlight, rainfall, and temperature cycling fractures these larger particles into smaller and smaller ones. The dissolution rate for these residues is a function of particle size, so the smaller the particles become, the faster they can dissolve into precipitation.

At present, the only personnel authorized to pick up and destroy chunks of residue on U.S. Department of Defense (DoD) training ranges are explosive ordnance disposal (EOD) technicians. These highly-trained individuals are in short supply in the military and the use of active duty EOD technicians for routine environmental cleanup is not possible at present.

As part of some of the routine range clearance activities conducted by the Military Services, unexploded ordnance (UXO) items present on the surface are destroyed. Sometimes during clearance activities, large chunks of energetic compounds such as 2,4,6-trinitrotoluene (TNT), Composition B, Tritonal, and Composition H6 are collected and detonated to remove explosive hazards from these ranges. These activities are not designed to reduce energetic residues at ranges, but have that effect as a side benefit.

The percentage of destruction of chunks of explosives residues when they are detonated with Composition C4 (C4) is difficult to estimate. To our knowledge, the only research on the destruction efficiency for unconfined residues was conducted by Brochu et al. (2004). In their research, different shapes of C4 (spheres, cylinders, blocks) and cylinders of TNT, PBX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were detonated with a #12 detonator, and the resulting residue estimated by collection on witness plates. The work indicated that residue deposition was low in all cases, but that the shape of the charge made a difference. The block of C4 produced the largest percentage of residue deposition. It is difficult to extrapolate these results to the case where a block of C4 is used to detonate a pile of explosive chunks, but it does suggest that if high-order detonation is achieved, the residue deposition will be small, thus making this a useful technique for the destruction of residues on ranges.

There has been some research on the use of a chemical approach for the destruction of chunk residues (Thorne, 2004). The on-range process would begin by decomposing the energetic compounds in hot, aqueous solvent causing the solid explosive to lose their bulk properties and form a slurry. The next step in the process would be to hydrolyze the slurry by adding it under controlled conditions to a strong aqueous base. The waste solution from the hydrolysis could then be fed to a thermal gasification system that completely destroys the organic explosives, producing only releasable gases and steam. One advantage of this technique is that it can be completed within the boundary of the range, thus negating the need to transport explosives off-range. This approach might not be useful for energetic formulations containing aluminum such as Tritonal and Composition H6, however, due to production of hydrogen gas by reaction with strong base.

The use of this technique for residue management would be most effective if it was implemented soon after a low detonation occurred. It is currently difficult to keep track of the number and locations of low-order events during training events. One idea that has been suggested, and in which some research has been conducted, is to use a combination of

acoustic/seismic signatures to pinpoint the locations of these events (Anderson and Weale, 2006). This would be particularly useful for large ranges, such as artillery or bombing ranges.

5.1.6.2 Cost and Ease of Implementation

The cost and ease of implementing a residue collection/destruction program designed for environmental sustainability of a range is unknown at this time. Data on residue collection/destruction activities performed to address safety concerns should be available from the EOD community. The cost and ease of implementation of a residue collection/destruction program designed for range environmental sustainability could be estimated from such data.

5.1.6.3 Limitations and Recommendations

Several DoD and Service Instructions prevent or limit the ability of the EOD personnel to remove energetic residues from ranges during operational range clearance activities. For example:

- DoD Instruction 3200.16 (Operational Range Clearance, June 13, 2005) excludes the "removal, treatment, or remediation of chemical residues or munitions constituents from environmental media" from the definition of "range clearance."
- Marine Corps Order (MCO) 3550.12, Operational Range Clearance Program (August 21, 2008) states that "range clearance does not include treatment or remediation of chemical residues or munitions constituents from environmental media, actions to address buried or discarded military munitions (e.g., burial pits), nor management programs to prevent the migration of munitions constituents off operational ranges."
- The Navy's Operational Range Clearance Policy states that "the term range clearance does not include removal, treatment, or remediation of chemical residues or munitions constituents from environmental media, nor actions to address discarded military munitions (e.g., burial pits) on operational ranges." (OPNAVINST 3571.4 [N4 3], October 9, 2009).
- Air Force Instruction 32-3001 (EOD Program, June 2011) states that the "AF EOD Program is neither equipped, trained, nor manned for environmental requirements-based response actions."

Clearly, the collection and destruction of chunks of energetic chemicals at ranges by EOD personnel for the management of energetic residues is disallowed at present. However, during routine range safety clearance activities at bombing range impact areas, Air Force EOD destroys UXO and does pick up and destroy chunks of explosive residues by detonation using C4 (Thomas Jenkins, personal observation). While this is not intended as environmental management, it does have that as a side benefit.

In order to use this technique for routine range management, personnel other than EOD would have to be allowed to do the work on active ranges. UXO technicians are available through a number of UXO contractors and these personnel are either retired EOD or graduates of a UXO Technician Training program. These individuals conduct similar operations on closed ranges and should be fully competent to conduct these maintenance activities. Clearly, this approach would be the most successful if implemented after some sort of wide range screening technology was used to identify the areas of a large range where low-order detonations have occurred, or even better, if a technology was available to pin point the locations of low-order detonations as they occurred. As with other management approaches requiring physical access to the ranges, and

perhaps disruption of the soil surface, safety concerns must be paramount. Thus, residue collection activities can only be conducted after the area has been cleared by EOD or UXO personnel using magnetometers or other geophysical techniques. This is true even for HGRs where undetonated grenades can sometimes get buried within craters.

The major advantage of this approach to range management is the effectiveness in reducing the mass of energetic residues in source zones. Collecting large pieces of residue and destroying it using an explosive charge or in another manner is likely to be the least expensive means of preventing migration of residues. For example, a few large chunks of residue that contain 1 kilogram (kg) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), when dissolved, has the potential to contaminate 500 million liters (L) of water to 2 micrograms per liter (µg/L), assuming no natural attenuation occurs. The 2 µg/L concentration is the U.S. Environmental Protection Agency's (USEPA's) health advisory concentration for RDX (USEPA, 2011).

This approach does not require the installation of wells within the range or a detailed understanding of the direction of the plume. It could be implemented via a contract to companies that do routine UXO destruction on Formerly Used Defense Sites (FUDS) or other types of closed ranges and are thus familiar with the identification and destruction of UXO and surficial residues.

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DoD Instruction Number 3200.16 (June 13, 2005) Operational Range Clearance.

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5.1.7 Field-portable Burn Pan for Destruction of Excess Propellant Charges

Propellant burn pan test, Firing Point Neibar, Fort Richardson, Alaska, March 2011 (Walsh et al., 2011).

Description: Burn pans are portable devices that allow propellant charges to be loaded and burned in a controlled setting. When training with large-caliber weapon systems (e.g. howitzers, mortars), a full complement of propellant charges is issued with each round. However, the charges are seldom fully utilized during training. Excess propellant charges are disposed of by burning on the ground, which creates propellant residues.

Where It Can Be Used: Ranges where large caliber weapons are fired.

Advantages: Field disposal of excess propellants is an integral part of field artillery training. Use of burn pans increase the efficiency of propellant disposal and greatly reduce the deposition of explosives and heavy metals in soils. Portable burn pans allow troops to train as they fight without compromising range sustainability.

Limitations: Portable burn pans are designed for burning up to 120 kilograms of propellant charges. The turn-around time between batches is estimated to be less than 20 minutes.

Lead foil is used in some propellant charges as a de-coppering agent and may be of concern if released to the environment. Burn-pan studies conducted by the Defence Research and Development Canada-Valcartier (DRDC) using lead-containing propellants indicate that the majority of lead is contained in and around the burn pans (Thiboutot et al., 2012). It was estimated that less than 2% of the lead was volatilized and released to the air. Additional tests examining the fate of lead during burn pan operations are underway by researchers at the U.S. Army Cold Regions Research and Engineering Laboratory.

Maintenance: Periodic inspections are recommended to verify the structural integrity of the burn pans (e.g., no structural warping or corrosion has occurred). It is recommended that the burn pan is emptied after each burn event. This allows for proper documentation of the propellants burned and aids in proper labeling of the waste residue. Users are advised to contact the installation hazardous waste manager to determine appropriate handling and disposal procedures for the residue.

Cost Information: The cost to construct the portable burn pan is estimated at $5,000 with a predicted unit life of 20 years based on material selection and proper use. Additional cost considerations include the maintenance of the burn pans, safety training, and periodic soil sampling/analysis and air monitoring if deemed necessary.

Recommendation: **Recommended for the management of energetic residues at ranges where large caliber, indirect-fire weapon systems are used.**

Key Resources:

ESTCP. 2012. Fact Sheet: A Portable Burn Pan for the Disposal of Excess Propellants. ESTCP ER-201323. http://www.serdp.org, accessed March 14, 2014.

Thiboutot S, Ampleman G, Pantea D, Whitwell S, Sparks T. 2012. Lead emissions from open burning of artillery propellants. In Longhurst JWS, Brebbia CA, eds, Air Pollution XX, pp 273-284. Volume 157 in WIT Transactions on Ecology and the Environment, published by WIT Press, Southampton, U.K.

U.S. Army National Guard. 2012. Best Management Practices for Army National Guard Operational Ranges: Burn Pans Fact Sheet. Provided by the Army National Guard and URS Group, Inc.

Walsh MR. 2013. U.S. Army ERDC-CRREL, Hanover, NH, personal communication. July.

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Walsh MR, Thiboutot S, Walsh ME, Ampleman G, Martel R, Poulin I, Taylor S. 2011. Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges. ERDC/CRREL TR-11-13. U.S. Army ERDC-CRREL, Hanover, NH.

Walsh MR, Thiboutot S, Walsh ME, Ampleman G. 2012. Controlled expedient disposal of excess gun propellant. J Hazard Mat 219–220:89–94.

5.1.7.1 Technology Description

When training with howitzer or mortar munitions, a full complement of propellant charges is issued with each round. These charges are seldom fully utilized during training due to range restrictions and weapon system limitations. This results in the accumulation of unused propellant charges. The ammunition supply point does not want the unused propellant charges returned due to safety and quality concerns, and it is common practice to burn the excess propellant charges on the ground at firing points following the training activity.

Propellant charges contain materials that are detrimental to the environment. The propellants are largely composed of nitrocellulose and most contain smaller amounts of 2,4-dinitrotolune, nitroglycerin, or nitroguanidine. In addition to organic compounds, some propellant charges incorporate a lead foil, which is used as a decoppering agent for gun barrels. These materials are found not only surrounding the firing positions but in the vicinity of existing fixed propellant disposal structures and propellant disposal locations (burn points) at the training sites.

Soil and snow sampling results from propellant disposal locations have shown that the current practice of burning excess propellant charges on the ground or in remote fixed burn pans is not effective. Up to 18% of the propellant remains unburned, and lead concentrations in soils can exceed 5,000 mg/kg (see Figure 5-5 and Walsh et al., 2010).

Figure 5-5. Example of burning excess propellant on the ground (left). Propellant residue remaining after burn is completed (right). Photographs provided courtesy of Michael R. Walsh, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H.

As part of the Strategic Environmental Research and Development Program (SERDP) project ER-1481, alternatives to the current propellant disposal practices were investigated. One alternative pursued was the improvement of the design of the fixed burn pan. Over the past several years researchers at Defence Research and Development Canada-Valcartier (DRDC) have optimized the design of a large fixed propellant burn pan. Testing of these structures indicates that the new design is successful in reducing residue deposition on soils from burning excess propellants and enables the collection of most of the unburned propellant compounds from within the pan (Thiboutot et al., 2011; Walsh et al., 2012). Use of the burn pan in Canada is now mandated by the National Defence Canada (Thiboutot et al., 2012).

In the United States, due to the doctrine of training as we fight and environmental restrictions on fixed disposal facilities, the collection and destruction of excess propellants at a centralized area is less desirable. Thus, an effort was initiated by the U.S. Army Cold Regions Research and

Engineering Laboratory (CRREL) to develop a smaller transportable version of a burn pan as a training aid for expedient use at firing points. Initial tests of this portable design were successful in substantially reducing propellant residue deposition but further development work was required.

Figure 5-6. Propellant burn pan test, Firing Point Neibar, Fort Richardson, Alaska, March 2011 (Thiboutot et al., 2011).

Field tests conducted by CRREL with prototype burn pan units at Canadian Forces Base Valcartier, Quebec and Fort Richardson, Alaska (see Figure 5-6) demonstrated that 99.9% of the combustible components of the propellant charges were destroyed within the pans. Less than 0.02% of the propellant material was recovered outside the burn pan and the recovered lead was largely contained within the pan (Walsh et al., 2012). These results indicate that the concept of a portable propellant burn pan is viable.

5.1.7.2 Technology Demonstrations

The field portable burn pan is being further refined and demonstrated under an ESTCP-funded effort (ESTCP ER-201323). The portable burn pan is a box-like structure with perforated sides integrated into an open-topped removable bonnet. The bonnet is made of perforated stainless steel and designed to prevent a chimney effect that could loft propellant charge constituents out of the pan and into the environment while containing charge debris within the burn zone. The lightweight aluminum base contains a removable stainless steel false bottom that protects the structure from the high heat developed during deflagration. The pan provides a dry, semi-enclosed platform that contains the debris (ash) from the propellant burn for easy removal and treatment. The device is small enough to transport in a standard small military trailer and light enough to be handled by four or fewer personnel. The target propellant charge load capacity will be in the 120 kg range for a full-size unit. The portable device can be transported to the training site, enabling troops to burn excess propellant following training without having to

transport the charges to a central burn facility, thus reducing transportation hazards. Currently, no portable burn devices exist in the United States military inventory. The performance objectives for the ESTCP demonstration are a 99.9% reduction of the original combustible mass, less than 0.1% total propellant material remaining following the burn, and less than 0.01% of the original mass of propellant material recovered outside the burn pan. The performance objective for lead is less than 10% of the original mass ejected from the burn pan. Turnaround time for burns should be less than 30 minutes between loadings. In addition, integration of the pan into the standard training doctrine will be a major measure of success.

The initial test of the improved prototype was conducted at Camp Grayling, Michigan in 2013 at the invitation from the U.S. Army National Guard Bureau, the Camp Grayling Environmental Compliance Office, and the Ohio Army National Guard. (Figure 5-7) Results indicated that the project performance objectives were met with the exception of the lead, which was not a constituent of the propellant charges consumed in the tests (M.R. Walsh, CRREL, personal communication, July 2013, Walsh et al., 2013). A Final Report will be posted on the ESTCP web site in 2015. In the interim, information on this technology can be obtained by contacting Michael Walsh at ERDC-CRREL (Michael.Walsh@usace.army.mil).

Figure 5-7. Redesigned portable burn pan (left) prior to use. In use burning 65 kilograms of M1 propellant charges (right). Photographs taken at Camp Grayling, Michigan and are provided courtesy of Michael R. Walsh, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H.

5.1.7.3 Maintenance and Cost Information

The cost to construct the portable burn pan is estimated at $5,000 with a predicted unit life of 20 years based on material selection and proper use. Operations and maintenance costs include the cost of periodic inspections to verify the structural integrity of the burn pans (e.g., no structural warping or corrosion has occurred). It is recommended that the burn pan be emptied

after each burn event. This allows for proper documentation of the propellants burned and aids in proper labeling of the waste residue. Users are advised to contact the installation hazardous waste manager to determine appropriate handling and disposal procedures and costs for residue disposal. Additional cost considerations include the cost for conducting safety training and the cost of periodic soil sampling/analysis and air monitoring if deemed necessary

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Thiboutot S, Ampleman G, Pantea D, Whitwell S, Sparks T. 2012. Lead emissions from open burning of artillery propellants. In Longhurst JWS, Brebbia CA, eds, Air Pollution XX, pp 273-284. Volume 157 in WIT Transactions on Ecology and the Environment, published by WIT Press, Southampton, U.K.

Walsh MR, Walsh ME, Hewitt AD. 2010. Energetic residues from field disposal of gun propellants. J Hazard Mat 173:115-122.

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5.2 Groundwater/Surface Water Technologies

Several technologies are available to manage energetic compounds in groundwater and surface water. These technologies all were originally developed to treat contaminants such as fuel hydrocarbons or chlorinated solvents. Over the past few decades, field demonstrations and validations of their efficacy for energetic compounds have been performed.

Monitored natural attenuation (MNA) has been selected as the solution at numerous sites impacted with a variety of chemicals, including energetic compounds. Section 5.2.1 discusses the MNA process and the use of a novel approach—compound specific isotope analysis (CSIA)—to estimate the extent of degradation occurring.

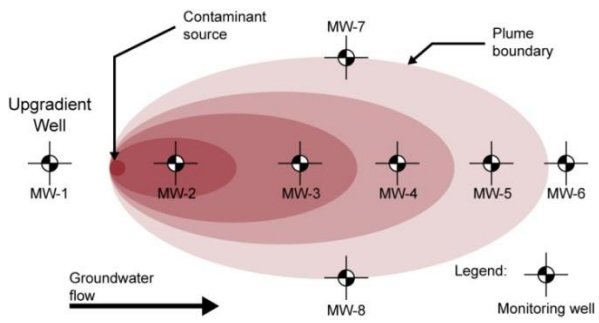
The passive *in situ* mitigation approach for groundwater was first implemented in the early 1990s primarily to treat chlorinated solvent groundwater plumes. Since that time, this *in situ* technology has evolved with the development of innovative reactive materials to treat different contaminants—including energetic compounds—and innovative construction methods. This approach can be used near source zones to reduce energetic chemical mass flux and act as a source zone management remedy or downstream from the source zone to protect downgradient receptors (Section 5.2.2).

Another *in situ* technology is active *in situ* management of groundwater. This approach involves the injection of an amendment in the subsurface to stimulate microbial growth and degradation of the energetic compounds. Section 5.2.3 describes the engineering approaches that can be used to implement active *in situ* management and the results from a recent field trial at an energetic-contaminated groundwater plume.

One of the oldest approaches used to manage impacted groundwater is to pump the contaminated groundwater aboveground followed by treatment. This is known as hydraulic control or containment. Section 5.2.4 discusses the ways hydraulic control can be implemented to manage training range issues: (1) for source control near the source of contamination to prevent long-term expansion of a plume or (2) for downgradient hydraulic control to prevent energetic chemicals from migrating past a boundary.

Constructed wetlands have been widely used to treat municipal wastewaters and a variety of other contaminated water streams. Section 5.2.5 discusses the different types of constructed wetlands and their applicability for managing energetic chemicals in groundwater or surface water.

5.2.1 Monitored Natural Attenuation (MNA)



Recommended groundwater well network for demonstrating MNA (Pennington et al., 1999 [source: USEPA, 1994]).

Description: Monitored natural attenuation (MNA) is defined by the USEPA (1999) as the "reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." Natural attenuation processes include physical, chemical, and biological processes such as dispersion, dilution, adsorption, and volatilization, abiotic transformation, and biodegradation.

Where It Can Be Used: MNA has been selected as the solution (or part of the solution) at numerous U.S. Department of Defense (DoD) sites impacted with chlorinated solvents, petroleum hydrocarbons, and energetic compounds, such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). However, the authors are not aware of instances where MNA was implemented to manage energetic chemicals in groundwater beneath an operational range.

Advantages: No active groundwater pumping or injection of treatment amendments or materials is required.

Disadvantage: This approach requires a thorough understanding of the plume's shape, information on the rate of release of the contaminant to the environment, and variable hydrogeological data. Gathering such data requires installation of monitoring wells throughout the plume. Analytical techniques, such as compound specific isotope analysis (CSIA), may be required to demonstrate and quantify the loss of energetic chemical mass due to biological processes.

Cost Information: Cost information and tools to use in developing site-specific cost estimates for MNA are available from a number of federal agency websites and associated documents (see resources provided below). Additional cost factors may need to be considered when implementing MNA on an operational range (e.g., unexploded ordnance [UXO] clearance costs).

Recommendation: **MNA should be considered as a management strategy at ranges with energetic chemicals in groundwater. It can be used at both large and small ranges, and when appropriate, it may be the least expensive approach to manage a significant groundwater plume of energetic contaminants.**

Key Resources:

http://www.epa.gov/ada/gw/mna.html, accessed March 6, 2014.

http://toxics.usgs.gov/definitions/natural_attenuation.html, accessed March 6, 2014.

Pennington JC, Zakikhani M, Harrelson DW. 1999. Monitored natural attenuation of explosives in groundwater. ESTCP Completion Report – Project CU-9518. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

5.2.1.1 Technology Description

Natural attenuation is defined by the ASTM (2003) as the “reduction in mass or concentration of a compound in groundwater over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as; biodegradation, dispersion, dilution, adsorption, and volatilization." Monitored natural attenuation (MNA) is defined by the USEPA (1999) as the “reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods.”

Initial work on natural attenuation for explosives was conducted by Pennington and co-workers at the U.S. Army Engineer Research and Development Center (ERDC) (Pennington et al., 1999a; 1999b; 2001) for the Strategic Environmental Research and Development Program (SERDP). Because there was no direct way to measure the extent of natural attenuation at the time, Pennington used the “lines of evidence” approach that had been developed by the Air Force Center for Engineering and the Environment (AFCEE) to demonstrate the natural attenuation of fuel hydrocarbons. These were:

1. Historical groundwater or soil chemical data that showed a clear trend of declining contaminant mass or concentrations at appropriate monitoring points.
2. Hydrogeologic or geochemical data that can be used to indirectly demonstrate the types of natural attenuation mechanisms that are active on the site.
3. Data from a field or microcosm study that demonstrates a specific natural attenuation process at the site that is able to degrade/stabilize the contaminants of concern.

Pennington et al. (1999a; 1999b; 2001) conducted their research at the Louisiana Army Ammunition Plant (AAP) and at the Joliet AAP in Illinois, where the major energetic contaminants of concern in groundwater were 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and the manufacturing impurities and environmental degradation products of TNT. Pennington’s study included: (1) an analysis of pre-project data from groundwater monitoring wells, aquifer soil samples collected using a cone penetrometer, and groundwater samples, (2) statistical analysis of this data, (3) determination of estimates of the natural assimilative capacity of the aquifer system to degrade the various energetic compounds, (4) identification of biomarkers, and (5) attempt to use stable isotope analysis of ^{13}C and ^{15}N and groundwater modeling. Biomarkers are various techniques that are used to detect whether biodegradation is involved in the transformation of various contaminants.

The conclusions from Pennington’s work at Louisiana AAP (Pennington et al., 2001) were that there were declines in explosives concentrations at a number of locations within the groundwater plume, but this was not correlated with any measured geochemical parameters. Mass transport limitations appeared to restrict the movement of energetic contaminants more than specific sorption to aquifer material. Biomarker studies indicated that the potential for microbial degradation was present, but that additional work was required to improve some of the biomarker approaches. Results from the stable isotope work indicated that ^{15}N measurements for energetic compounds in groundwater had potential for tracking the attenuation process (Miyares et al., 1999). Numerical models predicted a continued decline in contaminant concentrations. Overall, Pennington et al. (2001) concluded that “each site will require the careful development of a data set on which a decision to use MNA can be based.”

The use of MNA is an attractive option for energetic residues at training ranges; however, it requires locating and characterizing the source zones and installing groundwater monitoring wells near the source and both crossgradient and downgradient along the plume pathway.

RDX is the energetic compound that is the most mobile in groundwater plumes below sites with residues of energetic compounds. RDX may naturally attenuate in groundwater through either aerobic or anaerobic biodegradation (see Section 3.5).

Sampling and modeling conducted in support of an MNA approach can be used to predict whether concentrations of energetic compounds in groundwater will decline to acceptable concentrations before the groundwater leaves the boundaries of a military range and reaches off-range receptors. The approach demonstrated by Pennington et al. (2001), however, requires a knowledge of the plume's shape, information on the rate of release of the contaminant to the environment, and variable hydrogeological data to quantify biodegradation using modeling techniques (Bernstein et al., 2010). What was needed was a technique that directly measured the rate of biodegradation in the groundwater plume.

5.2.1.2 Use of Compound Specific Isotope Analysis (CSIA) to Quantify Extent of Degradation

Monitoring a reduction in the concentration of energetic compounds in a plume does not necessarily mean that the compounds are being degraded or stabilized. The observed reduction in concentration may be due to other processes, such as dilution or dispersion, or that the monitoring wells failed to adequately sample the groundwater plume. It appears that CSIA can provide the data needed to document that the observed reduction in contaminant concentration is due to biodegradation or abiotic transformation processes. When organic contaminants are degraded in the environment, the ratio of stable isotopes within these contaminants will often change, and the extent of degradation can be recognized and predicted from the change in the ratio of stable isotopes (USEPA, 2008). CSIA has been used to generate data to support an MNA approach for chlorinated solvents, petroleum hydrocarbons, and fuel oxygenates. The U.S. Environmental Protection Agency (USEPA) recently published general guidance on the use of CSIA to determine biodegradation rates (2008).

CSIA also has been used to quantify the biodegradation of RDX. Two stable isotopes of N (^{14}N and ^{15}N) are present in RDX, as well as two non-radioactive isotopes of O (^{16}O and ^{18}O). The ratios of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ for RDX change as RDX is degraded to form other compounds because the chemical bonds of the lighter isotopes are more readily cleaved than those of heavier isotopes. This results in the isotopic composition of the remaining mass of contaminant being enriched in the heavier isotopes.

Bernstein et al. (2008) reported on the use of CSIA of RDX in groundwater to obtain isotopic nitrogen and oxygen enrichment factors during biodegradation. Given appropriate stable isotope fractionation factors, and the respective stable isotope values of the contaminants in the field, it is possible to quantify the extent of biodegradation along a contamination plume. Using this approach, Bernstein et al. (2010) estimated the reaction rates for RDX bioremediation for a groundwater plume in Israel. Combined with an estimate of the transport rate of RDX in the aquifer, they estimated the first-order rate constants for biodegradation. Because it was uncertain whether the biodegradation was going via an aerobic or anaerobic process, rates of reaction were estimated for both processes. For their site, the half-life of RDX was computed to be between 4.4 and 12.8 years (yrs) in the upper 15 meters (m) of the plume if aerobic biodegradation was occurring, and between 10.9 and 31.2 yrs if anaerobic biodegradation was

taking place. The estimated half-lives in the deeper aquifer were an order of magnitude longer. Knowledge of the flow velocity of RDX in the plume was needed to make these estimates. For this site, the RDX flow velocity was between 20 and 45 m/yr. CSIA is a major breakthrough in developing an approach to generate the data needed to enable the use of MNA for sites with RDX in groundwater.

ESTCP is currently funding the development of a validated field method for evaluating RDX biodegradation using CSIA.[21]

5.2.1.3 Use of MNA for Application at Training Ranges

To date, the authors are not aware of any use of MNA for energetic compounds at U.S. Department of Defense (DoD) training ranges.[22] However, this approach, together with CSIA, has the potential to determine whether plumes of RDX or other contaminants will migrate to receptors at concentrations that will require more aggressive management strategies.

To use this approach, it is necessary to locate and quantitatively characterize major source zones and install groundwater monitoring wells along the projected plume. Groundwater samples will require analysis using a sophisticated isotope ratio mass spectrometer that is generally not available at most commercial environmental laboratories. Such equipment is available at some universities and government research labs.

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Pennington JC, Miyares P, Ringleberg D, Zakikhani M, Reynolds CM, Felt D, Coffin RB, Gunnison D, Cifuentes L, Fredrickson HL, Jenkins TF. 1999b. Natural Attenuation of Explosives in Soil

[21] http://www.serdp.org/; see ER201208

[22] A search of the USEPA National Priorities List (NPL) Record of Decision (ROD) database (http://cumulis.epa.gov/superrods/index.cfm?fuseac tion=main.splash) indicated that MNA has been selected as part of the selected remedy at a number of DoD energetic-contaminated sites. Examples include: (1) Shell Washout Wastewater Ditch, Building 700B, Aberdeen Proving Ground, MD (contaminants of concern [COCs]—TNT, 4-ADNT) (September 2010), (2) Picatinny Arsenal, Group 1 Sites, Response Action GW-2, NJ [COCs—TNT, RDX] (July 2010), and (3) Former Naval Ammunition Depot Sitewide Groundwater, Hastings, NE [COCs—TNT, RDX].

and Water Systems at Department of Defense Sites: Final Report. Technical Report SERDP–99–1. U.S. Corps of Engineers Waterways Experiment Station, Vicksburg, MS.

Pennington JC, Zakikhani M, Harrelson DW. 1999c. Monitored natural attenuation of explosives in groundwater. ESTCP Completion Report – Project CU-9518. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Pennington JC, Brannon JM, Gunnison D, Harrelson DW, Zakikhani M, Miyares P, Jenkins TF, Clarke J, Hayes C, Ringleberg D, Perkins E, Fredrickson H. 2001. Monitored natural attenuation of explosives. *Soil Sed Contam* 10:45–70.

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USEPA. 2008. A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA). EPA 600/R-08/148. USEPA Office of Research and Development, National Risk Management Research Laboratory, Ada, OK, USA. 82 p.

5.2.2 Passive *In Situ* Mitigation Approach for Groundwater

Installation of zero-valent iron (ZVI) passive *in situ* mitigation approach at Cornhusker Army Ammunition Plant (AAP), Nebraska (Johnson and Tratnyek, 2008).

Description: An *in situ* method for managing groundwater impacted by energetic chemicals that combines a passive chemical or biological zone with subsurface fluid flow management.

Where It Can Be Used: Soil is excavated and a wall of permeable material that reacts with the energetic chemicals in the groundwater is installed. The wall (amended zone) removes the energetic chemicals as the groundwater flows through the reactive zone. Both chemical and biological zones have been shown to be effective.

Advantages: The major advantage of the passive *in situ* mitigation approach is that the groundwater can be managed *in situ* with no pumping required and no disposal issues for the treated water.

Disadvantages: Can only be used with relatively shallow impacted groundwater with depths <40 feet. How long a specific reactive zone will function is difficult to predict at present.

Cost Information: Cost drivers for this technology are: (1) the depth of the impacted groundwater, (2) the required thickness of the reactive zone, (3) the mobilization costs for the trenching machinery, (4) disposal costs (if any) for the trench cuttings, (5) the width of the impacted groundwater plume, and (6) anticipated longevity of the reactive zone.

Capital costs for installing a full-scale ZVI PRB to treat explosives-contaminated groundwater at Cornhusker AAP, Nebraska were estimated to be $150/ft^2 of wall and annual operations and maintenance costs (to include monitoring) were $200K (ESTCP, 2008a). Unit costs for an *in situ* mulch biowall have been estimated at $0.08/gallon of contaminated groundwater treated over a 10-year period of operation (ESTCP, 2008b). This cost was based on data from a pilot-scale field demonstration of an *in situ* mulch biowall at Pueblo Chemical Depot, Colorado. For comparison, the investigators estimated a unit cost of $0.11/gallon of contaminated groundwater for ZVI PRB technology.

Recommendation: **Recommended for the management of shallow, narrow plumes of impacted groundwater. This would be particularly appropriate for managing impacted groundwater from hand grenade ranges (HGRs) and demolition ranges, and it could be used at antitank rocket ranges as well.**

Key Resources:

ESTCP. 2008a. Remediation of TNT and RDX in Groundwater Using Zero-Valent Iron Permeable Reactive Barriers. ESTCP Project No. ER-0223 Cost and Performance Report. April. 66 p.

ESTCP. 2008b. Treatment of RDX and/or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) Using Mulch Biowalls. ESTCP Project No. ER-0426 Cost and Performance Report. April. 47 p.

ITRC. 2011. Permeable Reactive Barrier: Technology Update. June.

Johnson R, Tratnyek P. 2008. Remediation of Explosives in Groundwater Using a Zero-Valent Iron Permeable Reactive Barrier. ESTCP Project No. ER-0223 Final Report.

5.2.2.1 Overview

A passive *in situ* mitigation approach consists of a permeable subsurface zone that is constructed with a reactive material to intercept and destroy (or immobilize) contaminants in groundwater. The purpose is to bring the contaminant and the specific reactant in contact under environmental conditions that lead to the removal of the contaminant from the subsurface plume. Typically, this approach is designed to operate in a hydraulically passive fashion so that contaminants flow through the zone without mechanical assistance. This approach has been used near source zones to reduce contaminant mass flux and act as a source zone management remedy, or it can be used downstream to protect downgradient receptors (see Figure 5-8) (ITRC, 2011). The major advantage is that contaminated groundwater can be managed *in situ* with no pumping required and no disposal issues for treated water. A major limitation is the depth of the plume. Since the reactive zone is generally established via trenching, only relatively shallow plumes (<40-foot [ft] depth) can be treated using this technology. Trenching equipment is available to establish 1.5-, 2-, and 3-ft-thick trenches in which the reactive material is placed. The 3-ft trenching equipment is much more expensive to use than the 2-ft equipment (Ahmad et al., 2007). Thus, if thicknesses >2 ft are desired, installation of parallel 2-ft walls is recommended.

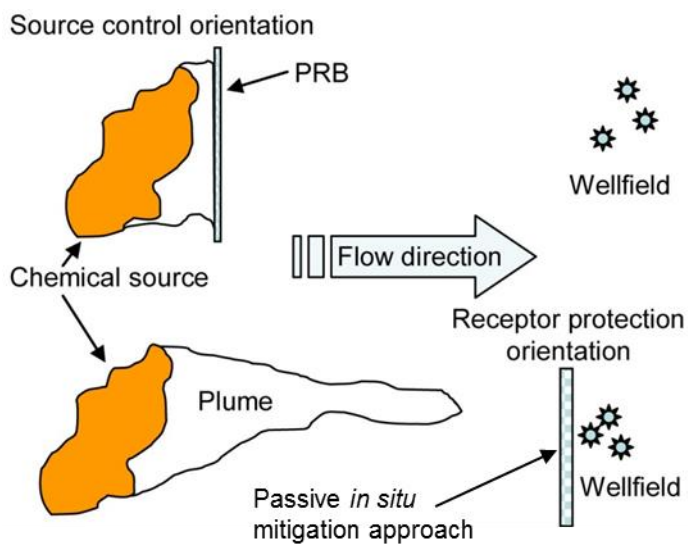

Figure 5-8. Examples of passive *in situ* mitigation approach configurations for source control (top) and protection of a downgradient receptor (bottom) (modified from ITRC, 2011).

The intent of this approach is to create a barrier for the contaminant of interest but not to the flow of the water itself. Thus, the reactive zone must be as permeable, or more so, than the surrounding aquifer media (Figure 5-9).

Passive *in situ* mitigation approaches are now accepted standard engineering practice. The most common type used is an “iron” wall made of zero-valent iron (ZVI), although other barriers have been made from peat, apatite, mulch, or zeolite, with our without additional substrate. An e-barrier concept (created by buried electrodes) has also been evaluated. Depending on the specific technology, treatment may result from physical, chemical, electrolytic, or biological processes.

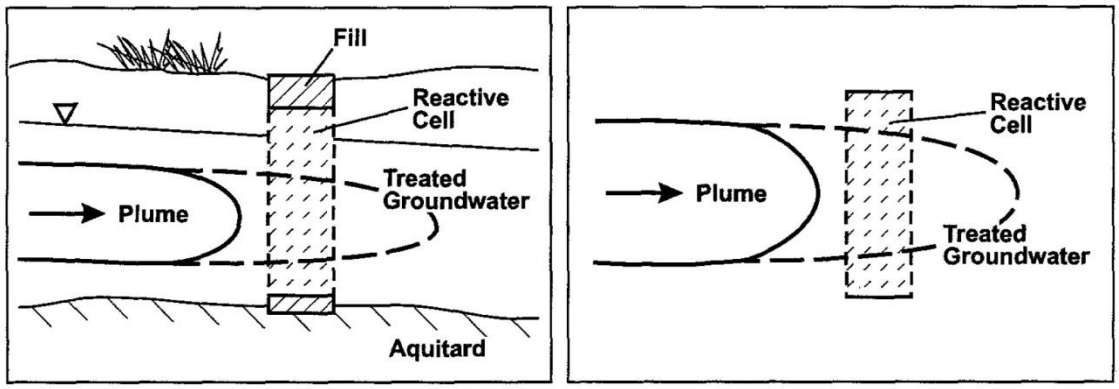

Figure 5-9. Elevation view (left) and plan view (right) of a continuous permeable reactive barrier configuration (from Battelle, 1998).

The success or failure of a passive *in situ* mitigation approach to meet intended goals is dependent on the following:

1. Providing hydraulic conditions where the plume is directed through the reactive media without being deflected around or under the reactive zone, and the reactive zone is able to maintain the flow conditions for an adequate length of time (generally many years) and
2. Providing conditions within the reactive zone that result in contaminant destruction or sequestration (ITRC, 2011) with the presence of other co-contaminants present in the groundwater at the site (Roberts et al., 2002).

The initial application of this approach was for the treatment of chlorinated solvents in groundwater, but research in the last decade or so has identified reactants that are capable of transforming/destroying energetic compounds including 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). In order to manage these energetic compounds, the approach must create a zone where reactions between the energetic compound and the reactive material take place or create an anaerobic zone with a residence time long enough to biologically treat the most recalcitrant contaminant of interest. Three types of passive *in situ* mitigation approaches have been studied for this purpose: the iron wall, the biowall, and the electrically induced redox barrier. In addition, a bioaugmented iron wall has been investigated (Shrout et al., 2004).

The dimensions of the reactive zone must be adequate to intercept the contaminant plume without bypassing around or under the zone. The reactive zone is established perpendicular to the flow of the plume, and the length of the reactive zone must be long enough to treat the width of the plume. Sometimes gates of impermeable material are established on either end of the reactive zone to force the plume to pass through the reactive zone (Figure 5-10). The width (thickness) of the reactive zone must be adequate to maintain a residence time for reaction that is long enough to achieve the desired treatment. The required residence time in the reactive zone depends on the degradation rate expected for the least reactive contaminant of interest and the flow rate of the plume through the reactive zone. The depth of the reactive zone should be deeper than the lowest depth of the plume, and when possible, it should be deep enough to extend to bedrock or an aquitard (a flow restricting layer).

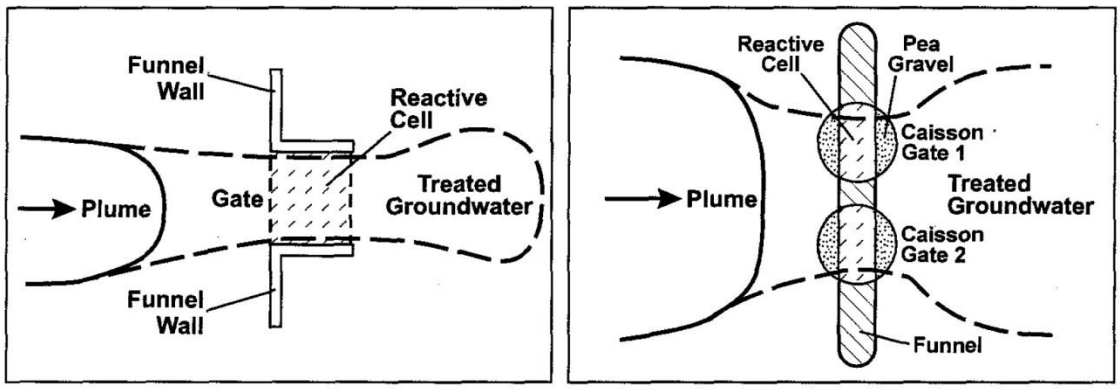

Figure 5-10. Plan view of funnel-and-gate system (left) and of a funnel-and-gate system with two caisson gates (right) (from Battelle, 1998).

5.2.2.2 Treatment Processes for Energetic Compounds

Iron-Based Passive In Situ Mitigation Approach

The iron wall is a barrier that chemically reduces contaminants as the contaminated groundwater comes in contact with ZVI particles. A trench is dug to an adequate depth and ZVI is placed in the trench. ZVI mitigation approaches have been used to remove energetic compounds from groundwater at Cornhusker Army Ammunition Plant (AAP), Nebraska (ESTCP, 2008a). The ZVI used has a high iron metal content (generally >90%) and generally comes from recycled iron scrap. The grain size of the material is generally from 2 to 2.25 millimeter (mm), which provides an adequate surface area for treating the contaminant, but does not reduce hydraulic conductivity. Sometimes sand or pea gravel is included to increase the permeability of the wall.

TNT and RDX are chemically reduced by contact with ZVI. For TNT, the reaction proceeds as follows (Equation 5.1), resulting in a complete conversion of TNT to triaminotoluene (TAT), which is presumably naturally attenuated as the plume moves beyond the reactive zone (Tratnyek and Johnson, 2011).

$$\text{TNT} \rightarrow \text{2- or 4-aminoDNT} \rightarrow \text{2,4- or 2,6-diaminoNT} \rightarrow \text{TAT} \qquad \text{(Eq. 5.1)}$$

For RDX, the reaction proceeds via two mechanisms as shown in Equation 5.2 (McCormick et al., 1981) and Equation 5.3 (Hawari, 2000) and results in some low molecular weight organics that can be further mineralized to innocuous products such as carbon dioxide (CO_2), nitrous oxide (N_2O), and water.

$$\text{RDX} \rightarrow \text{MNX} \rightarrow \text{DNX} \rightarrow \text{TNX} \rightarrow \text{formaldehyde + dimethyhydrazine} \qquad \text{(Eq. 5.2)}$$

$$\text{RDX} \rightarrow \text{methylenedinitramine + bisdimethynitramine} \rightarrow \text{formaldehyde + nitramine} \qquad \text{(Eq. 5.3)}$$

Presumably, HMX reacts in a similar manner as RDX. Reduction rates are in the order TNT > RDX > HMX. Thus, if a plume contains TNT, it will be preferentially reduced. At ranges, TNT is generally absent from plumes, and barriers would be designed to treat RDX and HMX predominantly.

As the Fe^0 (ZVI) reacts, it is oxidized to Fe^{++}, which raises the pH of the groundwater and can result in the precipitation of some minerals. In some cases, this can reduce the hydraulic conductivity of the reactive zone and that is a reason why the concentrations of other constituents must be studied before the long-term performance of a ZVI passive approach can be predicted (Gravaskar et al., 2000).

Iron wall passive approaches have been evaluated for use in treating explosives-contaminated groundwater. Johnson and Tratnyek (2008) conducted a pilot scale study at Cornhusker AAP in Grand Island, Nebraska. The shallow aquifer at the site (15–20 ft below ground surface [bgs]) consists of medium sands with some silty material and the groundwater velocity at the site is 1–2 ft/day. The demonstration activities included installation of a mixed iron wall/sand reactive zone (30% by weight iron). The reactive zone was approximately 50-ft long by 15-ft deep by 3-ft thick. Monitoring activities were conducted over a 20-month period to evaluate the performance of the mitigation approach. The reactive zone was located within a large groundwater plume from a diffuse source resulting from production of munitions.

Groundwater concentrations upstream of the reactive zone ranged from 30–200 micrograms per liter (µg/L) TNT and 1–2 µg/L RDX. Over the 20-month test, concentrations of TNT and RDX downstream of the reactive zone were consistently <0.1 µg/L.

A detailed cost and performance evaluation of this study is presented in ESTCP (2008a). The installation cost of this 50-ft by 15-ft reactive zone (3-ft thick) was estimated at $180 per square foot ($ft^2$). Some flow diversion under the barrier was observed but this was attributed to the use of guar during the iron wall construction and a failure to remove it completely after construction of the wall. Construction details are presented in ESTCP (2008).

Factors that affect the cost and performance of the iron wall reactive zone include (Johnson and Tratnyek, 2008):

1. The concentration and distribution of explosives in the groundwater to be treated. Higher concentrations of explosives will require longer residence times in the reactive zone.
2. The chemistry of the aquifer to be treated. The primary issues of concern will be the presence of dissolved oxygen, carbonate, nitrate, sulfate, or other species that may passivate the surface of the iron or plug the reactive zone.
3. The depth to groundwater will impact the cost of barrier installation.
4. The hydraulic conductivity of the aquifer will impact the design of the reactive zone (e.g., barrier thickness, iron content).
5. The hydraulic gradient in the aquifer will impact the design of the reactive zone (e.g., barrier thickness, iron content).
6. Geological heterogeneities in the aquifer
7. Seasonal variation in groundwater flow direction will impact the design of the reactive zone.

Biowalls

The biowall uses a wall of organic matter to deplete dissolved oxygen in the groundwater and to develop an anaerobic zone conducive to anaerobic biodegradation. Biowalls have utilized a number of different organic amendments including mulch, molasses, and vegetable oils to develop anaerobic conditions needed for biological degradation of RDX and HMX (Hawari, 2000).

Organic mulch is an inexpensive, complex carbon material that is typically populated with its own consortium of microorganisms. These organisms slowly break down complex insoluble organics (lignin, cellulose) releasing soluble carbon, which can then be utilized by these and other microorganisms as an electron donor for treating contaminants via reductive pathways. Mulch has advantages over other electron donors in that it is cheaply available, long lasting, and is naturally present in the environment (Ahmad et al., 2007). When mulch is used in a biowall, the dissolved organic carbon released by the mulch biowall can travel downstream with the plume, thereby increasing the effective zone of treatment beyond the thickness of the wall itself. Mulch biowalls have been demonstrated to treat chlorinated solvents, perchlorate, and nitrate ion.

For a mulch biowall system, it is essential to combine the mulch with pea gravel or sand to maintain the structural integrity of the wall over time as the mulch degrades. The effectiveness of the biowall depends on the composition of the groundwater. For example, if the need is to treat RDX, the presence of TNT or nitrate can reduce the effectiveness because these chemicals are preferentially reduced relative to RDX. For groundwater at training ranges, however, TNT is generally absent or at very low concentrations relative to RDX.

A pilot-scale mulch biowall was tested at Pueblo Chemical Depot (PCD), Colorado, to treat a groundwater plume of RDX and HMX (Ahmad et al., 2007). A trash-pine mulch was selected for the biowall and mixed 2:1 with pea gravel. A 105-ft biowall was established with a 30-ft bentonite funnel to serve as a hydraulic control to ensure that the water did not bypass the reactive zone. The biowall varied in depth from 14 to 24 ft bgs and was 2-ft thick. The trencher simultaneously cut the trench and backfilled with the mulch/gravel material. Wells were drilled both upgradient and downgradient of the biowall to allow sampling to characterize the RDX and HMX removal efficiency.

The mulch biowall demonstration was conducted for 22 months. Concentrations of RDX were reduced from 2–3 µg/L to <0.2 µg/L by passage through the biowall. None of the intermediate reduction products of RDX were detected downstream of the biowall. No loss of permeability was found over the 22-month demonstration.

Pilot-scale costs of the Pueblo demonstration and extrapolated costs for a full-scale system is provided in Ahmad (2007). Cost drivers for this technology include:

1. The depth of contamination, which determines the selection of a trenching procedure,
2. The required thickness of the reactive zone,
3. Mobilization costs for the trenching machinery,
4. Disposal costs (if any) for the trench cuttings, especially for saturated zone soils, and
5. Anticipated length of operation to achieve cleanup goals.

Ahmad (2007; ESTCP, 2008b) also compared costs of the biowall system to an iron-based system. The major difference in cost is the material cost for ZVI versus mulch. Overall, the biowall was about 25% less expensive according to their assumptions. This assumes that the longevity of both systems would be identical.

Electrically Induced Redox Barriers

A third type of passive *in situ* mitigation approach is called the electrolytic barrier (e-barrier) has also been evaluated for treatment of a plume of energetic compounds in groundwater at the PCD (Sale et al., 2010). In this technology, the contaminated groundwater passes through a reactive zone consisting of a set of titanium screen electrodes placed within the aquifer that are charged with low voltage direct current (DC). Contaminants are exposed to varying reductive conditions at the negatively charged electrode and oxidative conditions at the positively charged electrode, potentially treating compounds that are difficult to treat using other passive *in situ* mitigation approaches. Sale et al. (2010) list the following as the potential advantages of the e-barrier:

1. The e-barrier is environmentally benign, requiring no chemical introduction,
2. No *in situ* mixing of reagents or nutrients is required,
3. Electrical power costs associated with driving the chemical transformations are low (i.e., \$0.05–0.01/day/m^2),
4. With additional optimization, the cost of construction materials may be less than that for comparable niche technologies,
5. Rates of chemical transformation can be modified remotely by adjusting applied voltage,
6. The potential at the electrodes can be periodically reversed or adjusted to remove inorganic precipitates (e.g., calcium carbonate [$CaCO_3$]), a common constraint of other technologies,
7. Electrode materials appear to be resilient under standard treatment conditions; it is expected that subsurface components of the system can remain effective for ten or more years. This compares favorably against other passive *in situ* mitigation approaches (e.g., ZVI), in which reactive materials are consumed, and
8. The process of sequential oxidation and reduction has the potential to degrade a wide range of contaminants.

The e-barrier demonstration was conducted at PCD, but on a different groundwater plume than that used for the biowall demonstration. This plume was contaminated with a variety of energetic compounds including RDX, HMX, 2,4-DNT, TNT, and 1,3,5-trinitrobenzene (1,3,5-TNB), as well as nitrate ion. The highest concentrations of TNT and RDX in groundwater on the upstream side of the barrier during the test were 134 and 12 µg/L, respectively.

A 35-ft long e-barrier was established immediately downgradient of a former washout lagoon. The primary component of the barrier was composite panel containing four titanium mesh electrodes coated with mixed metal oxides (Ti/MMO) separated by high-density polyethylene (HDPE) geonet and bounded on the outside by a geotextile. The composite panels were mounted on vinyl sheet pile sections. A total of 15 panels were constructed. The panels were installed in the trench and backfilled with a well-sorted course sand.

The barrier was operated at voltages ranging from 1.4 to 6.3 volts over 777 days. For 1 hour each day, the polarity of the electrodes was reversed to reduce scale buildup. Concentrations of energetic compounds were measured in the groundwater plume just upstream and downstream of the e-barrier. Concentration reductions observed across the barrier were 40% RDX, 60% 2,4,6-TNT, 82% HMX, 67% 2,4-DNT, and 65% trinitrobenzene (TNB) (Sale et al., 2010). The results from the demonstration failed to show large improvement in water quality downgradient of the e-barrier. In general, site cleanup goals were not achieved, although decreasing upgradient contaminant concentrations during operations complicated analysis of the results.

5.2.2.3 Overall Considerations for the Use of Passive *In Situ* Mitigation Approaches

This technology is an alternative to hydraulic control for the management of RDX-impacted groundwater on ranges. Both the iron wall and biowall appear to be effective at managing plumes of RDX. The advantage of this type of approach is that it is an *in situ* technology with very little operation and maintenance (O&M) costs compared with *ex situ* approaches requiring pumping of the groundwater to the surface and subsequent reinjection into the aquifer.

Before a passive *in situ* mitigation approach is considered, aquifer characteristics must be known to include the groundwater depth, depth to bedrock or aquitard, groundwater velocity, lateral and vertical gradients, site stratigraphy/heterogeneities, hydraulic conductivities of the different layers, porosity, and dimensions and distribution of the plume, and the other constituents present in the groundwater plume (Gravaskar et al., 2000). If the plume is >50 ft deep, this technology is not appropriate due to the limitations associated with trenching equipment required for the installation of the barrier.

Both the iron wall and biowall technologies can treat an RDX plume effectively, based on pilot-scale tests. The major uncertainty is the longevity of the system. Most RDX plumes will require long-term management over many years. A thorough discussion of these approaches is provided in ITRC (2011).

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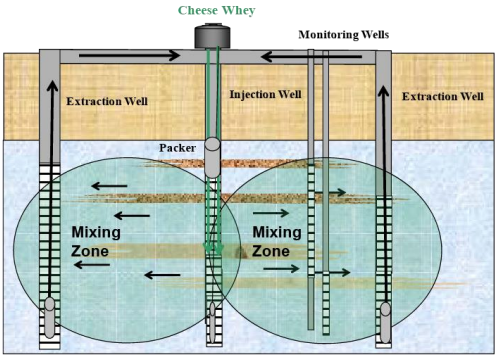
5.2.3 3.11 Active *In Situ* Management Approach for Groundwater



Schematic of the semi-passive extraction-reinjection system used at Area 157, Picatinny Arsenal, Dover, New Jersey (Hatzinger and Lippincott, 2012).

Description: Active *in situ* management of groundwater involves the addition of amendments (e.g., electron donors, carbon substrates) to the subsurface to stimulate the microbial growth and degradation of the energetic chemicals of concern.

Where It Can Be Used: Several engineering approaches have been developed to include: (1) "active systems" that meter and mix soluble amendments into groundwater during continuous active pumping, (2) "semi-passive systems" that mix soluble amendments into groundwater during intermittent pumping, and (3) "passive systems" that apply slow-release amendments in trenches, wells, or using direct-push methods, and rely upon natural groundwater flow to mix the amendment with the impacted groundwater (Hatzinger et al., 2009).

Advantages: Active *in situ* management approaches have application for impacted groundwater source zones and as a downgradient cutoff to groundwater migration. The energetic chemicals are treated *in situ*.

Disadvantages: Biofouling of the wells is a frequent problem that must be controlled. Adverse impacts on secondary groundwater quality can be of concern and requires monitoring. The active and semi-passive approaches require aboveground infrastructure, which may be problematic in or near active training areas.

Cost Information: Krug et al. (2009) presents a cost analysis of the three engineering designs for application to perchlorate-contaminated groundwater. Aspects of this analysis should be relevant to estimating the cost of these systems for energetic-impacted groundwater. ESTCP (2012) provides a cost analysis of several in situ management approaches for groundwater containing TNT and RDX including: semi-passive bioremediation of the entire plume using cheese whey, a semi-passive biobarrier using cheese whey, passive injection biobarrier using emulsified vegetable oil, a passive trench mulch biowall, and a passive zero-valent iron passive trench barrier.

Recommendation: **Recommended for the management of groundwater source zones and for halting migration of an impacted groundwater plume. Site characteristics (depth to groundwater, hydrogeologic parameters, etc.), management goals, and possible regulatory constraints (due to reinjection of contaminated groundwater) will influence the selection of the optimum engineering approach. This technology would be appropriate for managing impacted groundwater at hand grenade ranges (HGRs), demolition ranges, and antitank rocket ranges.**

Key Resources:

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Hatzinger PB, Lippincott D. 2012. In Situ Bioremediation of Energetic Compounds in Groundwater. ESTCP Project No. ER-0425 Final Report. March. 240 p.

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5.2.3.1 Technology Overview

Active *in situ* management of groundwater involves the addition of amendments to the subsurface to stimulate the microbial growth and degradation of the contaminants of concern. A variety of microorganisms have the ability to degrade/transform energetic compounds (see Kalderis et al., 2011). However, the addition of a cosubstrate is often needed to create a biologically active zone conducive for the degradation processes.

The development and practice of the active *in situ* management approach has progressed rapidly over the past decade, especially for application to chlorinated solvents and perchlorate contamination in groundwater. This has generated a body of information on the technology's cost and performance to allow reliable cost comparisons with other groundwater technologies (Henry, 2010 citing AFCEE, 2007; 2008; ITRC, 2008a; 2008b; see also AFCEE et al., 2004). Recently, attention has turned to demonstrate the utility of this approach to manage energetic compounds in groundwater.

5.2.3.2 Engineering Approaches

Active *in situ* management of groundwater requires that microorganisms capable of degrading the contaminants of interest are present in the site groundwater. Additionally, the aquifer geochemistry must be such that reducing conditions can be achieved and maintained through the addition of a cosubstrate. Confirming the presence of microorganisms with the desirable metabolic capabilities and determining the optimum cosubstrate is done by conducting site-specific treatability studies.

The effective delivery and mixing of bioamendments is one of the biggest challenges with active *in situ* management. Several engineering approaches have been developed: (1) "active systems" that meter and mix soluble amendments into groundwater during continuous active pumping, (2) "semi-passive systems" that mix soluble amendments into groundwater during intermittent pumping, and (3) "passive systems" that apply slow-release electron donors in trenches, wells, or using direct-push methods and rely upon natural groundwater flow to mix the amendment with the contaminated groundwater (Hatzinger et al., 2009). These systems have been widely used to treat chlorinated solvents and perchlorate in groundwater and information on their design and operation can be found in Henry (2010), Hatzinger et al. (2009), Krug and Cox (2009), and Borden and Lieberman (2009). Recently, Kitanidis and McCarty (2012) published a monograph volume on *Delivery and Mixing in the Subsurface: Processes and Design Principles for In Situ Remediation*. This volume contains useful information on the design and implementation of *in situ* technologies involving amendment addition that would be relevant to designing such systems for energetic contamination.

Active Systems

The design of an active treatment system is typically based on the extraction, amendment, and reinjection of groundwater or on a groundwater recirculation system (Figure 5-11). Active systems can be designed to treat source areas in groundwater and as cutoff barriers to prevent further migration of large contamination plumes (see Hatzinger et al., 2009).

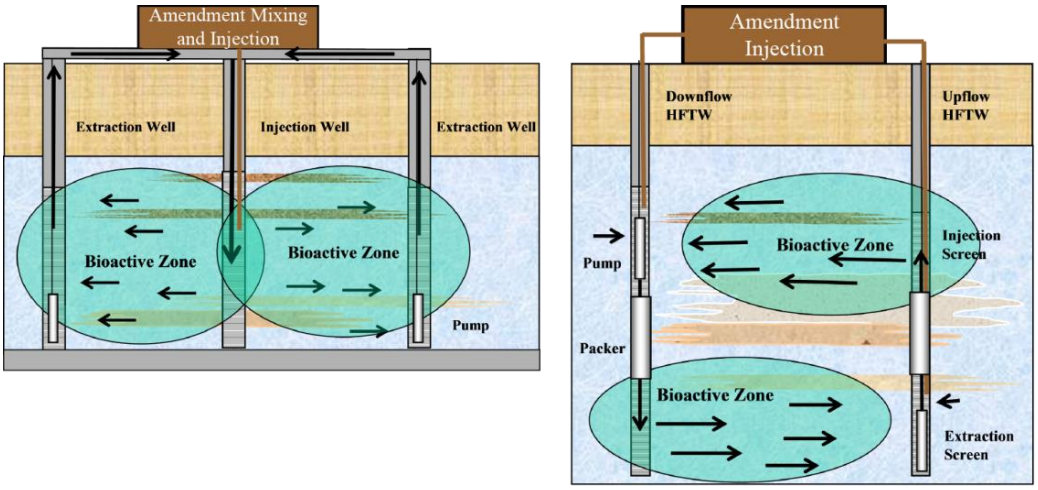

Figure 5-11. *Left:* Schematic of an active system consisting of two extraction wells and a single injection well. Water is pumped to the surface from each extraction well where the bioamendment is added, then the amended water is re-injected into the formation through the injection well. *Right:* Schematic of an active horizontal flow treatment well (HFTW) consisting of two treatment wells. In the upflow HFTW, water is amended and pumped from the lower screened interval (extraction screen) through the packer to the upper screened interval (injection screen), where it is released into the formation. The downflow HFTW operates in reverse. Modified from Hatzinger et al., 2009.

The primary advantages of an active treatment system include the following (Hatzinger et al., 2009):

- It is applicable in deep as well as shallow aquifers.
- It can serve as a groundwater capture and treatment system to prevent plume migration.
- The effective treatment zone does not rely on the natural groundwater flow and is applicable over a range of hydraulic conductivities.
- The systems are flexible, so modifications in pumping rates, amendment type, and quantity are possible at any time in order to respond to changing flow and transport conditions.
- It minimizes the potential for secondary adverse impacts on groundwater geochemistry.

Disadvantages with active *in situ* treatment systems include the following (Hatzinger et al., 2009):

- Biofouling of the injection wells is a frequent problem and must be actively controlled.
- Infrastructure and operation and maintenance (O&M) requirements are often greater than for comparable passive or semi-passive systems.
- Regulatory permitting may be required in some states to allow the reinjection of groundwater containing contaminants.

Semi-Passive Systems

A semi-passive *in situ* management system involves the addition of the bioamendment on an intermittent basis to simulate the native microorganisms. A semi-passive system is designed similar to the active system in that groundwater is circulated between injection and extraction wells. However, with a semi-passive system, the groundwater is circulated for a limited duration (the 'active phase') to distribute the amendment, and then the circulation system is shut off for a longer period of time (the 'passive phase') (Krug and Cox, 2009).

Figure 5-12 shows the induced and natural groundwater flow patterns generated during the active and passive phases of operation of a semi-passive system.

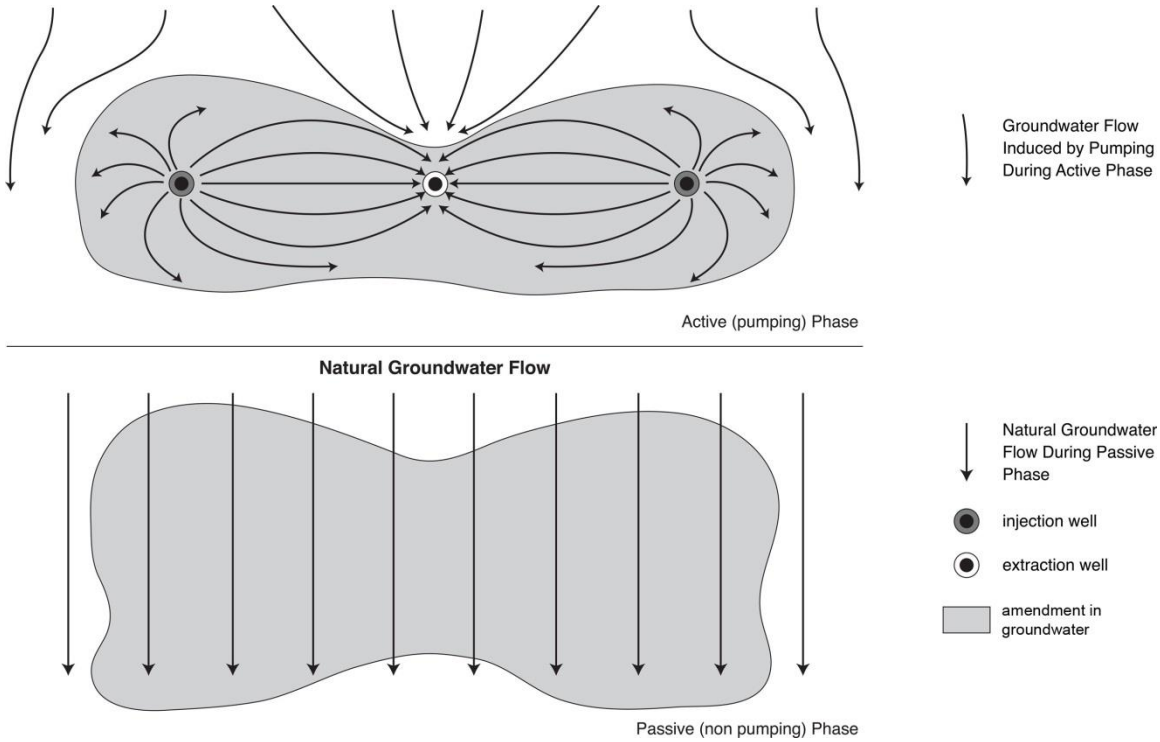

Figure 5-12. Plan view of the groundwater flow for a semi-passive *in situ* management system (Krug and Cox, 2009). Copyright 2009, Springer Science+Business Media, reprinted with permission.

A semi-passive *in situ* management design may be favored over either a passive or active design for the following site characteristics (Krug and Cox, 2009):

- Deep sites (>12–15 meters [m] below ground surface [bgs]) where creating a passive biobarrier would be difficult and expensive.
- Wide plumes where the number and cost of injection points would be prohibitive.
- Sites where the injection of large quantities of bioamendments (as with a passive approach) may create secondary water quality problems.
- Sites where the high capital and O&M costs of an active design are uneconomical.

Passive Systems

The most commonly used passive *in situ* management system involves the injection of amendments through injection wells in either a grid formation or through lines of injection wells to create a biobarrier (Borden and Lieberman, 2009) or the installation of an emplaced trench of amendment, such as organic mulch, that the groundwater flows through. The term passive *in situ* mitigation approach is also used to describe this engineering approach. More information is provided in Section 5.2.2.2.

The primary advantages of passive *in situ* management systems are the following (Borden and Lieberman, 2009):

- Rapid establishment of reducing conditions *in situ*.
- Long-lasting *in situ* treatment (depending on the amendment used).
- No permanent aboveground infrastructure required.
- Low O&M costs.

Factors to consider when evaluating the appropriateness of a passive *in situ* management approach include:

- Hydrogeologic conditions that will allow the effective distribution of the amendment, and
- Adequate groundwater flow conditions since this approach does not involve active pumping of groundwater to aid in amendment distribution.

5.2.3.3 Field Demonstration

Picatinny Arsenal, Dover, New Jersey: An Environmental Security Technology Certification Program (ESTCP)-funded demonstration of passive *in situ* management was conducted at Picatinny Arsenal, Dover, New Jersey (Hatzinger and Lippincott, 2012). The site selected for the study was Area 157 near a former explosives production area contaminated with energetic compounds including 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). The delivery and mixing system consisted of a recirculation cell design with semi-passive operation. Laboratory testing was conducted to identify the most effective amendment to promote biodegradation of the energetic compounds. Lactate, citrate, benzoic acid, yeast extract, cheese whey, hydrogen, glucose, acetate, and ethanol were tested. Cheese whey promoted the most rapid and extensive degradation of the target energetic compounds and was selected for the field demonstration.

The system consisted of two extraction wells and a single injection well. The system was operated in a semi-passive mode, pumping for 3–5 days during the injection of soluble cheese whey constituents (active phase) and then was shut down for 6–12 weeks (passive phase) once the cheese whey was adequately distributed and mixed in the aquifer. A total of 830 kilograms (kg) of cheese whey (dissolved constituents only) was added to the system in four active cycles, beginning on Day 0, Day 41, Day 103, and Day 181. The final groundwater sampling event was conducted on Day 565, more than a year after the final bioamendment addition.

The primary performance objective was to reduce levels of energetic compounds in groundwater to below concentrations of regulatory concern—0.5 micrograms per liter (µg/L) RDX, 1 µg/L TNT,[23] and 400 µg/L HMX.[24] Initial concentrations of TNT and RDX in the groundwater, prior to injection of the bioamendment, ranged from 5 to 190 µg/L and from 5 µg/L to 170 µg/L, respectively. Initial concentrations of HMX in the treatment zone monitoring wells (TZMWs) ranged from 3.5 to 130 µg/L, all below the U.S. Environmental Protection Agency (USEPA) Health Advisory Value of 400 µg/L.

The concentration of TNT was reduced to below the analytical detection limit (Practical Quantitation Limit [PQL] = 0.25 µg/L) in all of the treatment zone monitoring wells by Day 62 of the study. Concentrations remained at this level for the remainder of the study, with the exception of one monitoring well sample. Biodegradation of RDX occurred more slowly than for TNT. However, by Day 148, RDX concentrations had decreased to <1.5 µg/L in five of the six TZMWs (the sixth TZMW concentration was ≤5 µg/L). From Day 222 to Day 565, RDX concentrations in all of the downgradient TZMWs was <1 µg/L and all were <0.2 µg/L on Day 565. As long as total organic carbon (TOC) remained >5 milligrams per liter (mg/L), rebound of RDX was not observed. A significant decline in HMX concentrations was observed in all downgradient TZMWs and by Day 274, concentrations were <0.4 µg/L.

The accumulation of degradation intermediates was also monitored during the study. 4-amino-2,6-dinitrotoluene (4-ADNT) and 2-amino-4,6-dinitrotoluene (2-ADNT), two common TNT daughter products, were present in the site groundwater from 1 to 120 µg/L prior to the injection of cheese whey. A rapid reduction in concentration was observed after cheese whey was injected, and by Day 148, neither daughter product was present above 0.25 µg/L (the analytical PQL). 2,4-diamino-6-nitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,6-DANT) increased in concentration, as expected, after the injection of cheese whey, and then declined in concentration to below their respective PQLs by Day 98. The transient production of RDX daughter products (hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine [MNX], hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine [DNX], TNX) was observed, followed by a reduction in their concentrations to below their PQL by Day 420 of the study.

The use of the following techniques successfully controlled problems with microbial biofouling during the demonstration:

- Pumping groundwater intermittently rather than continuously.
- Reducing the length of the active pumping phase as much as possible.
- Injecting large quantities of cheese whey during the active pumping phase.
- Injecting groundwater through a pressurized packer to promote movement of water into the formation.

Reasonably high concentrations of iron, manganese, and methane (secondary groundwater contaminants) were observed in some of the monitoring wells during the demonstration. The

[23] New Jersey Department of Environmental Protection (NJDEP) Interim Groundwater Quality Criteria. http://www.nj.gov/dep/wms/bwqsa/gwqs_interim_criteria_table.htm, accessed March 14, 2014.

[24] USEPA 2011 Edition of the Drinking Water Standards and Health Advisories. EPA 820-R-11-002. USEPA Office of Water, Washington, D.C. http://water.epa.gov/action/advisories/drinking/upload/dwstandards2011.pdf, accessed March 14, 2014.

investigators attributed this to the addition of relatively high concentrations of cheese whey during each injection cycle and slow groundwater transport. These contaminants were deemed to not be an important issue because there were no nearby drinking water wells or close downgradient receptors at this site.

U.S. Department of Energy Pantex Plant, Amarillo Texas:

In situ bioremediation (ISB) is being used at the Pantex Plant to treat two groundwater plumes containing multiple contaminants, including high explosives. A pilot-test of *in situ* biological treatment was performed in a perched aquifer to determine the technology's effectiveness (Seitz et al., 2007). A carbon source consisting of soybean oil and lactic acid was injected into the aquifer to adjust the geochemical conditions and stimulate the bacteria in the aquifer to degrade the high explosives. A total of 315,800 gallons of carbon source (containing 13,100 gallons of Newman Zone® amendment) was injected in two events over a two-year period. After the second injection event, RDX concentrations declined to less than 97% of the baseline concentrations in the treated wells.

Following the pilot study, full-scale ISB systems were installed at the leading edge of two separate contaminated groundwater plumes (Krembs and Clayton, 2011; Clayton and Krembs, 2011). The contaminated zone is very deep, approximately 270 feet below ground surface, and includes high explosives, chlorinated solvents, perchlorate, and hexavalent chromium. Injection wells were installed on a relatively wide spacing of 100 feet due to the high drilling costs. For each amendment injection event, a volume of 0.15 pore volume of the target zone at a 5% amendment concentration is added. To date, approximately 9 million gallons of diluted buffered emulsified oil amendment have been injected. Reinjection on a 12-18 month frequency is being implemented to maintain the desired reducing conditions within the treatment zones. Process monitoring conducted to date indicates that contaminant concentrations have been reduced to non-detect concentrations (~99% reductions) in the treatment zone and at downgradient monitoring wells.

5.2.3.4 Overall Considerations for the Use of Active *In Situ* Management Approach

An active *in situ* management system is an alternative to hydraulic control for the management of groundwater plumes of RDX and TNT on ranges. The advantage of these approaches is that the treatment occurs *in situ*, so no aboveground treatment plant is needed. However, depending on the engineering approach used, some permanent aboveground infrastructure may be required. With the active engineering approach, aboveground tanks, pumps, meters, and piping will be required to meter, mix, and inject amendment in the groundwater. With the semi-passive approach, the equipment needed to implement the approach may be mobile and moved from one area to another as required or may be installed permanently and operated on an intermittent basis. The passive approach (one design being the biowall discussed in Section 5.2.2.2) requires access to amendment injection wells to periodically add amendment to the subsurface. These requirements limit the technologies use to areas accessible to workers and that are not constrained by training activities.

Before active *in situ* management is considered, the microbial, hydrogeologic, and geochemical characteristics of the aquifer must be determined. Factors such as depth to groundwater, the amount of geologic heterogeneity, and geochemistry of the groundwater will help determine the optimum engineering design and cosubstrate. Much cost and performance information for the engineering design of a an active *in situ* management system for perchlorate and

chlorinated solvent plumes is available in the literature and is relevant to energetic-contaminated plumes. Readers are encouraged to visit the Strategic Environmental Research and Development Program (SERDP)/ESTCP website for publication updates on the Picatinney Arsenal demonstration discussed above and the results of on-going efforts (Section 5.2.3.5).

5.2.3.5 Ongoing Research and Development

ESTCP recently funded two efforts to further develop this technology for energetic contaminants. The first project[25] will develop a bioaugmentation approach to enhance RDX biodegradation in groundwater under aerobic conditions. The goals of this effort are to develop an aerobic RDX-degrading culture with suitable growth, activity, and cell transport characteristics and then conduct field-scale tests at an RDX-contaminated groundwater site. This approach, if successful, has the potential to address large, dilute RDX plumes where it is not economically feasible to create and maintain anaerobic conditions throughout the entire plume. The second project[26] will field test for the first time the use of an injected emulsified vegetable oil substrate passive *in situ* mitigation approach at a site contaminated with energetic compounds. This technique could offer a long-term solution for contaminant migration on active ranges.

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Hatzinger P, Lippencott D. 2012. In Situ Bioremediation of Energetic Compounds in

[25] http://www.serdp.org/; ER-201207.

[26] http://www.serdp.org/; ER-201028.

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5.2.4 Hydraulic Control

Hydraulic control (e.g., pump-and–treat) system at the Lagoons Groundwater Plume at Umatilla Chemical Depot, Oregon (photograph provided courtesy of Harry Craig, U.S. Environmental Protection Agency [USEPA] Region 10).

Description: Hydraulic control refers to the use of extraction wells to pump impacted groundwater aboveground where it can be managed using various technologies.

Where It Can Be Used: This technology can be used as a source control option or at an installation boundary to prevent the migration of impacted groundwater. The effectiveness of pump-and-treat is dependent on a number of factors, including the geologic conditions and groundwater flow parameters. Characteristics such as site stratigraphy, degree of heterogeneity, structural geology, hydraulic conductivity, vertical flow, and distribution of the energetic compounds must be considered when assessing this technology.

Advantages: This technology, while expensive, is effective at halting the migration of impacted groundwater and does allow for the reliable removal of energetic chemicals from the groundwater, typically by using granulated activated carbon (GAC).

Disadvantages: Disadvantages include the high capital costs for installation of the extraction wells and construction of the aboveground management system, and the operation and maintenance (O&M) costs of pumping groundwater to the surface and treating for extended periods of time. Siting pump-and-treat aboveground infrastructure on an operational range without interfering with training activities may be problematic. The efficacy of pump-and-treat can be adversely impacted by subsurface heterogeneities, fractured bedrock and zones of low hydraulic conductivity.

Cost Information: Total estimated costs for extraction, treatment, and long-term monitoring of the J1 northern and southern plumes at Massachusetts Military Reservation (MMR) are $4.9M and $14.6M, respectively, with the time required to reduce contaminant levels to risk-based acceptable concentrations estimated at 14 and 37 years (yrs), respectively (USEPA, 2011).

Recommendation: **Use of hydraulic control appears to be a last resort for training range applications for situations where other management options are not possible or are ineffective, and/or an important receptor such as a sole-source aquifer must be protected.**

Key Resources:

ESTCP. 2004. Application of Flow and Transport Optimization Codes to Groundwater Pump-and-Treat Systems. ESTCP Cost and Performance Report Project CU-0010. January.

USEPA. 1997. EPA Ground Water Issue: Design Guidelines for Conventional Pump-and-Treat Systems. EPA/540/S-97/504. USEPA Office of Solid Water and Emergency. September.

USEPA. 2011. EPA Reaches Cleanup Decision for J1 Range and Groundwater Plumes at Camp Edwards. Press Release. May 31. Available at http://yosemite.epa.gov/opa/admpress.nsf/0/ED524B82E3040B36852578A100578A21, accessed March 6, 2014.

5.2.4.1 Overview

In some cases, management of a groundwater plume of energetic compounds at a U.S. Department of Defense (DoD) range may be necessary and require containment and/or treatment of a source zone or a downstream groundwater plume. Some other management approaches have been discussed in previous sections, but the most commonly utilized approach for this situation for other contaminants, such as chlorinated solvent dense nonaqueous phase liquid (DNAPL), has been hydraulic control using extraction wells to remove the contaminated groundwater followed by treatment aboveground. This technology has been used with or without subsequent treatment prior to discharge in a surface water body or reinjection into the subsurface. When the extracted groundwater is treated prior to discharge, this technique is commonly referred to as hydraulic control and has been used extensively by the U.S. Environmental Protection Agency (USEPA) Superfund program for many years for a wide range of contaminated groundwater plumes (USEPA, 1997).

Hydraulic containment can be used in two different ways for training range issues. When the source of contamination cannot be removed, source control can be achieved using hydraulic containment near the source of contamination. In most cases where this has been used, the goal was to achieve long-term containment of contaminated groundwater to prevent continued expansion of the contaminated zone.

The second option is to use hydraulic control at range or installation boundaries to prevent the contamination from migrating off-range and degrading groundwater resources used by off-range receptors. This approach would be a last resort if other management schemes were unsuccessful or not feasible. The volume of water that would need to be pumped for this approach to be successful would be very large in most cases and the technology would be very expensive to implement.

To implement hydraulic control, the aquifer must be thoroughly characterized to obtain a three-dimensional (3-D) picture of the subsurface. Sometimes the subsurface can be fairly simple in structure and in others quite complex with several different aquifers at various depths. Extraction wells need to be placed strategically to capture the zone of interest and minimize the volume of groundwater that must be pumped. Often mathematical modeling is used to optimize extraction well placement (ESTCP, 2003a; 2003b; 2003c; Zheng and Wang, 2001). A design manual for conventional hydraulic control systems is available (USEPA, 1997).

5.2.4.2 Hydraulic Control for Energetic Contaminants on DoD Installations

Hydraulic control has been used for energetic contaminants in groundwater at a number of military ammunition plants and depots including Umatilla Army Depot, Oregon; Milan Army Ammunition Plant (AAP), Tennessee; Bangor Sub Base, Washington; and a former firing range at Camp Bonneville, Washington. Hydraulic control has been selected as the remedy for groundwater contamination at the Camp Edwards portion of the Massachusetts Military Reservation (MMR) for the hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)/perchlorate plumes originating at the J1 range (USEPA, 2011). For the northern J1 plume, extraction wells will be used with treatment using granulated activated carbon (GAC) and ion exchange. For the southern J1 plume, two extraction wells will be used—one on Camp Edwards and one offsite with treatment using GAC. The cost of treating the northern plume has been estimated at $14.6M with treatment required for at least 37 years (yrs) to achieve risk-based acceptable

concentrations. The cost of treating the southern plume is estimated at $4.9M and a minimum treatment period of 14 yrs will be required.

For removal of RDX and 2,4,6-trinitrotoluene (TNT), most hydraulic control systems have relied on GAC for the aboveground treatment of the extracted groundwater. Several different advanced oxidation techniques have been tried, but most have reverted to GAC for reliability and cost. The GAC must be periodically replaced to ensure that breakthrough does not occur, but the carbon can be regenerated reducing the cost of replacement carbon somewhat.

5.2.4.3 Problems with the Use of Hydraulic Control for Groundwater Impacted by Energetic Compounds

Siting pump-and-treat aboveground infrastructure on an operational range without interfering with training activities may be problematic. Additionally, the efficacy of pump-and-treat can be adversely impacted by subsurface heterogeneities, fractured bedrock and zones of low hydraulic conductivity.

Operation and maintenance (O&M) costs for hydraulic control systems are typically very high. For example, the estimated O&M for the hydraulic control system at Umatilla Army Depot is $430K/yr for the cleanup of a RDX/TNT plume (ESTCP, 2004). Similarly, the projected cost for O&M at the former Naval Ammunition Plant Blaine, Nebraska, was $2M/yr with a projected lifetime of 50–80 yrs (ESTCP, 2004). Often it has been difficult to achieve site closure once a hydraulic control system has been implemented. When pumping is stopped, the groundwater table rises and interacts with the smear zone in previously unsaturated zones where contaminants still reside. This interaction results in desorption of the contaminants and an increase in contaminant concentrations in the groundwater, often to unacceptable concentrations.

References

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ESTCP. 2003b. Application of Flow and Transport Optimization Codes to Groundwater Pump and Treat Systems. ESTCP Final Technical Report Volume 2. September.

ESTCP. 2003c. Application of Flow and Transport Optimization Codes to Groundwater Pump and Treat Systems. ESTCP Final Technical Report Volume 3. September.

ESTCP. 2004. Application of Flow and Transport Optimization Codes to Groundwater Pump-and-Treat Systems. ESTCP Cost and Performance Report Project CU-0010. January.USEPA. 2011. USEPA Press Release: EPA Reaches Cleanup Decision for J1 Range and Groundwater Plumes at Camp Edwards, May 31.

Zheng C, Wang P. 2001. Application of Flow and Transport Optimization Codes to Groundwater Pump-and-Treat Systems: Umatilla Army Depot, Oregon. The Hydrogeology Group, University of Alabama, Technical Report, October, Revised 2003.

5.2.5 Constructed Wetlands

Pilot-scale constructed wetland at Milan AAP, Milan, Tennessee (ESTCP, 1999)

Description: A constructed wetland is a form of hydraulic control where impacted groundwater is pumped to the surface and passed through an artificial wetland that has been designed to remove energetic compounds as the water flows through the wetland.

Where It Can Be Used: Constructed wetlands are designed to mimic the powerful cleansing effects of natural marsh ecosystems by relying on different aerobic and anaerobic conditions with various aquatic plant species.

Advantages: The major advantage of this system is that it combines both plant-based mitigation with anaerobic/aerobic cycling to remove both nitroaromatics and nitramines.

Disadvantages: The main disadvantage of this type of groundwater management is the high annual operation and maintenance (O&M) costs of pumping groundwater to the surface. For treating energetic compounds, an energy source such as molasses must be added to create anaerobic conditions. The constructed wetland technology is also temperature dependent and implementation at sites in colder climates may be problematic.

Cost Information: A pilot-scale constructed wetland system was tested at Milan Army Ammunition Plant (AAP), Tennessee. Based on data collected during this demonstration, the total cost (capital and O&M) for a 10-acre, full-scale, gravel-based wetland system designed to treat 200 gallons per minute (gpm) of contaminated groundwater was estimated at $1.78 per thousand gallons of groundwater (ESTCP, 1999). The reported costs do not include the cost of well construction.

Recommendation: **This is a very expensive technology and does not seem to have an advantage over classical hydraulic control using granulated activated carbon (GAC) for managing contaminated groundwater. The only potential application for energetic residues on ranges seems to be the treatment of surface water drainage from a detonation area**.

Key Resources:

ESTCP. 1999. The Use of Constructed Wetlands to Phytoremediate Explosives-Contaminated Groundwater at the Milan AAP, Milan, Tennessee. ESTCP Project CU-9520 Cost and Performance Report. July. 46 p.

5.2.5.1 Technology Description

Natural wetlands have been used to treat municipal sewage for centuries, but the use of constructed wetlands to treat contaminated groundwater is relatively new (Vymazal, 2011). Numerous papers were published on this subject from the 1970s through the end of the century describing treatment systems to treat municipal wastewaters, as well as various waste streams containing organic chemicals such as landfill leachate, hydrocarbons, and other types of contaminants from manufacturing activities, chlorinated organic volatiles, and explosives (Haberl et al., 2003).

There are several different types of constructed wetlands: surface flow systems, horizontal subsurface flow systems, and vertical subsurface flow systems. Surface flow systems are densely vegetated with water depths usually <0.4 meters (m) (Haberl et al., 2003). In the subsurface flow systems, the water depth is greater—up to 1 m—and the treatment occurs mainly by facultative microorganisms living in association with the plant roots and substrate. Facultative organisms are those that can live with or without oxygen. Many successful subsurface flow systems have used emergent plants, those that have a portion of the plant above the water surface.

For systems treating municipal wastewaters, treatment occurs by a combination of settling of suspended solids, filtration, chemical precipitation, microbial degradation (both aerobic and anaerobic), adsorption, ion exchange, and plant uptake of nutrients. For municipal wastewater systems, the waste stream generally contains sufficient organic carbon to result in the development of anaerobic conditions in a portion of the system. For groundwater systems, however, an added source of organic carbon, such as molasses, and nitrogen and phosphorus fertilization has been used.

5.2.5.2 Systems to Treat Explosives Contaminated Groundwater

The use of constructed wetlands for management of groundwater contaminated with energetic compounds is a form of hydraulic control in that the groundwater must first be pumped to the surface. Several microcosm studies have investigated the use of constructed wetlands as a means of treating groundwater contaminated with explosives, mainly 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Best et al., 1997; 1998a; 1998b; Sikora et al., 1997). In general, rapid removal of TNT occurs with slower removal of RDX. Transformation of TNT occurs by several processes including photochemical degradation (Best et al., 1998b). Removal of RDX is by anaerobic microbial degradation and some plant uptake.

A pilot-scale field demonstration of this technology was conducted at the Milan Army Ammunition Plant (AAP), Tennessee, from 1996 to 1998 (Sikora et al., 1998). The goal of this project was to treat groundwater contaminated with TNT and RDX to concentrations <2 micrograms per liter (µg/L) for TNT and <50 µg/L total nitrobodies (including RDX). Groundwater from two different extraction wells was used during the demonstration. The initial concentrations in the two wells were 1,250 and 4,440 µg/L for TNT, and 3,250 and 9,200 µg/L for total nitrobodies.

Two different treatment schemes were evaluated. In one, a gravel-based system (4-feet [ft] deep) using emergent plants was evaluated. This system had two units connected in series. The first unit was maintained anaerobic by the addition of either milk replacement starter or molasses, while the second unit was maintained in an aerobic condition using a Tennessee Valley Authority-patented process (Sikora et al., 1998). The second scheme evaluated was a

lagoon-based system. This system used two 4-ft deep lagoons connected in series planted with submergent plants.

Both systems were built aboveground using 4-ft-high, prefabricated, PolyWall panels supported by earthen berms. The cells were lined with cross-grain laminated polyethylene. The gravel-based system was equipped with a nutrient delivery system. Influent and effluent manifolds were used to distribute the groundwater for each system. For the gravel system, water entered through a distribution header near the top of the anaerobic cell. Flow out of the first cell was collected using a collection header and flowed into the second cell using an outlet control sump to regulate the flow into the second cell. A more detailed description of the design of this system is available elsewhere (Sikora et al., 1998).

Four types of emergent plants were used in gravel-based cells: canary grass, wool grass, sweetflag, and Parrotfeather. Canary grass was used in the lagoon system because it can be a submerged plant as well as an emergent one. The anaerobic cell of the gravel-based system was initially inoculated with commercially available anaerobic bacteria that are commonly used in household septic tanks. The gravel-based system outperformed the lagoon-based system, thus no further description of the lagoon-based system is provided.

The treatment mechanism for the gravel-based system is complex and appears to be due to a combination of emergent plants and microbiological populations. Reduction in explosive concentrations occurs mainly in the anaerobic cell, with further treatment of explosive by-products, nutrients, and residual biological oxygen demand (BOD) in the aerobic cell.

The gravel-based system was operated by continuously pumping 5 gallons per minute (gpm) of groundwater into the 0.088-acre anaerobic cell. The water had a resident time of 8 days in the first cell and then flowed into the 0.030 acre aerobic cell with a resident time of 2 days. In the second year of operation, 1 gallon of molasses and 40 grams (g) of diammonium phosphate was added to the anaerobic cell each day.

The gravel-based system worked best and met treatment goals except for RDX in the coldest months when the activity of the microorganisms was reduced. The treated water was suitable for discharge directly to surface streams as well.

The battery limit cost of the system was estimated for a 1-acre system designed to treat 200 gpm at $3,466,000 (in 1998 dollars), however, this did not include the cost of extraction well installation (ESTCP, 1999). The annual operation and maintenance (O&M) costs were estimated at $62,666.

This technology was also evaluated to treat contaminated groundwater at several other U.S. Department of Defense (DoD) ammunition plants including the Volunteer AAP, Tennessee (Best et al., 2001) and the Iowa AAP (Kiker et al., 2001). The results were similar to those found for the gravel-based system with emergent plants at Milan AAP. At Volunteer AAP, the treatment goals for TNT were met, but not the goals for 2,4-DNT or 2,6-DNT. RDX was not present in the groundwater at Volunteer AAP.

5.2.5.3 Explosives-Contaminated Surface Water

A pilot-scale constructed wetland was evaluated for treatment of surface water drainage from a detonation area at a training range in Germany. At this location, the detonation area was rebuilt to include a drainage system and the water from the drainage system was passed through the constructed wetland basin (Gerth and Hebner, 2007). The basin was designed to contain

reactive iron, and molasses was added to the basin to promote the necessary reducing conditions. Maximum concentrations of explosives observed in the influent water were 7.4 mg/L TNT, 0.37 mg/L RDX and 0.055 mg/L HMX. The authors indicate that target values for the explosive compounds were met during the test phase; unfortunately, the target values were not defined in this paper.

5.2.5.4 Overall Assessment

Overall, the use of constructed wetlands would be a very expensive approach to treat explosives-contaminated groundwater or surface water at any DoD training range. The construction and operational costs of extraction wells would add to the expense of this technology for groundwater applications (see Section 5.2.4). In addition, the system may or may not meet treatment goals during winter, depending on the location of the system.

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Gerth A, Hebner A. 2007. Risk Assessment and Remediation of Military and Ammunition Sites. In Advanced Science and Technology for Biological Decontamination of Sites Affected by Chemical, Radiological Nuclear Wastes. NATO Science Series IV: Earth and Environmental Sciences, vol 75, part 1, pp 45-57.

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Explosives-Contaminated Groundwater Using Constructed Wetlands at the Milan Army Ammunition Plant, Milan, Tennessee (Volumes I through IV). Report No. SFIM-AEC-ET-CR-97059. Prepared for ESTCP. December.

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6 Status of Research and Development for Innovative Approaches

The U.S. Department of Defense (DoD) and the Military Services continue to invest in research, development, testing, and evaluation (RDT&E) projects to improve our understanding of the deposition, fate, and transport of the munitions constituents (MCs) from military training activities on ranges and in technologies to characterize and manage MCs in soil and groundwater.

Tables 6-1 and 6-2 provide a list of ongoing Strategic Environmental Research and Development Program (SERDP)- and Environmental Security Technology Certification Program (ESTCP)-funded efforts, respectively, with relevance to MCs and range sustainment. Additional information on these efforts can be found on the SERDP/ESTCP website by searching by the specific project ID number. Table 6-3 lists the projects relevant to range sustainability that were selected for funding in fiscal year 2012 by SERDP and ESTCP. Readers are encouraged to check the SERDP/ESTCP website[27] periodically for updated information on these efforts. Technical Reports and Cost and Performance Reports are posted as projects are completed.

Representatives from the Air Force, Navy, and Army were queried to identify RDT&E efforts focused on the deposition, fate, transport, and management of MCs in soil and groundwater that are funded directly by the Services. The Air Force does not currently have any RDT&E investments in this area.[28] The Navy is funding one field study of alkaline hydrolysis at a simulated demolition area at Pinecastle Range, Florida (see Section 5.1.1.2).[29] RDT&E efforts funded by the Army are listed in Table 6-4.

Table 6-1. Ongoing SERDP-Funded Efforts with Application to Range Sustainment

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Fate of Plant Tissue Associated RDX in Surface Soil	Dec-04	ER-1412	Charles Reynolds, U.S. Army ERDC/CRREL	Improve the understanding of RDX transformation in plant tissues and the subsequent cycling of tissue-associated RDX and daughter products among soil mineral and humic fractions following plant senescence.	Final Report Available

[27] www.serdp.org.

[28] Major Timothy D. Dalby, USAF/A7CAN, Arlington, VA; personal communication, 2011.

[29] Leslie A. Karr, NESDI Program Manager, Port Hueneme, CA; personal communication, July 2011.

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Defining Munitions Constituent Source Terms in Aquatic Environments on DoD Ranges	Apr-05	ER-1453	William Wild, SPAWAR Systems Center Pacific	Develop a scientific basis for quantitatively estimating the source terms associated with breached or broken projectile casings along with the fate and transport of MC contamination in the aquatic environments on DoD ranges as a component of a future risk assessment process. Specifically, to provide a predictive modeling capability of MC fate and transport associated with an unexploded breached projectile.	Final Report Available
Development of Toxicity Benchmarks and Bioaccumulation Data for N-Based Organic Explosives for Terrestrial Plants and Soil Invertebrates	Dec-05	ER-1416	Geoffrey Sunahara, National Research Council of Canada	Develop toxicity benchmark values, based on ecologically relevant soil biota, that are acceptable for derivation of Eco-Soil Screening Levels for energetic materials.	Final Report Available
Sustainable Range Management of RDX and TNT by Phytoremediation with Engineered Plants	Feb-06	ER-1498	Neil Bruce, University of York	Engineer transgenic grasses to contain and degrade RDX in the root zone of explosives-contaminated soil. Since munitions often consist of both RDX and TNT, it also will be necessary to engineer resistance to TNT as this explosive is highly toxic to plants.	2013
Rhizosphere Bacterial Degradation of RDX, Understanding and Enhancement	Apr-06	ER-1504	Stuart Strand, University of Washington	Develop an improved understanding of the relationship between rhizosphere bacteria and their host plants in environments exposed to MCs. Specifically, to (1) identify RDX-degrading bacteria in plant rhizospheres, (2) discover the factors that control their population levels, and (3) develop probes that can be used in the field to detect them.	2010
A Portable Fiberoptic Surface Enhanced Raman Sensor for Real-Time Detection and Monitoring of Perchlorate and Energetics	Oct-07	ER-1602	Baohua Gu, Oak Ridge National Laboratory	Develop a new, cost-effective tool for *in situ* quantification and monitoring of perchlorate (and energetics such as RDX) in groundwater via fiberoptic surface-enhanced Raman scattering (SERS).	Final Report Available

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Development of Biomarkers for Assessing *In Situ* RDX Biodegradation Potential	Jan-08	ER-1606	Alison Cupples, Michigan State University	Identify the microorganisms able to degrade RDX *in situ* and develop molecular tools so that the presence and abundance of these organisms can be investigated at different contaminated sites.	Phase I Final Report Available
Molecular Microbiology of Nitramine Degradation in Soils	Jan-08	ER-1608	Stuart Strand, University of Washington	Characterize the microbial communities of soils contaminated to varying degrees with RDX using molecular techniques, as well as to discover new RDX degrading bacteria, determine RDX metabolites, and elucidate the metabolic pathways mediating the degradation of RDX.	2012
New Approaches to Evaluate the Biological Degradation of RDX in Groundwater	Jan-08	ER-1607	Paul Hatzinger, Shaw Environmental	Combine state-of-the-art analytical techniques, molecular approaches, and biogeochemical studies to enhance understanding of the biodegradation of the nitramine explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in subsurface environments.	2011
Identification of Microbial Gene Biomarkers for *In Situ* RDX Biodegradation	Apr-08	ER-1609	Fiona Crocker, ERDC	Develop an understanding of the genetics, physiology, and biochemistry of RDX biodegradation to develop probes that can predict the potential for RDX biodegradation or monitor the progress of RDX bioremediation in the field.	Final Report Available
Periodic Mesoporous Organosilicas as Pre-Concentration Elements for Improved Long-Term Monitoring of Key Contaminants in Groundwater	Dec-08	ER-1604	Brandy White, U.S. Naval Research Laboratory	Develop the systems and methods necessary for applying novel periodic mesoporous organosilicate (PMO) materials to preconcentrate trace levels of key contaminants in groundwater and surface waters in order to improve in-line sensor performance for long-term monitoring.	Phase I Final Report Available
Fate and Transport of Colloidal Energetic Residues	Jan-09	ER-1689	Mark Fuller, Shaw Environmental	Assess the formation of these small-sized MC residues during controlled detonations and during weathering of larger residue particles and measure and model the transport (infiltration and surface runoff) and dissolution of these particles.	2012

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Dissolution Rate of Propellant Energetics from Nitrocellulose Matrices	Jan-09	ER-1691	Susan Taylor, U.S. Army ERDC	Characterize nitrocellulose-based propellant residues that result from firing commonly used military munitions and quantify how quickly 2,4-DNT in single-base propellants, NG in double-base propellants, and NQ in triple-base propellants leach from their nitrocellulose matrices.	Final Report Available
Mobility of Particulate and Dissolved Munitions Constituents in the Vadose Zone at Operational Ranges	Mar-09	ER-1690	Melanie Mayes, Oak Ridge National Laboratory	Understand, quantify, and predict the transport of particulate and dissolved MC in realistic vadose-zone conditions. Specific objectives are to determine the potential for preferential transport; quantify transport parameters for dissolved- and particle-phase MC under both normal vadose-zone conditions and under storm flow scenarios; and apply these parameters to site-specific subsurface models of operational ranges to predict the potential for mobility of explosive compounds through the vadose zone into underlying aquifers.	2012
Improving Understanding of the Fate and Transport of Munitions Constituents to Enhance Sustainability of Operational Ranges	Mar-09	ER-1688	Herbert Allen, University of Delaware	Develop models supported by appropriate data that can predict (1) the dissolution and release rate of NG and 2,4-DNT from NC matrix propellant residue and (2) the partitioning of military grade RDX, HMX, TNT, NG, DNT, NQ, and mixtures of these MCs to soils of varying physical/chemical characteristics.	2012
Antimony(V) Adsorption by Variable-Charge Minerals	Oct-09	ER-1741	Dr. Michael Essington, The University of Tennessee	Antimony (Sb) is a co-contaminant with lead (Pb) in shooting range soils at DoD installations. The objectives of this project are to (1) determine the mechanisms and thermodynamics of antimony adsorption by hydrous Fe and Al oxyhydroxides (goethite, gibbsite, and kaolinite) as a function of ionic environment, pH, temperature, and antimony concentration; (2) quantify the competitive effects of PO_4 and SO_4 on antimony adsorption; and (3) develop and evaluate the capability of chemical models to predict antimony adsorption within the holistic framework of a complex chemical environment.	2013

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Development of an Environmental Fate Simulator for New and Proposed Military-Unique Munition Compounds	Nov-09	ER-1736	Eric Weber, USEPA Office of Research and Development	Develop a Framework for Risk Analysis of Multimedia Environmental Systems (FRAMES)-based Environmental Fate Simulator (EFS) that will provide managers of military training and testing ranges estimates of the vulnerability of aquifers and surface waters to new and proposed energetic materials and their potential transformation products.	2013
Full In Silico Calibration of Empirical Predictive Models for Environmental Fate Properties of Novel Munitions Compounds	Nov-09	ER-1735	Paul Tratnyek, Oregon Health & Science University	Develop a novel, fully in silico approach to quantitative structure-activity relationships (QSAR) development, where all of the calibration data (both the target variable and the descriptor variables) are calculated from molecular structure theory. Rates of the most likely breakdown pathways (target variables) will be calculated with the highest level of theoretical accuracy, and these data will be correlated to molecular properties (descriptor variables) that are obtained with computational methods that are more available and feasible for most chemists. Once QSARs have been obtained by this approach, researchers will attempt to validate them by predicting data for safe and available model compounds and comparing them to measured experimental values.	2013
Developing Quantum Chemical and Polyparameter Models for Predicting Environmentally Significant Parameters for New Munition Compounds	Nov-09	ER-1734	Dominic Di Toro, University of Delaware	Develop models for predicting the physical chemical properties (aqueous solubility, octanol-water partition coefficient, and Henry's Law constant) and the potential bioaccumulation and metabolism of new munition compounds partitioning into soil organisms and plants.	2013

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Lead and Antimony Speciation in Shooting Range Soils: Molecular Scale Analysis, Temporal Trends, and Mobility	Apr-10	ER-1770	Thomas Trainor, University of Alaska Fairbanks	Improve the molecular- and nano-scale understanding of metal(loid) transport and bioavailability in range soils (lead and antimony in particular) with a focus on the rates and geochemical mechanism(s) of metallic fragment weathering, the rate and extent of oxidized metal(loid) dispersion, how metal(loid) dispersion is correlated with speciation, and how rates and extent of reaction are influenced by soil properties.	2013
Ecological Risk Assessment of Munitions Compounds on Coral and Coral Reef Health	Mar-11	ER-2125	Dr. Cheryl Woodley, NOAA National Ocean Service	Evaluate whether munitions compounds (MCs)–TNT, RDX, PETN, and HMX–or their breakdown products impact corals and determine the ecological risk they may pose to coral and coral reef health.	2015
Photochemical Transformation of Munitions Constituents in Marine Waters	Mar-11	ER-2123	Dr. Dianne Luning Prak, U.S. Naval Academy	Characterize the photochemical fate of MCs and the kinetics of such reactions at environmentally relevant concentrations in coastal waters. Specifically, to fill data gaps concerning (1) the mechanism of parent compound transformation, (2) the rates of photolysis of secondary products, and (3) the natural water characteristics that affect transformation rates (salinity, pH, chromophoric dissolved organic matter [CDOM], and nitrate concentration).	Final Report Available
Tracking the Uptake, Translocation, Cycling, and Metabolism of Munitions Compounds in Coastal Marine Ecosystems using Stable Isotopic Tracer	Mar-11	ER-2122	Craig Tobias, University of Connecticut	Quantify the pathways and rates of RDX and TNT processing in three typical coastal ecotypes: subtidal vegetated, subtidal unvegetated, and intertidal salt marsh.	2015

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
TNT Incorporation and Mineralization by Natural Microbial Assemblages at Frontal Boundaries between Water Masses and in Underlying Sediments in Coastal Ecosystems	Mar-11	ER-2124	Michael Montgomery, Naval Research Laboratory	Determine whether the environmental conditions at frontal boundaries enhance rates of TNT metabolism by natural microbial assemblages relative to those conditions found at other points along the salinity gradient.	Final Report Available

Table 6-2. Ongoing ESTCP-Funded Efforts with Application to Range Sustainment

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Passive Reactive Berm (PRBerm) to Provide Low Maintenance Lead Containment at Active Small Arms Firing Ranges	Apr-04	ER-200406	Steven Larson, U.S. Army ERDC	Training results in the deposition of metals, such as lead and copper, into berm soils ranging in size from whole projectiles to microscopic dust. Surface water runoff and leachate water represent two mechanisms with the potential to transport metals off-site. The technology to be demonstrated will address sites where high acidity soils are allowing high concentrations of lead in leachate water and surface water and the sites with high clay content soils that suspend well.	Technical Report Available
In Situ Bioremediation of Energetic Compounds in Groundwater	Apr-04	ER-200425	Paul Hatzinger, Shaw Environmental	Demonstrate an *in situ* technology for enhanced bioremediation of energetic compounds in groundwater.	Final Report and Cost and Performance Report Available
Open Burn/Open Detonation (OB/OD) Management Using Lime for Explosives Transformation	Apr-07	ER-200742	Andy Martin, U.S. Army ERDC	The technology to be demonstrated will address the reduction of RDX and TNT munitions constituents at an active OD range via the application of lime to induce alkaline hydrolysis. The lime addition also will immobilize the metals associated with common munitions. Minor erosion control measures will be established to reduce the surface water transport of sediments off-range through earthen berms.	Final Report and Cost and Performance Report Available
Modified Biopolymers as an Alternative to Petroleum-Based Polymers for Soil Modification	Jan-09	ER-200920	Steven Larson, U.S. Army ERDC	Establish the efficacy of scaling up to pilot production of Rhizobium tropici biopolymer, to determine industrial-scale cost information for production, and to perform a comparative performance evaluation of the biopolymer to a petroleum-based polymer.	Treatability Study Report Available
Improvement, Verification, and Refinement of Spatially Explicit Exposure Models in Risk Assessment	Jan-09	ER-200917	Mark Johnson, U.S. Army CHPPM	Test (verify) risk estimates for terrestrial wildlife (small mammals) and fish using spatially explicit exposure models. Field metrics will consist of a comparison of field-collected tissue data with tissue-based toxicity criteria, which are based on phenotypic biomarkers of effect. Model results will be compared with results from conventional deterministic risk estimates using the same data set.	2012

Title	Start Date	Project ID	Principal Investigator	Project Objective	Original Planned End Date
Demonstration of the Attributes of Multi-Increment Sampling and Proper Sample Processing Protocols for the Characterization of Metals on DoD Facilities	Apr-09	ER-200918	Jay Clausen, U.S. Army ERDC	Demonstrate the improved data quality that can be achieved by coupling multi-increment sampling with adequate sample processing for determining mass loading of metal constituents on military training ranges.	Technical Report Available
Passive Biobarrier for Treating Comingled Perchlorate and RDX in Groundwater at an Active Range	Nov-09	ER-201028	Paul Hatzinger, Shaw Environmental	Install a passive subsurface biobarrier at an operational DoD range (at an open burn/open detonation (OB/OD) site, munitions test range, explosive ordnance disposal (EOD) training area, target area, munitions disposal site, or other region where high concentrations of MCs are likely to occur). The barrier, which will be placed downgradient of one such area, will consist of an emulsified oil substrate applied using temporary injection wells. This barrier is expected to promote the rapid *in situ* biodegradation of perchlorate and explosives, including RDX, as well as HMX, TNT, DNTs and Tetryl.	2014
Generation of Biodegradation-Sorption Barriers for Munitions Constituents	Mar-11	ER-201123	Robert Borden, North Carolina State University	Demonstrate a process for enhancing the sorption and/or degradation of TNT, RDX, HMX, and perchlorate in soils by spray application of an amendment solution containing waste glycerol and a soluble humic material on the soil surface, followed by irrigation to carry the amendments deeper into the soil profile.	2015

Table 6-3. SERDP/ESTCP Efforts Selected for FY 2012 Funding

Project ID	Title	Principal Investigator	Organization	Original Planned End Date
SERDP ER-2219	Characterization of Residues from the Detonation of Insensitive Munitions	Sonia Thiboutot	Defense Research and Development Canada (DRDC), Valcartier	2015
SERDP ER-2220	Dissolution of NTO, DNAN and Insensitive Munitions Formulations and Their Fates in Soils	Katerina Dontsova	University of Arizona	2015
SERDP ER-2221	Interaction of Microbial and Abiotic Processes in Soil Leading to the (Bio)Conversion and Ultimate Attenuation of New Insensitive Munitions Compounds	James Field	University of Arizona	2015
SERDP ER-2222	Combined Biological and Chemical Mechanisms for Degradation of Insensitive Munitions in the Presence of Alternate Explosives	Kevin Finneran	Clemson University	2015
SERDP ER-2223	Development of Environmental Health Criteria for Insensitive Munitions (IMX-101-104)	Mark Johnson	U.S. Army Public Health Center	2015
ESTCP ER-201207	Bioaugmentation for Aerobic Bioremediation of RDX-Contaminated Groundwater	Mandy Michalsen	U.S. Army Corps of Engineers, Seattle District	2015
ESTCP ER-201208	Validation of Stable Isotope Ratio Analysis to Document the Biodegradation and Natural Attenuation of RDX	Paul Hatzinger	Shaw Environmental	2014
ESTCP ER-201213	A Flexible Permeable Reactive Barrier for Protection of Wetland Sediments from Heavy Metals in Runoff Water	Steven Larson	U.S. Army ERDC	2015

Table 6-4. ERDC-EL Efforts with Application to Range Sustainment (personal communication, Andy Martin, ERDC-EL, July 2012).

Title	Project ID	Principal Investigator	Project Objective	Project Start Date/ Original Planned End Date
Placement of Containment Berm (PRBerm) Connex at Active Firing Ranges	Containment Berm	Steve Larson and Andy Martin, U.S. Army ERDC-EL	Demonstrate that the Containment Berm (PRBerm™) connex will provide sufficient containment of bullets and bullet fragments for later removal from the berm material (i.e. sand) and recycling, ultimately demonstrating a closed loop SAFR system where the berm material (i.e. sand) can be placed back in the PRBerm™ connex following removal of bullets and bullet fragments.	Jul 2011/ 2012
Integration of Green Technologies at Training Ranges	Green Range	David Smith and Heather Smith, U.S. Army ERDC-EL	The project identifies green technologies potential for munitions constituent sequestration or degradation *in situ* with minimal to no impact on the training range or facility. Such technologies include a bioreactor for the degradation of munition constituents (i.e., RDX) migrating to and leaving the range via surface or groundwater.	Oct 2010/ 2013
Depleted Uranium (DU) Munitions & Munitions Residues Management for Range Sustainability and Legacy Sites	DU	Steve Larson and Vic Medina, U.S. Army ERDC-EL	Determine the environmental impact of munitions DU and residues in complex active range and legacy environments. Develop methods for the cost effective and environmentally protective management and/or removal of small metallic DU and residues from affected soils and sands.	Oct 2011/ 2014
Mechanistic Investigation of Lead Complexation by Plant Exudates	Pb Exudates	Afrachanna Butler, U.S. Army ERDC-EL	Determine the role of plant exudates in the observed enhancement of lead (Pb) mobility due to complexation and chelation mechanisms. Provide fundamental knowledge on the potential for plant exudates to mobilize Pb in the presence of environmentally relevant competing interactions.	Oct 2011/ 2014
Nanotechnology Development: Integrating Design with Environmental Sustainability Objectives	Nano-Technology	Jeffery Steevens, U.S. Army ERDC-EL	Develop quantitative relationships to characterize role of surface chemistry in the reactivity of nanomaterials with environmental media. Additional mechanistic studies focused on the role of surface chemistry and particle structure in the cellular mechanisms of action for nanomaterials.	Oct 2007/ 2010

Title	Project ID	Principal Investigator	Project Objective	Project Start Date/ Original Planned End Date
Nanotechnology for the Warfighter: Classification, Exploratory Design, Full Development	Nano-Technology	Jeffery Steevens, U.S. Army ERDC-EL	Integrate physical, chemical, and biological attributes of nanomaterials to develop computational chemistry approaches to predict the environmental risks of engineered nanomaterials. Use these computational approaches to proactively support warfighter technology development during its development. This focus area emphasizes materials in R&D which is different from life cycle of materials in demonstration or operations.	Oct 2009/ 2015
Role of Functionalization on Availability and Toxicity of Carbon Nanotubes	NanoTubes	Al Kennedy, U.S. Army ERDC-EL	Investigate the various carbon materials and determine the most appropriate approach to assess exposure and toxicity. Leveraging: analytical approaches, materials, and data generated.	Oct 2007/ 2010

Appendices

Appendix A – Canadian Approach

A.1 Strategic Vision

The Canadian Army has recognized that damaging the environment will pose a risk to military readiness in the 21st Century. They acknowledge their moral obligation to protect the environment and have developed a roadmap for the future. Their strategic vision is "by 2013, the Army will be an environmental leader among Federal organizations and allied armies, by providing a healthy sustainable environment in support of operations."[30]

The Canadian Army controls over 20% of all the federal land and buildings within Canada and, thus, has a huge footprint within the country. To comply with laws and regulations, and provide due diligence, the Canadian Army's Environmental Program has addressed the same sets of issues as faced by the U.S. Department of Defense (DoD), including contaminated sites, leaking fuel tanks, hazardous materials, effluents, and endangered species. Overall, the mission of the Canadian environmental program is to support the Army by contributing to sustainable military readiness through dedicated environmental stewardship.

A.2 Sustainable Training Ranges

One of the four strategic goals of the Canadian Army's Environmental Program (2008–2013) is: "Sustainable Ranges and Training Areas (RTAs): Ensure RTAs are managed in an environmentally sustainable manner." To pursue that goal, the Canadian Army has established a Range and Training Area Environmental Program. The objectives of this program are to:

- Identify key sources of contamination on the various types of military ranges,
- Describe the behavior of these contaminants in the environment (soil and water) associated with each type of training activity,
- Consolidate and summarize the key findings, and
- Identify knowledge gaps.

In response, they established a research program to address these issues.

A.3 Canadian Research Activities on Energetic Residues at Training Ranges

In the United States, the environmental attention on energetic residues was centered on ammunition plants and depots during the 1980s and early-1990s. This was because these facilities were Government Owned, Contractor Operated facilities located throughout the United States, and plumes of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) contamination were found in groundwater that had migrated beyond installation boundaries at a large number of these facilities.

In Canada, energetic compounds were manufactured by private companies, and, thus, the military did not have to deal with military facilities contaminated with the huge masses of explosives residues in disposal lagoons or burning grounds. Instead, they focused their attention

[30] Major Robert Lajoie, Director Land Environment, Canadian Army. 2011.

on military training facilities in the early 1990s. The Defence Research Establishment Valcartier (DREV) in Quebec took the lead and initiated a program to understand the situation at various types of training range complexes. In 1995, these researchers studied the Arnhem antitank rocket range at Canadian Forces Base (CFB) Valcartier, north of Quebec City. They found that the soil at the impact area at the Arnhem Range was contaminated with large concentrations of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) originating from M-72 light antitank weapon (LAW) Rockets (Thiboutot et al., 1998).

The researchers at DREV (now Defence Research and Development Canada [DRDC] Valcartier) subsequently developed a program to characterize the main training ranges within Canada and also collaborated with U.S. Army Engineer Research and Development Center (ERDC)-U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and ERDC-Environmental Laboratory (EL) on a number of Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) projects to develop an understanding of the issues associated with energetic residues at the various types of military training ranges.

The research team at DRDC Valcartier also characterized six of the major Canadian Army training bases with respect to munitions constituents (MCs), in particular metals and energetic residues. They conducted soil sampling utilizing much of the expertise gained by their collaboration on SERDP projects with ERDC and groundwater sampling and published many internal reports on each RTA. The Director Land Environment prepared a summary document that combined all the results obtained over the last years from the six RTAs which is entitled: “Army Bases Range and Training Area Characterization.”

A.4 Hydrogeologic Approach

The Canadian approach to determining if there is a groundwater issue with energetic compounds from a specific range is straightforward: install a set of groundwater monitoring wells in the area of concern and sample and analyze the groundwater on a routine basis. The wells installed at Canadian ranges are flush-mounted and do not provide a visual signature that might be tempting as an artillery target. Thus far, there have been no well losses due to detonations.

At present, wells have been or are being installed at six major Army training ranges within Canada. The method of well installation and well location selection was developed by Dr. Richard Martel, professor of Geohydrology at the University of Quebec (National Institute of Scientific Research, Earth Water and Environment Center). Because wells are being installed within impact ranges (on access roads or very near the impact area but not in the impact areas *per se*) where it is possible that unexploded ordnance (UXO) is present, care is taken to precede drilling with magnetometers to ensure that contact with UXO is prevented.

Two sampling campaigns are planned per year, to include groundwater and surface water samples. If necessary, sampling campaigns are scheduled to correspond with climatological events that impact dissolution and transport of surface residues. For instance, research conducted at the Arnhem range determined that leaching of contaminants from residues in the surface soil only occurred during periods of groundwater recharge; for Arnhem, this was largely in the spring after snow melt, and to a lesser degree in the fall (Martel et al., 2009).

A.5 Example of Canadian Approach at Arnhem Antitank Rocket Range

An example of the type of information that can be obtained by combining surface soil sampling, a geophysical survey using ground penetrating radar, and groundwater analysis is provided in Martel et al. (2009) for the Arnhem antitank range at CFB Valcartier near Quebec City. Details on the drilling and well installation within and near the range are presented in Mailloux et al. (2008).

The main objective of the work at Arnhem is "the hydrogeological characterization (stratigraphy, piezometry, and hydrological properties) of the area around the Arnhem Antitank Range, and its flow regime to better understand the migration of EM in the subsurface" (Mailloux et al., 2008). The weapon used predominantly at the Arnhem Range has been the 66-mm M-72 LAW Rocket, which contains Octol (HMX/TNT) in the warhead, and double-base propellant in the rocket motor containing nitrocellulose (NC), nitroglycerin (NG), and ammonium perchlorate.

Characterization of the surface soil in the source zones indicated that HMX was the predominant residue at the impact areas with concentrations as high as 1,230 milligrams per kilogram (mg/kg), whereas TNT was present at much lower concentrations, about 1/100th of the HMX concentration. NG was the predominant mobile residue behind the firing points with concentrations as high as 1,970 mg/kg (Jenkins et al., 2004). The concentrations of HMX in the groundwater beneath the Arnhem range ranged from less than detection to 230 micrograms per liter (µg/L) (Martel et al., 2009).

Based on the results of this study, conceptual site models (CSMs) for HMX and TNT behavior at the Arnhem range were developed. Octol is deposited as particles largely from ruptured M-72 rockets. The residues are scattered onto surface soils and the distribution of Octol is very heterogeneous resulting in concentrations that vary over several orders of magnitude from spot to spot. Precipitation slowly dissolves the Octol, with the dissolution of TNT occurring at a much faster rate, leaving crystals of HMX on the surface. HMX is weakly retarded in soil and does not biodegrade under the prevailing aerobic conditions. TNT both phototransforms and, once dissolved, is biotransformed but not mineralized. TNT's transformation products can be bound irreversibly to soils and both they and TNT are only rarely observed in groundwater wells located at the range. An HMX plume intercepts the regional aquifer, occurring as a series of slugs that are generated at each infiltration event via advective transport. The major infiltration of HMX into the aquifer occurs as a slug during spring snow melt with a smaller slug in the fall (USEPA, 2012).

A.6 Vulnerability, Hazard, and Risk Maps

The Canadians are also developing land use tools that can help reduce the potential for aquifer contamination from military training in the future. One approach being taken is the development of Risk and Vulnerability Maps for an installation. Using geologic and hydrogeologic properties such as infiltration and effective porosity, a Vulnerability Map based on the downward advective time (time of travel from the surface to the first aquifer) (Martel et al., 2011) is developed. This provides a comparison of the relative ease of transport of dissolved contaminants on the ground surface to reach the upper boundary of an aquifer (Figure A-1). The maps are color-coded for ease in locating the most vulnerable areas to avoid in the future development of range areas.

Next, a Hazard Map is developed based on the risk of environmental contamination from various military activities, such as firing point and impact area locations. The numbers of rounds fired and the number of low-order detonations that occur in specific areas are estimated (Figure A-2) to assess the severity of the hazard. The maps are then combined to produce color-coded Risk Maps (Figure A-3), with risk indices ranging from 1 (very low) to 5 (very high). These maps are very useful for planning new range locations that avoid areas where leaching and offsite contaminant migration potential is highest, and could be used to establish new target areas at existing ranges.

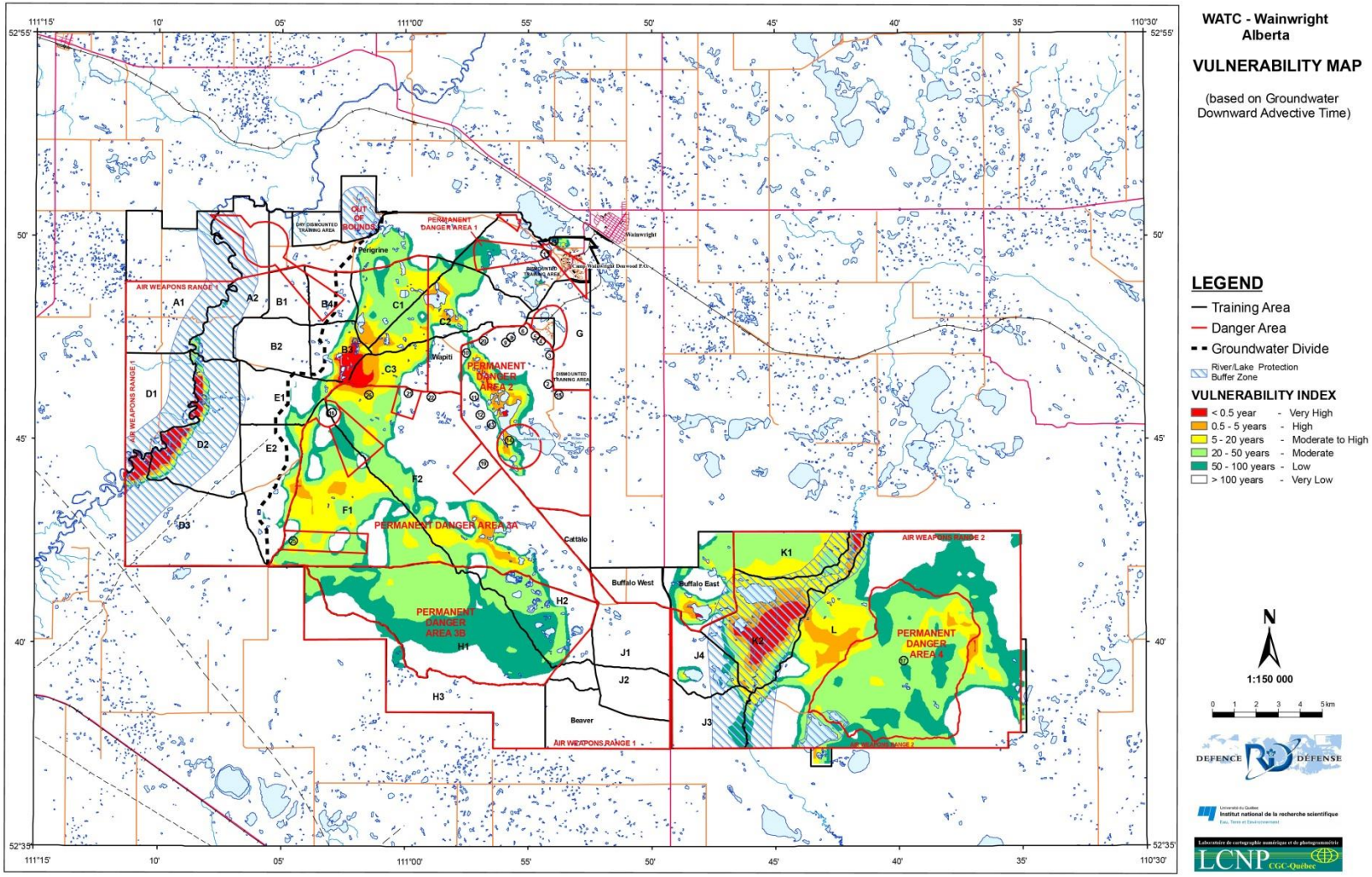

Figure A-1. Vulnerability Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

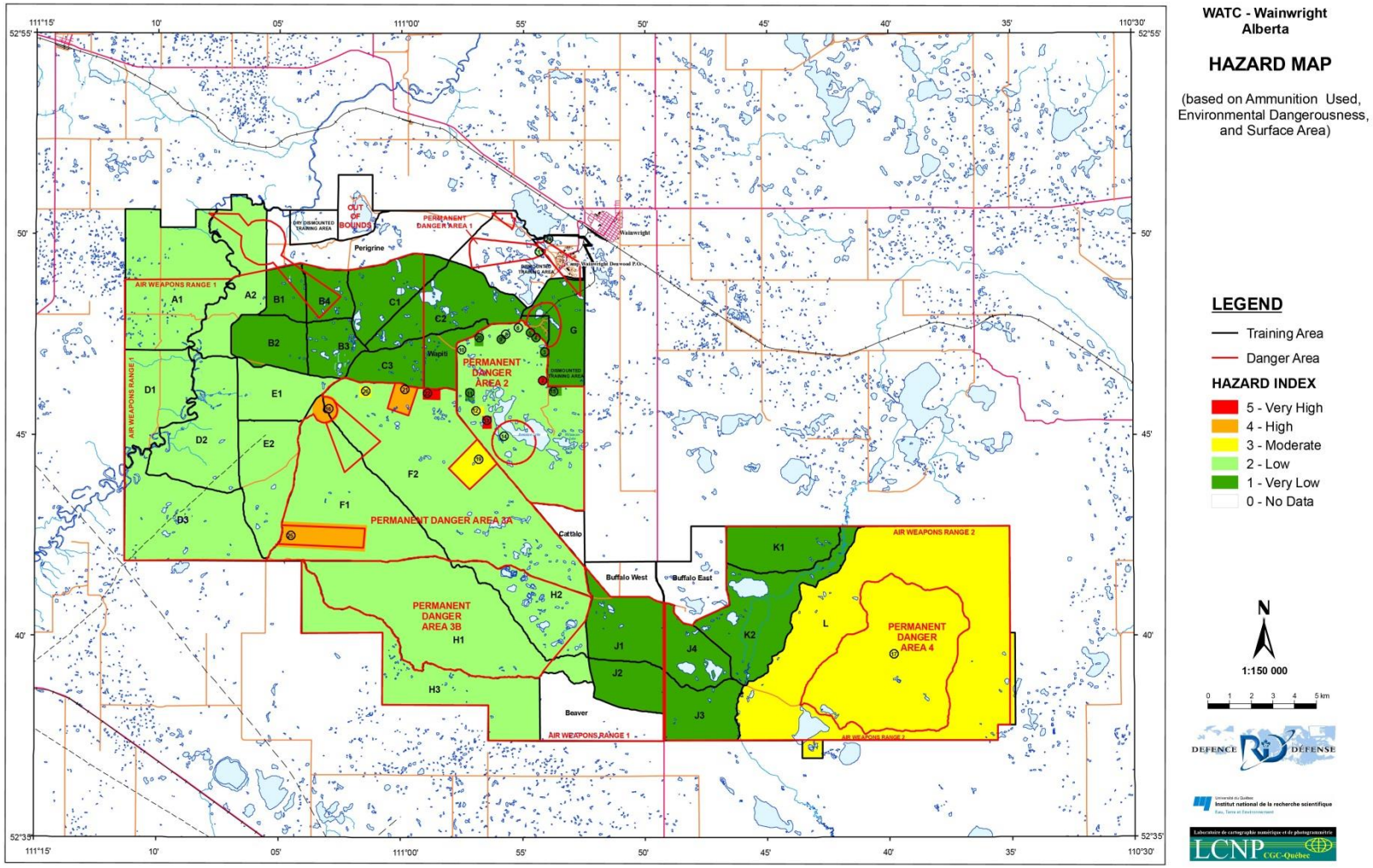

Figure A-2. Hazard Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

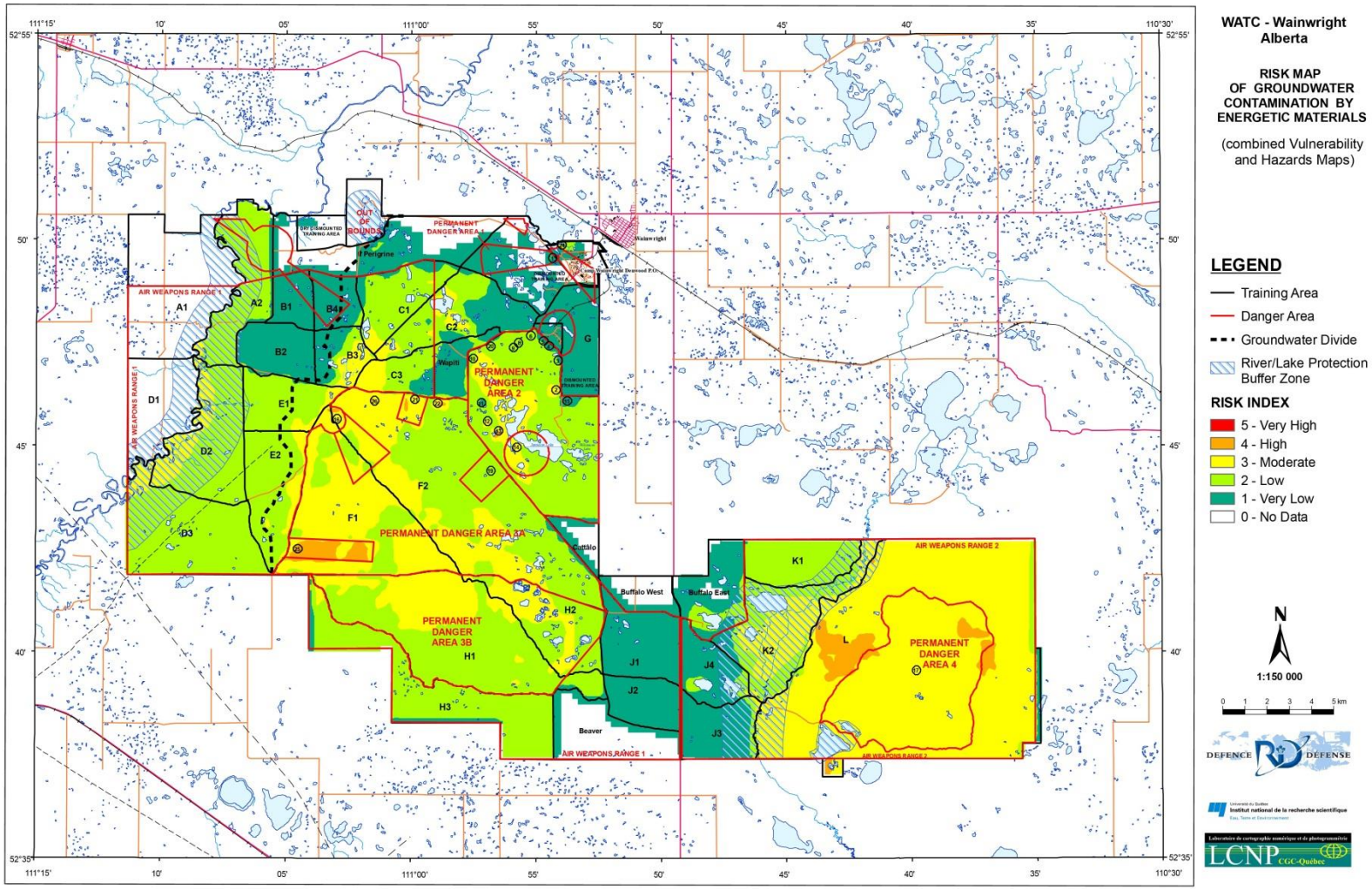

Figure A-3. Risk Map for CFB Wainwright. Map is provided courtesy of Dr. Sylvie Brochu, Defence Research and Development Canada - Valcartier, Québec, Canada and reprinted with the permission of Director Land Environment from the Canadian Department of the National Defence.

A.7 Status

Groundwater wells have been installed at six major Canadian Army installations, and routine analysis of groundwater samples is ongoing. Thus, direct evidence of whether there are, or are not, issues with energetic residues in groundwater is being generated at each installation. The cost of well installations at Canadian ranges has been estimated at $1M/installation (an average of 120 wells per installation). Risk and Vulnerability Maps have been completed for three of the Canadian Army training bases thus far.

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Appendix B – Acronyms and Abbreviations

°C	degree Celsius
µg	microgram(s)
µg/L	microgram(s) per liter
1,3,5-TNB	1,3,5-trinitrobenzene
2-Am-DNT	2-amino-4,6-dinitrotoluene
2-NT	2-nitrotoluene
2,4-DANT	2,4-diamino-6-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
2,6-DNT	2,6-dinitrotoluene
3-D	three-dimensional
3-NT	3-nitrotoluene
3,5-DNA	3,5-dinitroanaline
4-Am-DNT	4-amino-2,6-dinitrotoluene
4-NT	4-nitrotoluene
AAP	Army Ammunition Plant
AEC	U.S. Army Environmental Command
AFB	Air Force Base
AP	ammonium picrate
APG	Aberdeen Proving Ground
atm	atmosphere
bgs	below ground surface
BIP	blow-in-place
BMP	best management practice
C4	Composition 4
cal	caliber
CBU	cluster bomb unit
CFB	Canadian Forces Base
CJ-20	China Lake-20
cm	centimeter(s)
CMDB	composite modified double base
CRREL	Cold Regions Research and Engineering Laboratory, one of the ERDC laboratories in Hanover, NH.
CSIA	compound specific isotope analysis
DEGDN	diethylene glycol dinitrate
DNB	dinitrobenzene
DNT	dinitrotoluene
DNX	hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine
DoD	U.S. Department of Defense
DPA	diphenylamine

DRDC	Defence Research and Development Canada
DREV	Defence Research Establishment Valcartier (now DRDC Valcartier)
EGDN	ethylene glycol dinitrate
EOD	explosive ordnance disposal
ERDC	U.S. Army Engineer Research and Development Center, a combination of four Corps of Engineers research laboratories
ERDC-EL	U.S. Army Engineer Research and Development Center, Environmental Laboratory in Vicksburg, MS
ESTCP	Environmental Security Technology Certification Program
FEP	fluorinated ethylene propylene
ft	foot/feet
FP	firing point
FUDS	Formerly Used Defense Site
g	gram(s)
g/L	gram(s) per liter
GAC	granulated activated carbon
GC	gas chromatography
gpm	gallon(s) per minute
HE	high explosive
HEP	high-explosive plastic
HFTW	horizontal flow treatment well
Hg	mercury
HGR	hand grenade range
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high-performance liquid chromatography
HTPB	hydroxyl-terminated polybutadiene
HTRW	hazardous, toxic, and radioactive waste
IA	impact area
in	inch(es)
K	Kelvin
K_{OW}	octanol/water partition coefficient
kg	kilogram(s)
L	liter(s)
LAW	light antitank weapon
LC/MS	liquid chromatography/mass spectrometry
m	meter(s)
m^2	square meter(s)
m^3	cubic meter(s)
MC	munitions constituent
MEC	munitions and explosives of concern

MG	machine gun
mg	milligram(s)
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per liter (also expressed as mg L^{-1})
MIDAS	Munitions Items Disposition Action System
min	minute(s)
MIS	*MULTI-INCREMENT*® sampling
mL	milliliter(s)
mm	millimeter(s)
mM	millimolar
MMR	Massachusetts Military Reservation
MMRP	Military Munitions Response Program
MNA	monitored natural attenuation
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
mol	mole(s)
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NB	nitrobenzene
NC	nitrocellulose
NDPA	N-nitrosodiphenylamine
NEW	net explosive weight
NG	nitroglycerin
NQ	nitroguanidine
O&M	operation and maintenance
OB/OD	open burn/open detonation
ORAP	Operational Range Assessment Program
ORC	operational range clearance
PA	picric acid
PCD	Pueblo Chemical Depot
PE	polyethylene
PETN	pentaerythritol tetranitrate
PFA	perfluoroalkoxy
PMSO	peat moss and soybean oil
PP	polypropylene
PQL	Practical Quantitation Limit
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RDT&E	research, development, testing, and evaluation
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
REVA	Range Environmental Vulnerability Assessment
RSD	relative standard deviation
RTA	range and training area
SAR	small arms range

sec	second(s)
SERDP	Strategic Environmental Research and Development Program
TAT	triaminotoluene
TATB	2,4,6-triamino-1,3,5-trinitrobenzene
TNB	trinitrobenzene
TNT	2,4,6-trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TTA	thermal treatment area
TZMW	treatment zone monitoring well
USACE	U.S. Army Corps of Engineers
USACHPPM	U.S. Army Center for Health Promotion and Preventive Medicine (now the U.S. Army Public Health Command [USAPHC])
USAEC	U.S. Army Environmental Command
USAF	U.S. Air Force
USAPHC	U.S. Army Public Health Command
USEPA	U.S. Environmental Protection Agency
USMC	U.S. Marine Corps
USN	U.S. Navy
UV	ultraviolet
UXO	unexploded ordnance
v/v	percent by volume
VOA	volatile organic analysis
VOC	volatile organic compound
yr(s)	year(s)
ZVI	zero-valent iron