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SITE CHARACTERIZATION FOR MUNITIONS CONSTITUENTS

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This Federal Facilities Forum Issue Paper: Site Characterization For Munitions Constituents was prepared to provide remedial project managers and other federal, state, and private personnel working on hazardous waste sites the technical information needed to make decisions regarding the nature of energetic residues on Department of Defense training ranges (and other munitions sites such as Formerly Used Defense Sites), sampling strategies that provide representative samples, and analytical methods developed to characterize these samples.

This paper is not intended to include discussions of the safety issues associated with sites contaminated with energetic residues. Examples of explosives safety issues include, but are not limited to: geophysical detection methods, explosion (detonation) hazards, toxicity of secondary explosives, and personal protective equipment. Information pertaining to geophysical investigations has been summarized by ESTCP/ITRC (2006) and toxicity concerns can be found in Roberts and Hartley (1992), Yinon (1990), and Sunahara et al. (2009). Also, this paper is not intended to serve as a guide for geophysical investigation of unexploded ordnance (UXO) or discarded military munitions (DMM), or chemical sampling and analysis of bulk high explosives, primary explosives where concentrations exceed 20,000 mg/kg (2%), or secondary explosives in soil where concentrations exceed 100,000 mg/kg (10%).

It is imperative that any persons working on sites thought to be contaminated with energetic residues thoroughly familiarize themselves with the physical and toxic properties of the materials potentially present and take all measures as may be prudent and/or prescribed by law to protect life, health, and property. These conditions present a potential detonation hazard; therefore, explosive safety procedures and safety precautions should be identified before initiating site characterization activities in such environments.

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Glossary of Terms[1]

Blow-in-place. Method used to destroy UXO/DMM, by use of additional explosives, in the location the item is encountered.

Caliber. The diameter of a projectile or the diameter of the bore of a gun or launching tube. Caliber is usually expressed in millimeters or inches. In some instances (primarily with naval ordnance), caliber is also used as a measure of the length of a weapon's barrel. For example, the term "5 inch 38 caliber" describes ordnance used in a 5-inch gun with a barrel length that is 38 times the diameter of the bore. [4]

Casing. The fabricated outer part of ordnance designed to hold an explosive charge and the mechanism required to detonate this charge.

Deflagration. A rapid chemical reaction occurring at a rate of less than 3,300 feet per second in which the output of heat is enough to enable the reaction to proceed and be accelerated without input of heat from another source. 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. [5]

Detonation. A violent chemical reaction within a chemical compound or mechanical mixture evolving heat and pressure. The result of the chemical reaction is exertion of extremely high pressure on the surrounding medium. The rate of a detonation is supersonic, above 3,300 feet per second. [2]

Discarded Military Munitions (DMM). Military munitions that have been abandoned without proper disposal or removed from storage in a military magazine or other storage area for the purpose of disposal. The term does not include unexploded ordnance, military munitions that are being held for future use or planned disposal, or military munitions that have been properly disposed of consistent with applicable environmental laws and regulations 10 U.S.C. 2710 (e)(2). [10]

Dud-fired. Munitions that failed to function as intended or as designed. They can be armed or not armed as intended or at some stage in between.

Explosion. A chemical reaction of any chemical compound or mechanical mixture that, when initiated, undergoes a very rapid combustion or decomposition, releasing large volumes of highly heated gases that exert pressure on the surrounding medium. Also, a mechanical reaction in which failure of the container causes sudden release of pressure from within a pressure vessel. Depending on the rate of energy release, an explosion can be categorized as a deflagration, a detonation, or pressure rupture. [2]

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[1] Terms as defined in US EPA. 2005. EPA Handbook on the Management of Munitions Response Actions; Interim Final.

Explosive. A substance or mixture of substances, which is capable, by chemical reaction, of producing gas at such a temperature, pressure and rate as to be capable of causing damage to the surroundings.

Explosive filler. The energetic compound or mixture inside a munitions item.

Explosive ordnance disposal (EOD). The detection, identification, field evaluation, rendering-safe recovery, and final disposal of unexploded ordnance or munitions. It may also include the rendering-safe and/or disposal of explosive ordnance that has become hazardous by damage or deterioration, when the disposal of such explosive ordnance is beyond the capabilities of the personnel normally assigned the responsibilities for routine disposal. EOD activities are performed by active duty military personnel. [7]

Explosive soil. Explosive soil refers to any mixture of explosives in soil, sand, clay, or other solid media at concentrations such that the mixture itself is reactive or ignitable. The concentration of a particular explosive in soil necessary to present an explosion hazard depends on whether the explosive is classified as "primary" or "secondary." Guidance on whether an explosive is classified as "primary" or "secondary" can be obtained from Chapters 7 and 8 of TM 9-1300-214, Military Explosives. [1]

Explosive train. The arrangement of different explosives in munitions arranged according to the most sensitive and least powerful to the least sensitive and most powerful (initiator - booster - burster). A small quantify of an initiating compound or mixture, such as lead azide, is used to detonate a larger quantity of a booster compound, such as tetryl, that results in the main or booster charge of a RDX composition, TNT, or other compound or mixture detonating.

Formerly Used Defense Site (FUDS). Real property that was formerly owned by, leased by, possessed by, or otherwise under the jurisdiction of the Secretary of Defense or the components, including organizations that predate DoD. [1]

Fragmentation. The breaking up of the confining material of a chemical compound or mechanical mixture when an explosion occurs. Fragments may be complete items, subassemblies, or pieces thereof, or pieces of equipment or buildings containing the items. [2]

Fuze. 1. A device with explosive components designed to initiate a train of fire or detonation in ordnance. 2. A non-explosive device designed to initiate an explosion in ordnance. [3]

Ground-penetrating radar. A system that uses pulsed radio waves to penetrate the ground and measure the distance and direction of subsurface targets through radio waves that are reflected back to the system.

Magnetometer. An instrument for measuring the intensity of magnetic fields.

Military munitions. All ammunition products and components produced for or used by the armed forces for national defense and security, including ammunition products or components under the control of the Department of Defense, the Coast Guard, the Department of Energy, and the National Guard. The term includes confined gaseous, liquid, and solid propellants, explosives, pyrotechnics, chemical and riot control agents, chemical munitions, rockets, guided and ballistic missiles, bombs, warheads, mortar rounds, artillery ammunition, small arms ammunition, grenades, mines, torpedoes, depth charges, cluster munitions and dispensers, demolition charges, and devices and components thereof.

The term does not include wholly inert items, improvised explosive devices, and nuclear weapons, nuclear devices, and nuclear components, other than non-nuclear components of nuclear devices that are managed under the nuclear weapons program of the Department of Energy after all required sanitization operations under the Atomic Energy Act of 1954 (42 U.S.C. 2011 et seq.) have been completed (10 U.S.C. 101 (e)(4). [10]

Munitions constituents (MC). Any materials originating from unexploded ordnance, discarded military munitions, or other military munitions, including explosive and nonexplosive materials, and emission, degradation, or breakdown elements of such ordnance or munitions. (10 U.S.C. 2710 (e)(4)).[10] Munitions constituents may be subject to other statutory authorities, including but not limited to CERCLA (42 U.S.C. 9601 et seq.) and RCRA (42 U.S.C. 6901 et seq.).

Munitions and Explosives of Concern (MEC). This term, which distinguishes specific categories of military munitions that may pose unique explosives safety risks, means: (1) Unexploded ordnance (UXO); (2) Discarded military munitions (DMM); or (3) Munitions Constituents (e.g. TNT, RDX) present in high enough concentrations to pose an explosive hazard. Formerly known as Ordnance and Explosives (OE). [10]

Open burning. The combustion of any material without (1) control of combustion air, (2) containment of the combustion reaction in an enclosed device, (3) mixing for complete combustion, and (4) control of emission of the gaseous combustion products. [6]

Open detonation. A chemical process used for the treatment of unserviceable, obsolete, and/or waste munitions whereby an explosive donor charge initiates the munitions to be detonated. [6]

Operational range. A range that is under the jurisdiction, custody, or control of the Secretary of Defense and (A) that is used for range activities; or (B) although not currently being used for range activities, that is still considered by the Secretary to be a range and has not been put to a new use that is incompatible with range activities. [10]

Practice ordnance. Ordnance manufactured to serve a training purpose. Practice ordnance generally does not carry a full explosive payload. Practice ordnance may still contain explosive components such as spotting charges, bursters, and propulsion charges. [9]

Projectile. An object projected by an applied force and continuing in motion by its own inertia, as mortar, small arms, and artillery projectiles. Also applied to rockets and to guided missiles.

Propellant. An agent such as an explosive powder or fuel that can be made to provide the necessary energy for propelling ordnance.

Range. Means designated land and water areas set aside, managed, and used to research, develop, test and evaluate military munitions and explosives, other ordnance, or weapon systems, or to train military personnel in their use and handling. Ranges include firing lines and positions, maneuver areas, firing lanes, test pads, detonation pads, impact areas, and buffer zones with restricted access and exclusionary areas. (40 CFR § 266.601) A recent statutory change added Airspace areas designated for military use in accordance with regulations and procedures prescribed by the Administrator of the Federal Aviation Administration. (10 U.S.C. 101 (e)(3)).

Unexploded ordnance (UXO). These Guidelines will use the term "UXO" as defined in the Military Munitions Rule. "UXO means military munitions that have been primed, fuzed, armed, or otherwise prepared for action, and have been fired, dropped, launched, projected, or placed in such a manner as to constitute a hazard to operations, installation, personnel, or material and that remain unexploded either by malfunction, design, or any other cause." This definition also covers all ordnance-related items (e.g., low-order fragments) existing on a non-operational range. (40 CFR Part 266.201, 62 FR 6654, February 12, 1997).[8]

Warhead. The payload section of a guided missile, rocket, or torpedo.

Sources:

1. U.S. Army Corps of Engineers Pamphlet No. 1110-1-18, "Engineering and Design Ordnance and Explosives Response," April 24, 2000.
2. DoD 6055.9-STD, Department of Defense Ammunition and Explosives Safety Standards.
3. Federal Advisory Committee for the Development of Innovative Technologies, "Unexploded Ordnance (UXO): An Overview," Naval Explosive Ordnance Disposal Technology Division, UXO Countermeasures Department, October 1996.
4. National Oil and Hazardous Substances Pollution Contingency Plan (more commonly called the National Contingency Plan), 40 C.F.R. § 300 et seq.
5. Department of Defense Directive 6055.9. "DoD Explosives Safety Board (DDESB) and DoD Component Explosives Safety Responsibilities," July 29, 1996.
6. Department of Defense. Policy to Implement the EPA's Military Munitions Rule. July 1, 1998.
7. Joint Publication 1-02, "DoD Dictionary of Military and Associated Terms," April 12, 2001.
8. Military Munitions Rule: Hazardous Waste Identification and Management; Explosives Emergencies; Manifest Exception for Transport of Hazardous Waste on Right-of-Ways on Contiguous Properties, Final Rule, 40 C.F.R. § 260 et seq.
9. Former Fort Ord, California, Draft Ordnance Detection and Discrimination Study Work Plan, Sacramento District, U.S. Army Corps of Engineers. Prepared by Parsons. August 18, 1999.
10. Department of Defense Memorandum, "Definitions Related to Munitions Response Actions," from the Office of the Under Secretary of Defense, December 18, 2003.

Nomenclature

Term	Description
1,3,-5-TNB	1,3,5-Trinitrobenzene
3,5-DNA	3,5-Dinitroanaline
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
2AmDNT	2-amino-4,6-dinitrotoluene
4AmDNT	4-amino-2,6-dinitrotoluene
AEC	Army Environmental Command
AEHA	Army Environmental Hygiene Agency
Akardite	1-methyl-3,3-diphenylurea
C4	Composition C4 (91% RDX, 9% oil)
CFB	Canadian Forces Base
CHPPM	Center for Health Promotion and Preventive Medicine
CL-20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
CMDB	Composite Modified Double Base
Comp B	Composition B (60% RDX, 39% TNT, 1% wax)
CRREL	US Army Cold Regions Research and Engineering Laboratory
DDNP	Diazodinitrophenol
DEGDN	Diethylene glycol dinitrate
Decision Unit	The area that a soil sample is intended to represent, called the sampling unit in this document
DMM	Discarded Military Munitions
DNA	Dinitroanaline
DNT	Dinitrotoluene
DoD	U.S. Department of Defense
DPA	Diphenylamine
DQO	Data Quality Objectives
EDGN	Ethylene Glycol Dinitrate
EIS	Environmental Impact Statement
EOD	Explosive Ordnance Disposal
EPA	Environmental Protection Agency
ERDC	Engineering Research and Development Center
ERF	Eagle River Flats
Ethyl Centralite	Diethyl-1,3-diphenylurea
Explosive D	Ammonium Picrate
FUD	Formerly Used Defense site

Term	**Description**
GC	Gas Chromatography
H-6	RDX, TNT, aluminum
HE	High Explosive
HEP	High-explosive Plastic
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetreazocine (High-Melting Explosive)
HPLC	High Performance Liquid Chromatography
HTPB	Hydroxy-terminated polybutadiene
KDNBF	Potassium Dinitrobenzofuroxane
LAW	Light Anti-armor Weapon
LC/ESI/MS	Liquid Chromatography/Electrospray Ionization/Mass Spectrometry
LIDAR	Light detection and ranging
LMNR	Lead Mononitroresorcinate
MC	Munition constituents
MEC	Munitions and Explosives of Concern
MIS	*MULTI-INCREMENT*® sample, sometimes called Incremental Sample (IS)
MLRS	Multiple Launch Rocket System
MMR	Massachusetts Military Reservation, also referred to as Camp Edwards
MMRP	Military Munitions Response Program
MS	Mass Spectrometry
NEW	Net explosive weight
NC	Nitrocellulose
NDPA	N-Nitrosodiphenylamine
NG	Nitroglycerin
NQ	Nitroguanidine
OB	Open Burn
Octol	70 % HMX, 30% TNT
OD	Open Detonation
OSW	Office of Solid Waste
PCN	Polychlorinated naphthalene
PETN	Pentaerythritol Tetranitrate
QA/QC	Quality Assurance/Quality Control

Term	Description
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive), cyclonite
RSD	Relative Standard Deviation
RPD	Relative Percent Difference
Sampling Unit	The area that a soil sample is intended to represent
SERDP	Strategic Environmental Research and Development Program
SI	Site Investigation
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
Tetryl	Methyl-2,4,6-trinitrophenyl nitramine
TNT	2,4,6-Trinitrotoluene
TNB	1,3,5-Trinitrobenzene
TOW	Tube-launched, Optically tracked, Wire-guided missile
Tritonal	70:30 or 80:20 mix of TNT and aluminum powder
TTU	Thermal Treatment Unit
UCL	Upper Confidence Limit
USACE	U.S. Army Corps of Engineers
US EPA	U.S. Environmental Protection Agency
UTTR	Utah Test and Training Range
UV	Ultraviolet detector
UXO	Unexploded Ordnance
WP	White Phosphorus

Introduction

Purpose and Scope

The main focus of this issue paper is to provide remedial project managers and corrective action project officers with a summary of information regarding the nature of munition constituents (MC) with an emphasis on energetic residues and metals at military training ranges and munitions open burn (OB) and open detonation (OD) demolition units. For this document, MC will refer to chemicals associated with military explosives and propellants. This will include some background on the physical and chemical properties of energetic chemicals and residues, how residues are deposited and amounts of residue produced from different detonations and firing activities, results of investigations describing the accumulation and distribution of residues at different types of military ranges and OB/OD units, a comparison of methods for the collection of representative soil samples on ranges, and a summary of laboratory methods designed to provide adequate characterization of these soil samples. White phosphorus is discussed in a case study in Appendix A1, but no other smoke munitions or illumination munitions will be discussed in this document.

Background

For the purpose of this document, energetic compounds are those chemicals used by the U.S. Department of Defense (DoD) as propellants and explosives in military munitions and blasting agents. In general, 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 propagation wave. If the velocity of this wave is less than the speed of sound for a given substance, the substance is said to undergo deflagration (rapid burning). If the velocity is supersonic, the substance is said to undergo a detonation (US Army 1993). Some energetic compounds that undergo deflagration are used by the DoD as propellants to send munitions projectiles or warheads down range. Compounds that can undergo detonations are used in the projectiles or warheads as explosives as shown in Figure 1. Although significant engineering differences exist between explosive trains and ignition trains, 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 main charge or propellant load. The major difference between the two types of chains is in the component charges' rates of reaction.

Because both propellants and explosives react at very high temperatures (for TNT about 3000 degrees K), the reactions tend to go to completion forming mainly gaseous products. For TNT (2,4,6-trinitrotoluene, or $C_7H_5N_3O_6$), the reaction is as shown in equation 1 below:

$$(1)\quad 4\ C_7H_5N_3O_6 \longrightarrow 7\ CO_2 + 21\ C + 6\ N_2 + 10\ H_2O.$$

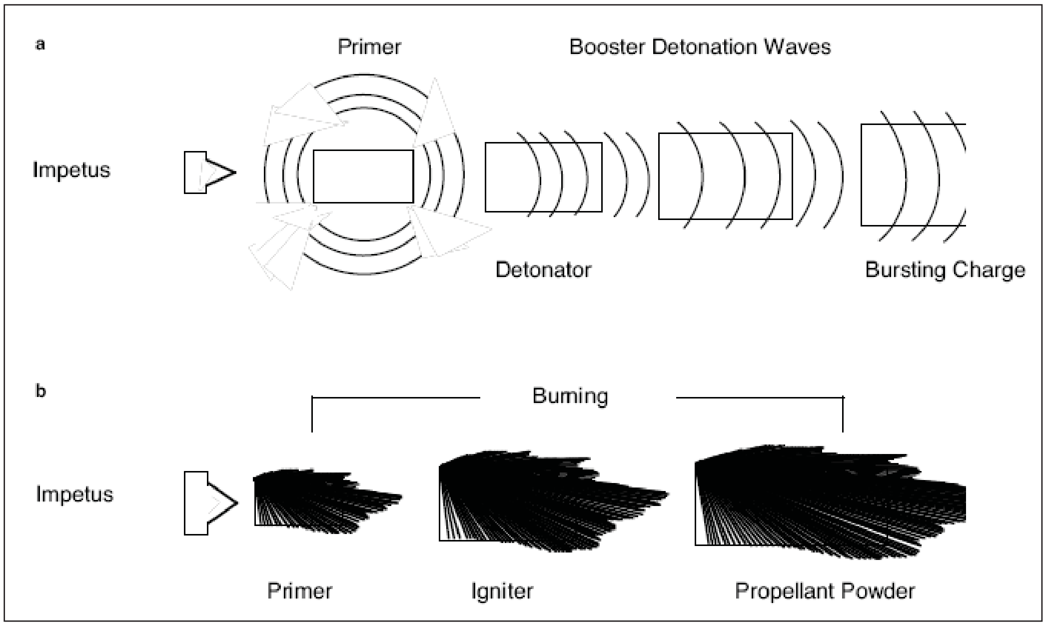


Figure 1. Comparison of explosive train (a) with ignition train (b).
Source: Boudeau (1993) as adapted from US Army (1993).

Because TNT has insufficient oxygen in the molecule relative to carbon, the detonation produces soot (solid C). 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.

Energetic chemicals

Most energetic chemicals used by the DoD fall into one of three groups – nitroaromatics, nitramines or nitrate esters (Fig. 2). Among the nitroaromatics, TNT (2,4,6-trinitrotoluene) is widely used as an explosive, and DNT (2,4-dinitrotoluene) as a component of many single-base propellants. RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetreazocine) are nitramines used in various explosives, and NG (nitroglycerin) and NC (nitrocellulose) are nitrate esters used in gun and some rocket propellants. Table 1 summarizes the energetic chemicals present in current military explosives. Some older energetic formulations contain compounds such as tetryl (methyl-2,4,6-trinitrophenyl nitramine) or ammonium picrate, but these compounds are rarely encountered at training ranges. Table 2 provides some compositions of other explosive formulations used in the past; this information may be useful for older active ranges or formerly used ranges. The discussions will concentration on the major energetic components present in current munitions. Other chemicals may be present in specific munitions but they have not been studied extensively and will not be discussed here.

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

- The Munitions Items Disposition Action System (MIDAS).
- MVS Munitions Datbase. [CD sent on request by U.S. Army Corps of Engineers Military Munitions Center of Expertise (EMCX)]
- ORDATA. http://ordatamines.maic.jmu.edu/default.aspx

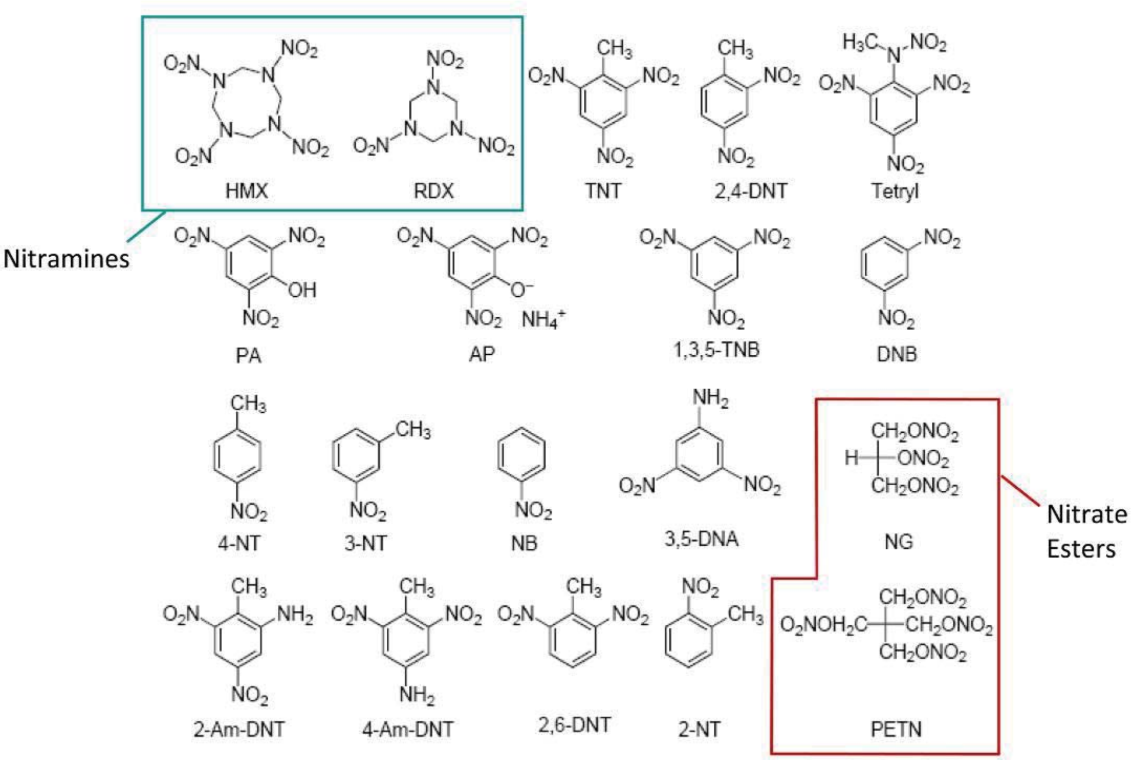


Figure 2. Structures of the nitramines (upper left), nitrate esters (lower right), and nitroaromatic explosives (all others) analyzed in the environment (from Tomkins 2000).

Table 1. Energetic chemicals present in current military explosive and propellant formulations.

Compound	Uses	Chemical Ingredients
Explosive formulations		
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	Military-grade TNT, aluminum
Composition A4	40-mm grenades	Military-grade RDX
TNT	Artillery	Military-grade TNT
Composition H-6	Navy and Marine bombs	Military-grade RDX and TNT, aluminum
Octol	Antitank rockets	Military-grade HMX and TNT
Explosive D	Naval projectiles	Ammonium Picrate

Table 2. Summary of explosive chemicals present in various military munitions (from 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			70–75	
Pentolite	f,g,i	25–90				PETN
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	i	Bursting charges
b	High energy projectiles	j	Fragmentation charge
c	Projectile filler	k	Former used demolition explosive
d	Boosters	l	Depth charges
e	Grenades	m	High energy charge
f	Shaped charges	n	Igniter powder
g	Demolition explosives	o	Time fuses
h	Ammunition	p	Land mines

Gun and Small Rocket Propellant Formulations

Composition

Solid propellants for small arms, artillery, and mortars are low-explosive materials designed to burn at a controlled rate and rapidly produce gases, creating the pressure to accelerate projectiles from guns or propel rockets toward targets (US Army 1993, Folly and Mäder 2004). 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, and lastly, stabilizer compounds that absorb nitrogen oxides, the breakdown products of NC, to increase propellant stability during storage. Solid propellants used for rocket fuel [termed “composite” or “composite modified double base” (CMDB)] include an oxidizing solid (such as ammonium perchlorate, or barium nitrate) together with a binder [e.g. HTPB (hydroxy-terminated polybutadiene)], which acts as a fuel.

Solid propellants with NC are divided into three classes based on presence of added energetic compounds. A summary of the major ingredients in some of these propellants is given in Table 3 (U.S. Army 1990). 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

Table 3. Summary of solid propellant classes with common examples.

Type	Uses	Examples	Particle type*	Principal ingredients
Single base	Small arms to cannons	M1 M6 M10	Single- or multi-perforated cylinder Multi-perforated cylinder Flake; Single- or multi-perforated cylinder	NC, 2,4-DNT NC, 2,4-DNT NC, diphenylamine
Double base	Multiple applications including small arms	M2 M5 M8	Single- or multi-perforated cylinder Single-perforated cylinder or flake Perforated increment sheet	NC, NG, ethyl centralite NC, NG, ethyl centralite NC, NG, diethyl phthalate
Triple base	Large caliber guns	M30 M31	Multi-perforated cylinder or hexagonal Multi-perforated cylinder; Single-perforated cylinder or stick	NC, NG, NQ, ethyl centralite NC, NG, NQ, ethyl centralite
Composite	Rockets and missiles	Class 1.3	Single grain	Ammonium perchlorate, Al, HTPB
CMDB	Rockets and missiles	Class 1.1	Single grain	NC, NG, Ammonium perchlorate, Al, HMX, HTPB

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

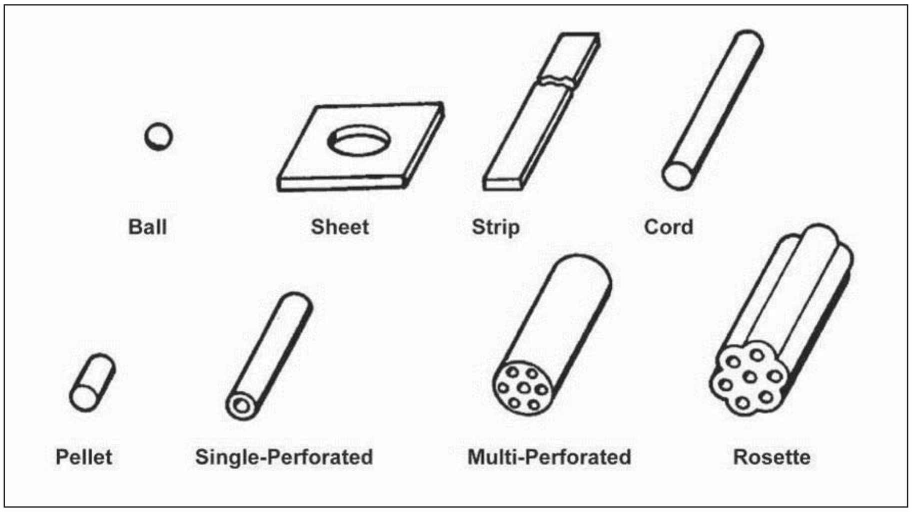
content of the formulation without raising the flame temperature, which reduces erosion in the gun barrel and also reduces flash. NQ tends to be found in the more powerful (higher charge number) artillery and tank propellants.

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.

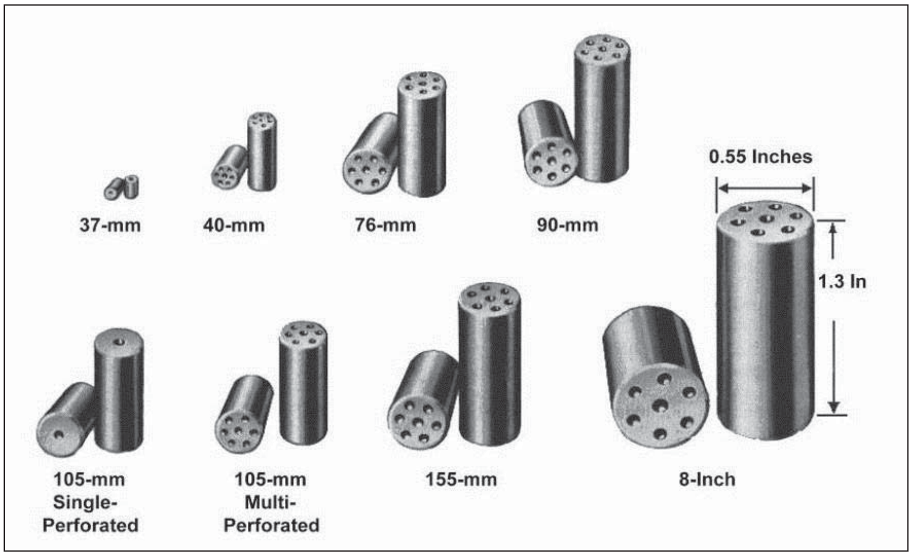
Deterrents or burn rate modifiers are added to propellants used in small arms and large-caliber artillery rounds. They are impregnated into the propellant surface, forming a coating that slows the initial burning rate. Commonly used deterrents include 2,4-DNT, 2,6-DNT, and ethyl centralite. A variety 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 and examples include the two esters of 1,2-benzenedicarboxylic (or phthalic) acids—dibutyl phthalate and diethyl phthalate. HTPB is commonly used as a binder for composite and CMDB rocket and missile propellants. A less commonly used binder is triacetin. 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 can be included to lower wear of the gun barrel liners such as wax, talc, and titanium dioxide. Tin and lead strips are often added to howitzer and tank propellants as decoppering agents. Copper is the primary ingredient of rotating bands on projectiles.

Grain size and shape

The properties of propellants are greatly influenced by the size and shape of the grains, which include a variety of small spherical balls, plates, or flakes, or in different forms of extruded cylinders or strips (Fig. 3). The propellant burns only on the particle surfaces; therefore, larger grains burn slower. Many of the cylindrical shapes have internal perforations to allow burning from the inside outwards simultaneously with burning from the surface inwards. Some cylinders have a single central perforation; others have multiple perforations, commonly with a central hole surrounded by six others. The size and shape of propellant grains used in a particular munition are balanced in an attempt to regulate the burn so an evenly constant pressure is exerted on the propelled projectile while it is in the barrel.



a. Propellant grain shapes.



b. Example sizes.

Figure 3. Propellant grain shapes and example sizes (From US Army 1990, 1993).

Ignition Train

Propelling charges are ignited through a chain reaction called an ignition train, usually a series of combustibles and explosives arranged according to decreasing sensitivity (Fig. 1b). To activate, a stimulus such as impact, heat, or spark ignites a small primer. In artillery ammunition, the primer then sets fire to the igniter charge, which intensifies the small flame produced by the primer and initiates combustion of the large quantity of propellant. In some cases, igniter charges are also sandwiched between layers of propellant. Commonly used igniter charges include black powder (a combination of potassium nitrate, charcoal, and sulfur) and potassium nitrate by itself.

Primer compositions for explosive fillers are a mixture of primary explosives, fuels, oxidizers, and binders. Primary explosives include lead azide, DDNP (diazodinitrophenol), lead styphnate, tetracene, KDNBF (potassium dinitrobenzofuroxane), and LMNR (lead mononitroresorcinate). Fuels used are metal thiocyanates, antimony sulfide, and calcium silicide. Oxidizing agents include potassium chlorate and barium nitrate.

Primers include three main types: percussion, stab detonator, and electrical. Several percussion and stab detonator priming compositions include the compounds lead styphnate, tetracene, barium nitrate, antimony sulfide, powdered zirconium, lead dioxide, and PETN (pentaerythritol tetranitrate).

The most commonly used electrical primers are the exploding bridge wire, the hot wire bridge, and the film bridge. In an exploding wire detonator, a large current passing through the wire causes it to burst, creating a shock wave that causes the detonation. With this type, no priming composition is needed; the wire is placed directly in a charge of RDX or PETN. Hot wire and film bridges use priming compositions that include potassium chlorate with various combinations of lead mononitroresorcinate, NC, lead thiocyanate, DDNP, charcoal, nitrostarch, titanium, and aluminum.

Summary

Table 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 percent by weight (Miller 1997, MIDAS 2007). Plasticizers and inert binders account for approximately 5 to 25 weight percent. Stabilizers and other compounds (flash reducers, primers, and igniters) account for the remainder, occurring at less than 5 weight percent each.

Table 4. Significant compounds in propellant formulations.

Energetic plasticizers	Stabilizers	Inert binders and plasticizers	Burn rate modifiers
Nitro-based	diphenylamine	dibutyl phthalate	**2,4-dinitrotoluene**
nitrocellulose	2-nitrodiphenylamine	diethyl phthalate	2,6-dinitrotoluene
nitroglycerin	diethyl-1,3- diphenylurea (ethyl centralite)	triacetin	ethyl centralite
nitroguanidine	1-methyl-3,3- diphenylurea (akardite)	wax	
diethylene glycol dinitrate		talc	**Flash reducers**
Oxidizers		titanium oxide	potassium sulfate
ammonium perchlorate		HTPB	potassium nitrate
potassium perchlorate			

Secondary (high) explosives

The most commonly used military high explosives by the United States and Canada today are TNT, RDX and HMX (Fig. 4). In the past, tetryl and ammonium picrate (Explosive D) were also used, but they are not generally found in modern munitions. New compounds are being considered for future use, but these compounds are not currently being used at military training ranges.

The energetic compounds present in the most common DoD explosive formulations are presented in Figure 4 and Table 1. All of these formulations contain one or more of TNT, RDX and/or HMX.

Important physical and chemical 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 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 used as a component of double- and triple-base propellants associated with the solid polymeric NC. The solubility of these compounds in water varies tremendously from a low of about 4.5 mg/L for HMX to about 4400 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 persist on the soil surface for many decades.

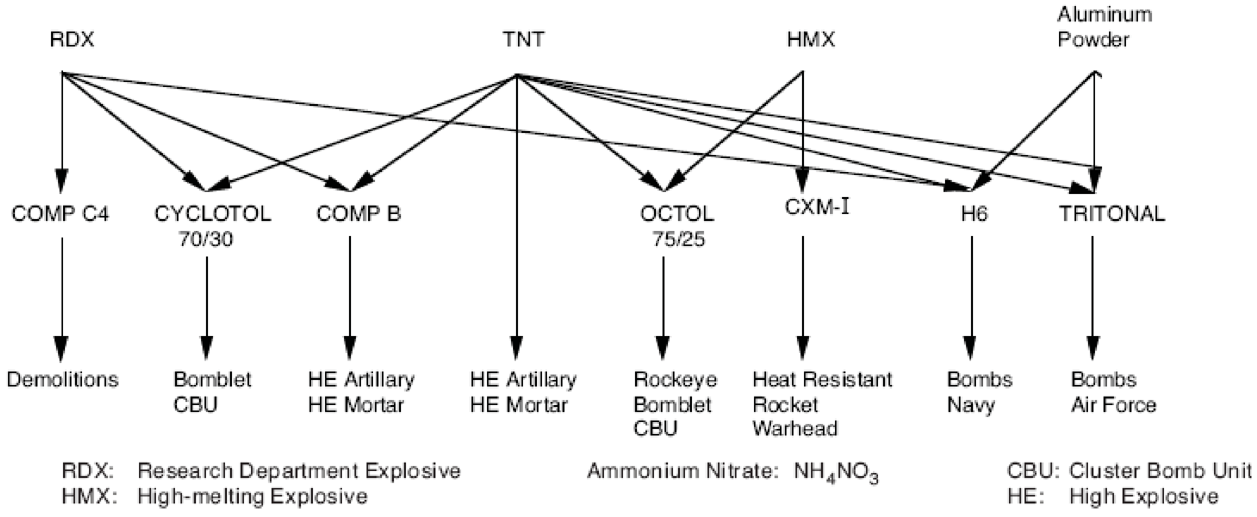


Figure 4. Energetic compounds present in the most common DoD explosive formulations [From Boudeau, (1993) as adapted from AEHA (1985)].

Table 5. Most commonly used physicochemical properties of some explosives utilized by military services (from Sunahara et al., eds. 2009, Sheremata and Hawari 2000, and M.E. Walsh et al 1993).

Common Name	Molecular Weight (g mol^{-1})	Melting Point (°C)	Water Solubility^{a} 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 x 10$^{-7\ a}$	1.99 x 10$^{-6\ a}$
2,4-DNT	182.15	71	270	1.98	1.86 x 10^{-7}	1.47 x 10^{-4}
2,6-DNT	182.15	64-66	206	2.02		5.7 x 10^{-4}
2-Am-DNT	197.17	176	42	1.94		4.0 x 10^{-5}
4-Am-DNT	197.17	171	42	1.91		2.0 x 10^{-5}
Tetryl	287.17	129.5	75	2.04	2.69 x 10^{-11}	5.69 x 10^{-9}
TATB	258.15	ND	32	0.7	5.8 x 10^{-12}	1.34 x 10^{-11}
Picric Acid	229.10	121.8	12800	1.33	1.7 x 10^{-8}	7.5 x 10^{-7}
NC	10^5–10^6	206 ^{b}	Insoluble	ND ^{c}	ND	ND
PETN	316.17	143.3	43*	3.71	1.7 x 10^{-9}	5.38 x 10^{-9}
NG	227.11	13.5	1800	1.62	3.4 x 10$^{-6\ a}$	2 x 10^{-4}
EGDN	152.08	-22.3	5200	1.16	2.52 x 10^{-6}	7.2 x 10^{-2}
RDX	222.26	205	56.3	0.90	1.96 x 10^{-11}	4.0 x 10^{-9}
HMX	296.16	286	4.5	0.17	2.60 x 10^{-15}	3.3 x 10^{-14}
CL-20	438.19	260^{b}	3.7	1.92	ND	ND
NQ	104.07	239	4400	-0.89	4.67 x I0^{-16}	1.43 x 10^{-11}

Note: ^{a} At 20°C; ^{b} With decomposition; ^{c} ND – Not determined;
* This value is uncertain; range of cited values from 2.1 to 43 mg L $^{-1}$

Once dissolved or leached from polymeric NC matrices, the tendency of energetic compounds to sorb to soil substrates varies substantially. The octanol/water partition coefficients are often correlated with soil/water partition coefficients for organic compounds and values for these compounds are shown in Table 5. Very low values for compounds such as NQ, HMX, and RDX indicate these substances will not be sorbed strongly to soil surfaces and hence will be more mobile in the environment than others such as TNT or especially PETN. The low soil/water partition coefficients and limited water solubility makes sampling soils in the subsurface problematic. Even when contamination has reached groundwater, the concentrations of RDX, in particular, may be below analytical detection limits in the subsurface soil. The reason for this is because RDX is present mostly within the soil moisture fraction, which is quite small compared to the mass of the soil. More thorough lists of these compounds' 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 many of them are thermally unstable, they are generally not analyzed using gas chromatography (GC) or gas chromatography/mass spectrometry (GC/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) (US EPA 2006). Because these compounds are not volatile (vapor pressures at 25°C vary from about 10^{-4} to 10^{-15} torr), soil increments containing these chemicals can be combined and processed without loss due to volatilization, a property that has been exploited when collecting, preparing, and subsampling representative samples.

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. Clausen et al. (2006) provide a detailed discussion of fate and transport issues and energetic chemical physiochemical properties.

The major sources of energetic residues at DoD training ranges are deposits of these chemicals, largely as particles of the energetic formulations. The surfaces of particles deposited on the soil surface are subject to reactions with sunlight (photodegradation) (Taylor et al. 2010). TNT is particularly subject to photodegradation leading to a complex array of reaction products, (Burlinson et al. 1978) that vary in their environmental stability, some of which are highly colored. 1,3,5-TNB (1,3,5-Trinitrobenzene) is the primary stable photodegradation product of TNT in environmental systems. For the solid explosives, photodegradation reactions occur only on the surface, but these products can be washed off by precipitation often producing a halo of reddish brown residue on the soil surface surrounding these TNT-containing particles. Tetryl photolyzes rapidly to N-methypicramide (Kayser et al. 1984). Photodegradation reactions of other energetics are less well studied but thought to be less significant than for TNT or tetryl.

While 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 soil. Some initial studies on the rates of dissolution of nitroaromatics and nitramines were conducted by Lynch et al. (2001, 2002a, b) using a stirred reactor and by Morley et al. (2006) using non-stirred batch reactors and columns. More recently, Taylor and co-workers (2009) have conducted rainfall simulation experiments with TNT, Composition B, Tritonal, and Octol, both in the laboratory and in outdoor experiments. In addition, Dontsova et al. (Ch. 5 in Jenkins et al. 2007 and Ch. 12 in Jenkins et al. 2008) reported on column experiments evaluating the mobility of propellant related compounds in soil columns.

Once dissolved, RDX and HMX in particular can migrate through the vadose zone and contaminate underlying groundwater aquifers, especially on training ranges that have permeable soils, a shallow groundwater table, and abundant rainfall (Clausen et al. 2004, Jenkins et al. 2001, Martel et al. 2009b, and Chapter 3 in Pennington et al. 2006). 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 Massachusetts Military Reservation (MMR; Clausen et al. 2004). However, TNT does not mineralize in the environment either aerobically or anaerobically, but TNT is environmentally transformed to several isomers of monoaminodinitrotoluene (2AmDNT and 4AmDNT). These compounds are more mobile in the environment than TNT, but they can chemically bind to natural organic matter in soils and become immobilized (Thorn et al. 2002). RDX and HMX do not degrade aerobically to any extent in surface soils, but they can be transformed to mono (and perhaps poly) nitroso compounds in the subsurface under reducing conditions (McCormick et al. 1981, Hawari et al. 2001).

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. The solubility of picrate is very high, about 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 US DoD. Kayser and Burlinson (1988) found that picrate migrated rapidly through four test soils in lysimeters and it was observed in a groundwater sampling well at the Louisiana Army Ammunition Plant (Jenkins, personal communication). 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 the impact area elsewhere. Apparently, picrate can also be transformed to picramic acid (2-amino-4,6-dintrophenol) due to microbial activity under anaerobic conditions.

Tetryl hydrolyzes in aqueous solution 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.

Microbial degradation of nitroglycerin has been studied by Wendt et al. (1978). 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 (Ch. 8 in Jenkins et al. 2008). The rate of degradation in soil is rapid in most soils (Jenkins et al. 2003). Using saturated columns, Dontsova et al. (Ch. 12 in Jenkins et al. 2008) found that in the absence of degradation, NG was mobile in soil columns, but was more retarded in its movement than NQ, that did not appear to be degraded in soils. Diphenylamine, however, was both retained and degraded in soil columns indicating that it would not be expected to penetrate soils to groundwater (Ch. 5 in Jenkins et al. 2007).

Residue deposition at training ranges

Propellant residues at firing points

Numerous experiments have been conducted on snow covered ranges to estimate the mass of energetic residue deposition at firing points, and from live-fire and blow-in-place detonations. Snow covered surfaces prevent cross contamination with past activities and provide a visual footprint where residues are deposited (Jenkins et al. 2002). In addition to energetic residues deposited at firing points other materials such as phthalates and N-nitrosodiphenylamine have been observed (Clausen et al. 2004).

The mass of propellant residues deposited was measured for artillery and mortar firing (M.R. Walsh et al. 2005a, b, 2006; Hewitt et al. 2003; M.E. Walsh et al. 2004), for several different shoulder-fired rockets (M.R. Walsh et al. 2009, Chapter 4 in Jenkins et al. 2008), one type of tank (Ch. 6 in Jenkins et al. 2008), and for the common military small arms (M.R. Walsh et al. 2007a, Faucher et al. Ch 5. in Jenkins et al. 2008). Measurements concentrated on the mass of NG or 2,4-DNT associated with the particles of NC deposited, and not NC itself. NC in soil is not thought to pose health risks, but may retain ignitable characteristics for long periods of time.

To make these measurements, surface snow was collected and the mass of NG and/or 2,4-DNT was determined in both the snowmelt and the filtered soot present in the snow (M.R. Walsh et al. 2007b). The total mass of these residues on a per-round-fired basis is presented in Table 6. 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 (Ch. 3 in Jenkins et al. 2007). The large mass of residue deposited for shoulder-fired anti tank 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 2004b). 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 50-caliber machine guns. Deposition extends out to 50 m behind where shoulder-launched rockets are fired (M.R. Walsh et al. 2009, Ch. 3 in Jenkins et al. 2007), and 10 to 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

Table 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	Residues/ round (mg)	Downrange Distance for deposition (m)	References
Howitzers						
105-mm	M1-I & II	DNT	71	34	ND[1]	M.R. Walsh et al. 2009
105-mm	M1	DNT	22	6.4	ND	M.R. Walsh et al. in Ch 4 Jenkins et al. 2007
155-mm	M1	DNT	60	1.2	ND	M.R. Walsh et al. 2005a
Mortars						
60-mm	Ignition cartridge	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[2]	Thiboutot et al. Ch 4 in Jenkins et al. 2008
84-mm AT4	AKB204	NG	5	20,000	50 m[2]	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)	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	

[1] ND Downrange distance for deposition was not determined.

[2] Major deposition is behind the firing line for shoulder-fired rockets, but downrange for other types of munitions.

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 established 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 a large quantity of unused propellant remaining because sufficient propellant is supplied to fire the weapons at maximum distance, and often that is not desired or possible. The general practice is 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. Sometimes it may be collected and burned in a burning pan. Several studies have been conducted to assess the residue remaining from these practices under different environmental conditions (M.R. Walsh et al. 2010a). Propellant burns were conducted in summer and winter, on wet and dry soil, snow, and frozen soil. The mass of NG or 2,4-DNT remaining after the burn was measured and compared to that present in the initial amount of propellant burned (Table 7). Propellant residues recovered in burn areas were large compared with those deposited from firing activities with the same propellant and were deposited over a smaller surface area resulting in higher concentrations in the soil. These results are preliminary and residue loading is quite variable. It appears to be influenced by surface condition (seasonal conditions) and the type or configuration of the propellant loads.

Table 7. Mass of initial propellant constituents recovered (%) after expedient propellant burning (M.R. Walsh et al. 2010a).

Test condition for burn	Propellant type	Mass recovered as % of initial mass in propellant
Summer (dry soil)	M1	0.95
Summer (wet soil)	M1	0.99
Winter (frozen soil)	M45	5.2
Winter (Snow)	M45 M9	18 1.7

Explosives residues at 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. The total explosive present in a given munition is referred to as the net explosive weight (NEW).

The mass of explosives residues deposited when a round detonates high order was estimated for a variety of munitions including: hand grenades (Hewitt et al. 2005b), mortars (Hewitt et al. 2005b, M.R. Walsh et al. 2005b), and artillery rounds (M.E. Walsh et al. 2004, M.R. Walsh et al. 2005a). 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 8 is a summary of the estimated deposition 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

Table 8. 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 (μg)	Plumes sampled	Percent 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	8500	5	2×10^{-3}	Hewitt et al. 2005b
	TNT	370	1100	5	3×10^{-4}	
120-mm	RDX	1794	4200	7	2×10^{-4}	M.R. Walsh et al. 2005b
	TNT	1166	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	1274	95	9	7×10^{-6}	Hewitt et al. 2003
	TNT	812	170	9	2×10^{-5}	
155-mm	RDX	4190	300	7	5×10^{-6}	M.R. Walsh et al. 2005a
	TNT	2730	ND	7	$< 10^{-5}$	
	*ND – Not Detected					

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.

Tests were also conducted to simulate the blow-in-place detonations used to destroy surface UXO (unexploded ordnance) on many ranges (Pennington et al. 2006, M.R. Walsh et al. 2007b). These items are detonated on active ranges by military EOD (Explosive ordnance disposal) teams using C4 (Composition 4) demolition explosive. On closed ranges, FUD (Formerly Used Defense) sites, and MMRP (Military Munitions Response Program) 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. 2006). 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, blow-in-place detonations take place from the outside in and do not use the detonation train built into the munition. Table 9 summarizes the results obtained for C4-initiated blow-in-place detonations of a variety of munitions that detonated at high order. Overall, the deposition from high order detonations during blow-in-place of duds is higher than from similar rounds that detonate as designed, but still much lower than from low-order detonations as described below. Pennington et al. (2006) also investigated the deposition of residues for ordnance detonated with a variety of donor charges including TNT blocks, C4, shaped charges, and binary explosives (Fig. 5). Results varied for different munition/donor

Table 9. RDX deposition from blow-in-place of military munitions using C4 demolition explosive.

Detonation type	Number of trials	Mean RDX deposition (mg)	(%)	Reference
C4 (alone)	11	20	3.9 x 10^{-3}	Pennington et al. 2006
Mortars				
60-mm	35	0.093	8.1 x 10^{-5}	Pennington et al. 2006
81-mm	11	95	2.2 x 10^{-2}	Pennington et al. 2006
Artillery				
105-mm	7	41	2.9 x 10^{-3}	Pennington et al. 2006
155-mm	28	13	3.1 x 10^{-4}	Pennington et al. 2006
Hand grenade (M-67)	7	26	2.4 x 10^{-2}	Hewitt et al. 2003

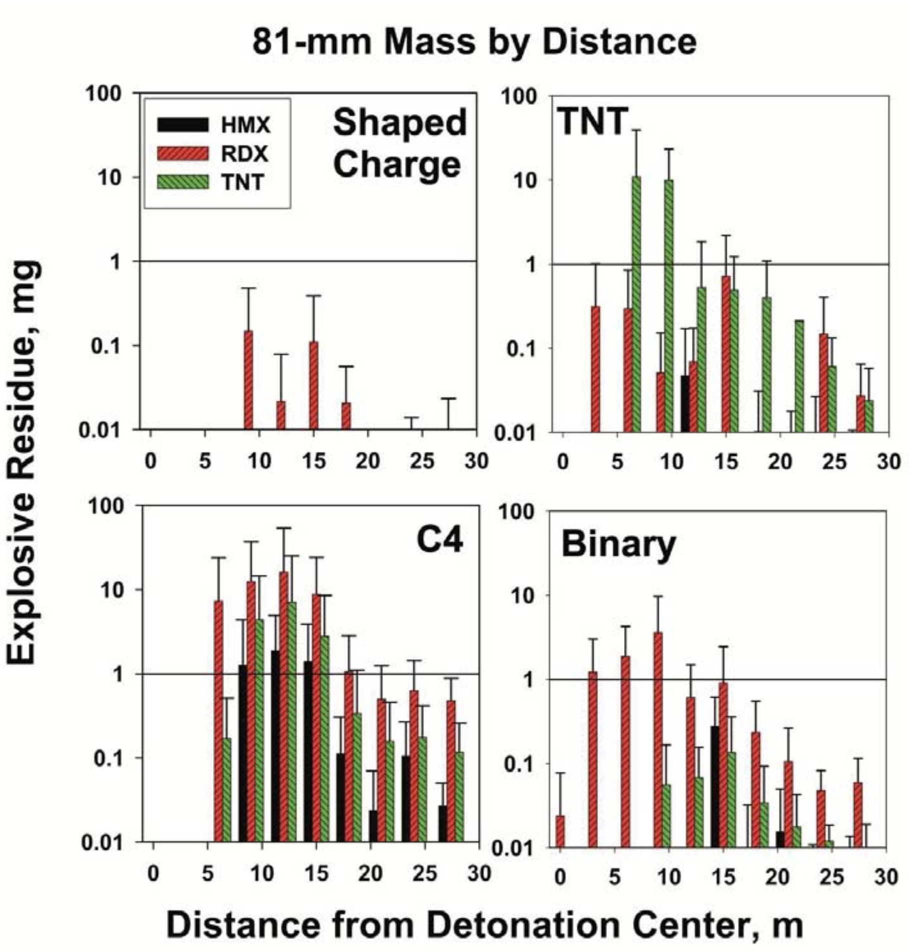


Figure 5. Mass of HMX, RDX, and TNT deposited with distance for each donor charge tested with the 81-mm mortar rounds (from Pennington et al. 2006).

charge combinations, but donor charges must be sufficient in size to ensure that a high order detonation of the UXO item occurs. Residue deposition was detected as far as 30 m from the detonation and contained contributions from the explosive contained in the UXO item and the donor charge. RDX predominates in the residue from detonations of items containing Composition B and from detonations using C4.

A percentage of fired rounds undergo low-order detonations. The frequency of occurrence has been estimated by Dauphin and Doyle (2000) and varies substantially from one munition type to another. To estimate the mass of energetic compounds remaining from low-order rounds, detonation tests were conducted at Blossom Point, Maryland on a raised table. The mass of compounds deposited was obtained after sweeping the residue from tarps covering the surrounding area and weighing the residue (Pennington et al. 2006). Five types of munitions were studied: 60-mm, 81-mm, and 120-mm mortars containing Composition B, 105-mm howitzer projectiles containing Composition B, and 155-mm howitzer projectiles containing either TNT or Composition B. Table 10 summarizes the results of this work with percent of original mass of explosives deposited ranging from 27 to 49%. This is an enormous mass of residue compared with that deposited from high-order detonations (Table 8). For a rule of thumb, it takes about 10,000 to 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 explosives residues at impact areas.

Observations from on-range investigations indicate that low-order detonations are not uncommon events for many munitions. Because low-order detonations are the major source of residues at impact areas, and the frequency of their occurrence is hard to predict, the mass of residues deposited at impact areas is difficult to estimate with any degree of accuracy (Dauphin and Doyle 2000). 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. For example, of 160 120-mm mortar rounds fired, eight did not

Table 10. Mass of explosives residue deposited from low-order detonation tests (from Pennington et al. 2006, 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	2989	49
Howitzer			
105-mm projectile	Composition B	2304	27
155-mm projectile	TNT	6985	29

detonate (duds) and four 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, these dud and low-order events often are not recorded. Thus, tabulated range record rates underestimate malfunctions, confounding efforts to predict the mass of residue deposition on live-fire impact ranges. The surface area over which low-order detonations of the various types of munitions deposit residues is still uncertain, i.e. are they co-located with high densities of craters, UXO, and metallic debris or more random in distribution, although some research to address this topic is underway. The resulting distribution at impact areas can be described as distributed point sources, complicating both site characterization as well as many approaches to remediation or best management practices to destroy residues on site.

Accumulation of energetic residues at various types of DoD ranges

Field studies have been conducted at over 30 military installations in the United States and Canada (Fig. 6) to identify the energetic residues present in the surface soils to understand the distributions of these residues on various types of training ranges (Jenkins et al. 2006a). Ranges

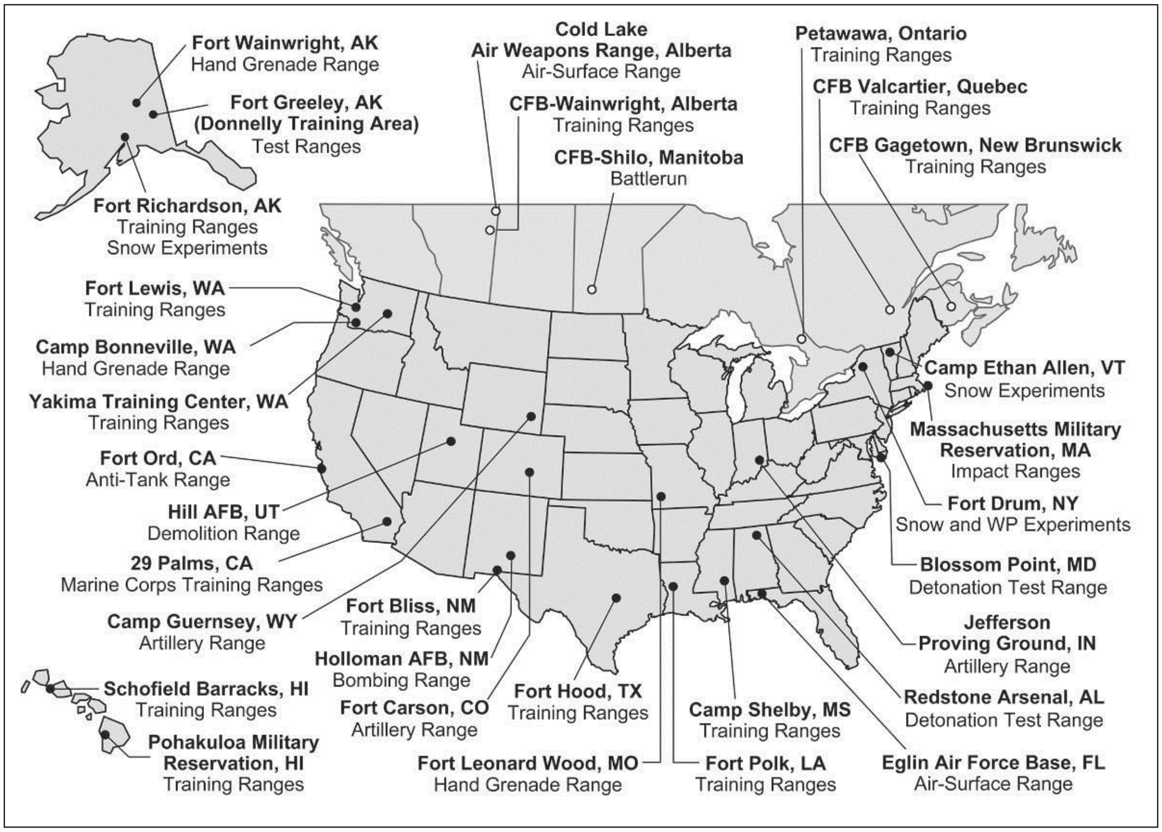


Figure 6. Field experiment sites at various U.S. and Canadian test and training ranges.

investigated included hand grenade, rifle grenade, antitank rocket, demolition, tank firing, mortar, artillery, bombing, demolition, small arms, and demolition ranges. Most ranges include an area where the weapon is fired and a separate impact area where detonations occur. Generally, energetic residues at the firing points are associated with propellants, whereas residues at the impact areas are compounds related to high explosives in the munition warheads, or white phosphorus (WP) from smoke rounds. Here we summarize the results of these studies. The sampling and analytical methods used to obtain these results evolved over time and are discussed elsewhere in this document.

Hand grenade ranges

Hand grenade ranges are only a few hectares in size and, because of the large number of individual detonations in a small area, the surface is usually bare or poorly vegetated (Fig. 7). These ranges often have several training bays from which soldiers throw grenades. Most of the detonation craters lie at distances between 15 and 35 m from the throwing pits. Thus compared with other types of ranges, only a very small area is subject to residue deposition. The most commonly used item at these ranges is the M67 fragmentation grenade. Its explosive charge is 185 g of Composition B. This means that compounds expected include RDX, TNT, HMX, and wax (Table 1), along with a few other isomers of TNT and DNT (Leggett et al. 1977).

Soil samples were collected at 11 active and two closed hand grenade ranges (Table 11). Concentration ranges of the major residue chemicals (RDX, TNT, and HMX) fell into two groups: one had concentrations generally less than 0.12 mg/kg and the other had concentrations

Figure 7. Old hand grenade range at Ft. Lewis, Washington.

generally above 1 mg/kg (Jenkins et al. 2006a). Live-fire studies indicate grenades that detonate high order do not deposit sufficient residues to account for the ranges with higher residue concentrations. However, remnants of grenades that did not completely detonate were found at these ranges (Fig. 8). These grenades either had undergone partial (low order) detonations or had been duds that were blown in place and did not fully detonate. When these types of detonations occur, much higher levels of residues are deposited, accounting for the higher concentrations of residues found at some ranges. In most cases, the highest concentrations of energetic compounds were in the top few cm of soil. These compounds can be deeper in the soil profile, though, if deep craters were allowed to develop before the surface was reconditioned.

Antitank rocket range

Impact areas

Antitank rocket ranges are direct fire ranges, up to several hundred hectares in size. They typically have only low-growing vegetation due to the necessity of maintaining a line of sight for training (Fig. 9). Targets are often derelict armored vehicles placed downrange at distances of 100 m or more from the firing points. The weapons fired most often at these ranges are the 66-mm M72 light anti-armor weapon (LAW) and the 84-mm AT4 rocket. These munitions contain

Table 11. Summary of results for energetic compounds detected in surface soils at hand grenade ranges.

Installation	Year sampled	Samples analyzed†	Mean concentration (mg/kg)					
			HMX	RDX	TNT	TNB	4ADNT	2ADNT
Fort Lewis, WA[1,3]	2000	23*	1.8	7.5	9.3	0.05	0.15	0.13
	2001	5** (50)	1.0	4.4	1.5	ND***	ND	ND
Fort Richardson, AK[1,3]	2000	27*	0.02	0.08	0.03	ND	0.01	0.01
Camp Bonneville, WA[2]	2000	48*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fort Leonard Wood, MO[1]	2001	18** (30)	0.19	0.45	<0.01	<0.01	<0.01	<0.01
CFB-Shilo, Manitoba[1,4]	2001	15** (20)	0.05	0.71	0.06	<0.01	0.02	0.02
Fort Wainwright, AK[1]	2002	25** (1,5,10,20,40)	2	11	1.2	0.15	ND	ND
Schofield Barracks, HI[1]	2002	3** (30)	9.1	51	36	0.28	0.40	0.03
Pohakuloa Training Center, HI[1]	2002	7** (30)	0.53	5.6	0.78	<0.01	<0.01	<0.01
CFB-Gagetown, New Brunswick								
Old Castle Range[2,5]	2002	5** (30)	0.02	0.12	0.12	<0.01	<0.01	<0.01
New Castle Range[1,6]	2002	5** (30)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
New Castle Range[1,7]	2003	15** (25)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fort Polk, LA[1]	2003	2** (30)	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
CFB-Petawawa, Ontario[1]	2004	9** (25,100)	0.18	0.65	0.16	<0.01	<0.01	<0.01

† * Discrete samples; ** Multi-increment samples with (n) increments per sample; *** ND – Not determined

[1] Active ranges
[2] Closed ranges
[3] Jenkins et al. 2001
[4] Ampleman et al. 2003a
[5] Pennington et al. 2004
[6] Thiboutot et al. 2003
[7] Thiboutot et al. 2004

Figure 8. Hand grenades that did not completely detonate.

Figure 9. View from firing point towards targets at the Arnhem anti-tank range, CFB-Valcartier, Quebec.

M7 double-base propellant; the warhead contains octol and a small amount of RDX in the booster charge. M7 propellant contains 54.6% NC, 35.5% NG, 7.8% potassium perchlorate, 0.9% ethyl centralite, and 1.2% carbon black. Octol includes 70% HMX and 30% TNT. At some ranges, practice rounds are fired that contain propellant but do not contain Octol (subcal rounds).

Field experiments were conducted at seven active antitank ranges and one closed range. The primary residue detected at antitank rocket impact areas is HMX; concentrations in surface soils adjacent to targets are generally in the hundreds of mg/kg (Table 12). Even though octol contains 30% TNT, TNT is generally only present at about 1/100th that of HMX in the soil at these ranges. Also present at detectable levels are RDX and two environmental transformation products of TNT (4AmDNT, and 2AmDNT), but the concentrations are always several orders of magnitude lower than that of HMX. The level of HMX in the soil declines as the distance from the target increases (Fig. 10). Observations indicate LAW rockets frequently rupture upon impact without detonating, thereby depositing crystalline explosive over the soil surface (Fig. 11). This deposition is thought to be the major source of explosives residues at these impact areas.

Because HMX has a low aqueous solubility (about 4–5 mg/L at 25°C), it tends to accumulate on the surface; the more soluble TNT (about 150 mg/L) dissolves and undergoes environmental transformations. Amino transformation products of TNT can covalently bind to soil organic matter and become immobilized (Thorn et al. 2002). The HMX that slowly dissolves does not

Table 12. Concentrations of energetic compounds detected in surface soils adjacent to targets at antitank rocket ranges.

Installation†	Year sampled	Samples analyzed††	Mean concentration (mg/kg)				
			HMX	RDX	TNT	4ADNT	2ADNT
CFB-Valcartier, Quebec [1,3,4]	1995	16*	803	4.6	24	<0.1	<0.1
	1995	5*	399	0.76	3	<0.1	<0.1
	1996	20*	662	<0.1	4	<0.1	<0.1
	2003	4**(30)	898	2.8	7	<0.1	<0.1
WATC-Wainwright, Alberta [1,3]	1997	11*	987	5.3	126	<0.1	<0.1
Fort Ord, CA [2,5]	1997	8***	307	0.25	0.2	0.69	0.55
Camp Edwards, MA [1,7]	1999	11**(5)	35	22	2.1	0.14	0.18
CFB-Gagetown, New Brunswick [1,4]	1998	10	680	<1	4	<0.1	<0.1
	2002	5**	874	0.5	6	0.8	0.7
	2003	8**	489	0.5	2	0.4	0.5
Yakima Training Center, WA [1,6]	2001	6**(30)	23	0.8	0.04	0.05	0.12
CFB-Petawawa, Ontario [1]	2004	3**(50)	745	0.32	73	<0.1	<0.1

† Impact areas at Pohakuloa and Fort Bliss anti-tank ranges were not sampled.

†† * Composite samples; ** Multi-increment samples with (n) increments per sample; *** Discrete samples

[1] Active ranges
[2] Closed range
[3] Thiboutot et al. 1998
[4] Jenkins et al. 2004a
[5] Jenkins et al. 1998
[6] Pennington et al. 2002
[7] Ogden 2000

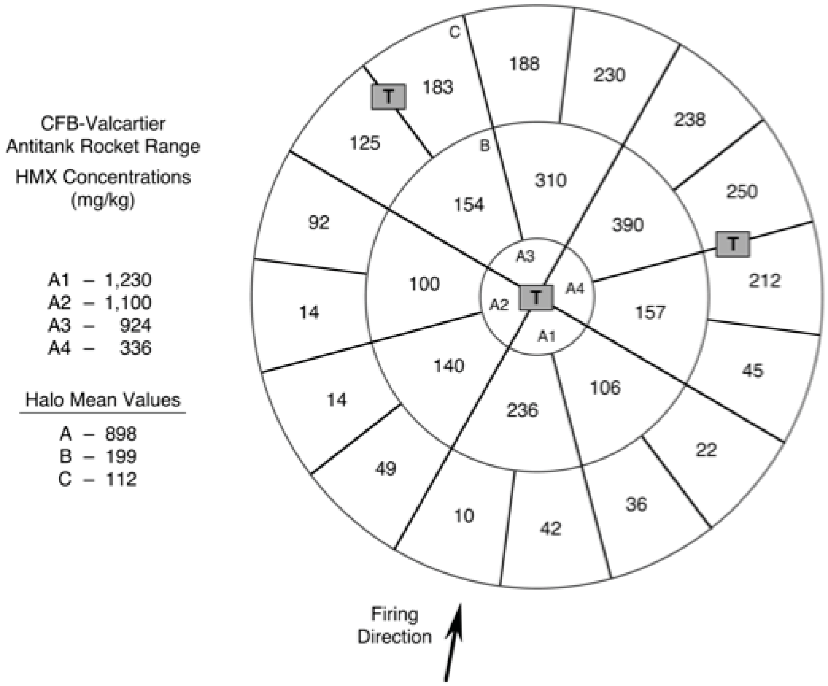


Figure 10. Distribution of HMX residues surrounding target vehicles at Valcartier, using an older-stylesampling design. Target positions are indicated by gray-shaded rectangles marked with a “T.” Sampling halos were divided at radii of 5 m (A), 5 –15 m (B), and 15 –25 m (C).

Figure 11. Ruptured LAW rocket at CFB-Valcartier, amber solid is octol, the color results from photolysis of the TNT component.

strongly interact with soils and can be carried through the vadose zone to underlying groundwater aquifers (Martel et al. 2009b).

Many anti-tank rockets are propelled all the way to the target, consequently propellants can still be present when these rockets detonate upon impact. Small pieces of propellant are thereby spread over the soil surface in the area surrounding the targets. These residues are often visible and NG has been detected at the impact areas at concentrations as high as 23 mg/kg. This may also be due to the poor burn characteristics of the propellant, as well.

Firing point areas

Sampling has been conducted at seven antitank rocket range firing points (Table 13). In all cases, NG was the primary energetic compound detected; however, only a few samples were

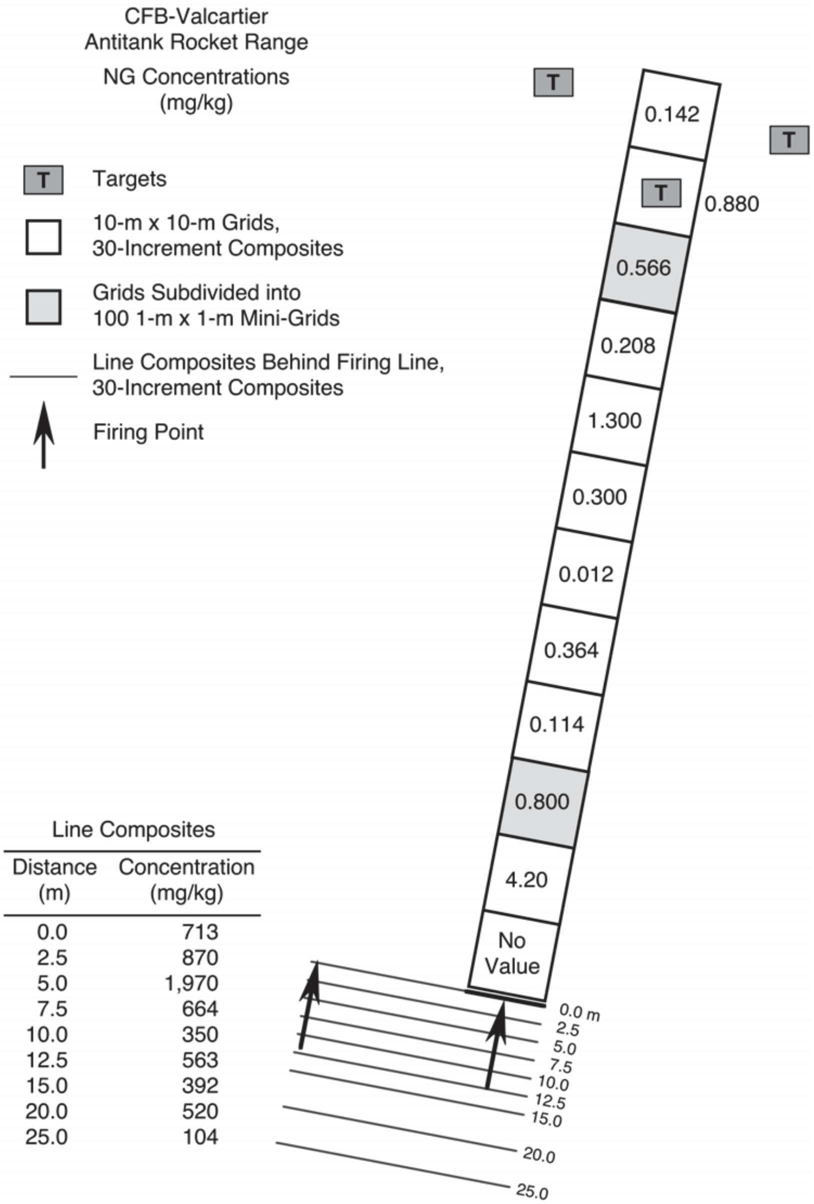
Table 13. Summary of results for nitroglycerin (NG) near firing points at active anti-tank rocket ranges.

			Mean NG concentration (mg/kg)								
			Position in front (m)					Position behind (m)			
Installation	Year sampled	Samples analyzed†	0–10	10–20	20–30	30-40	40-50	0–10	10-20	20–30	30–40
Yakima Training Center, WA[1]	2001	2 (30)	3	—*	—	—	—	—	—	—	—
Schofield Barracks, HI[2]	2002	4 (30)	—	—	—	—	—	1200	9.4	—	—
CFB-Gagetown, New Brunswick[3,4]	2002	4 (30)	176	65	—	—	14	1130	—	—	—
	2003	15 (30)	160	160	87	55	12	4700	2320	380	84
Fort Bliss, NM[5]	2002	10 (30)	1	0.5	<0.1	—	—	1	—	—	—
CFB-Valcartier, Quebec[6]	2003	13 (30)	NS	4.2	0.8	0.1	0.4	910	490	104	—
CFB-Petawawa, Ontario[7]	2004	8 (40)	—	—	—	—	—	2360	380	—	—
Ft. Lewis, WA											
Practice subcal area[8]	2006	16 (25)	—	—	—	—	—	632	175	82.4	13.0
Live fire area[8]	2006	8 (25)	—	—	—	—	—	936	206	—	—
Practice subcal area[9]	2009	4 (100)	—	—	—	—	—	860	—	—	—
Live fire area[9]	2009	4 (100)	—	—	—	—	—	1870	—	—	—
Camp Edwards, MA[10]											
TOW missile	1999	3 (5)	6.6	—	—	—	—	40	—	—	—
Dragon	1999	2 (5)	<0.12	—	—	—	—	<0.12	—	—	—
90-mm recoilless rifle	1999	2 (5)	2.9	—	—	—	—	13	—	—	—
LAW rocket	1999	10 (5)	5.7	—	—	—	—	268	—	—	—

† Number of multi-increment samples with (n) increments * — No sample collected

[1] Pennington et al. 2002
[2] Hewitt et al. 2004
[3] Thiboutot et al. 2003
[4] Thiboutot et al. 2004
[5] Pennington et al. 2003
[6] Jenkins et al. 2004a
[7] Brochu et al. 2009
[8] Jenkins et al. 2007
[9] Roote 2010
[10] Ogden 2000

analyzed for perchlorate. NG concentrations in surface soil samples from 0 to 25 m behind the firing line at Canadian Forces Base (CFB)–Valcartier were generally in the hundreds of mg/kg; whereas, concentrations between the firing line and the target were generally much lower (Fig. 12). In 2003 at CFB–Gagetown, soil cores were collected at a gravelly location behind the firing line at an antitank rocket range to depths reaching up to 63 cm below the surface (Ch. 4 in Pennington et al. 2005). In one soil profile, NG concentrations declined from 20 mg/kg in the surface 0–5-cm depth to 6.4 mg/kg at the 20–27-cm interval, and further declined to a concentration



Line Composites

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

Figure 12. Concentration of NG in composite soil samples collected in front of and behind the Arnhem rocket firing line at CFB–Valcartier.

of about 0.2 mg/kg from 40 to 60 cm deep. Thiboutot et al. (2003) found surface concentrations of NG as high as 11,300 mg/kg at this site. NG availability for dissolution is a function of its rate of release from the solid propellant residue and the amount of water in contact with the residues.

Perchlorate was generally either not determined in soil samples from antitank ranges or was not detected. Perchlorate is so soluble in water and mobile in soil that surface accumulation apparently does not occur as it does for nitroglycerin. Perchlorate is present in some antitank propellants, however, and it has been found in ground water plumes below the antitank firing range at CFB–Valcartier, QC (Fig. 13).

Artillery, tank, and mortar ranges

Artillery ranges are the largest training ranges used by the Army, covering areas of hundreds of square km, or about 40,000 square km throughout the country (DSB 2003, Fig. 14). Firing positions are often arranged around the circumference of the range with firing fans leading into the impact areas (Fig. 15). In the past, fixed firing points were used; with modern mobile artillery, firing activities have become more de-centralized as training has changed to support a “shoot and scoot” strategy. Once fired, artillery and mortar rounds can travel several km before impacting and detonating in the vicinity of targets. The flight path takes these rounds over an area referred

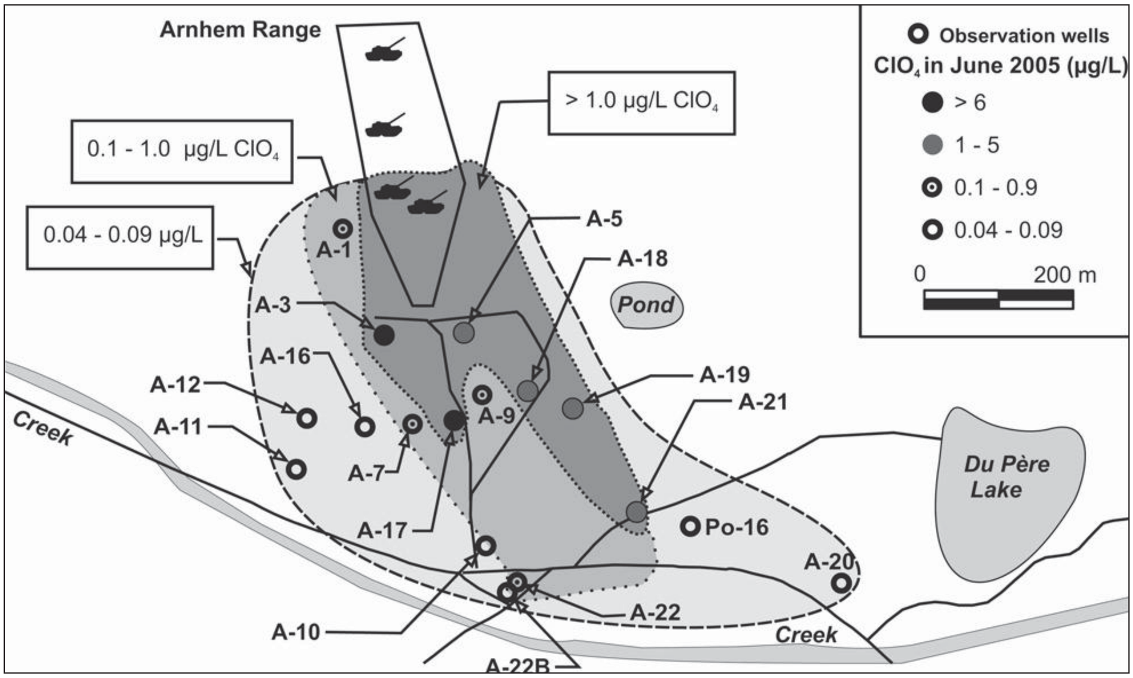


Figure 13. Dissolved perchlorate plume in ground water at CFB–Valcartier, June 2005. Wells A-11, A-12 and A-16 probably show the contribution from another perchlorate source (from the present three targets, only two have been shown) (from Martel et al. 2009b).

a. Ft. Bliss, New Mexico

b. Ft. Lewis, Washington

c. Ft. Richardson, Alaska

d. 29 Palms, California

Figure 14. Examples of artillery range impact areas.

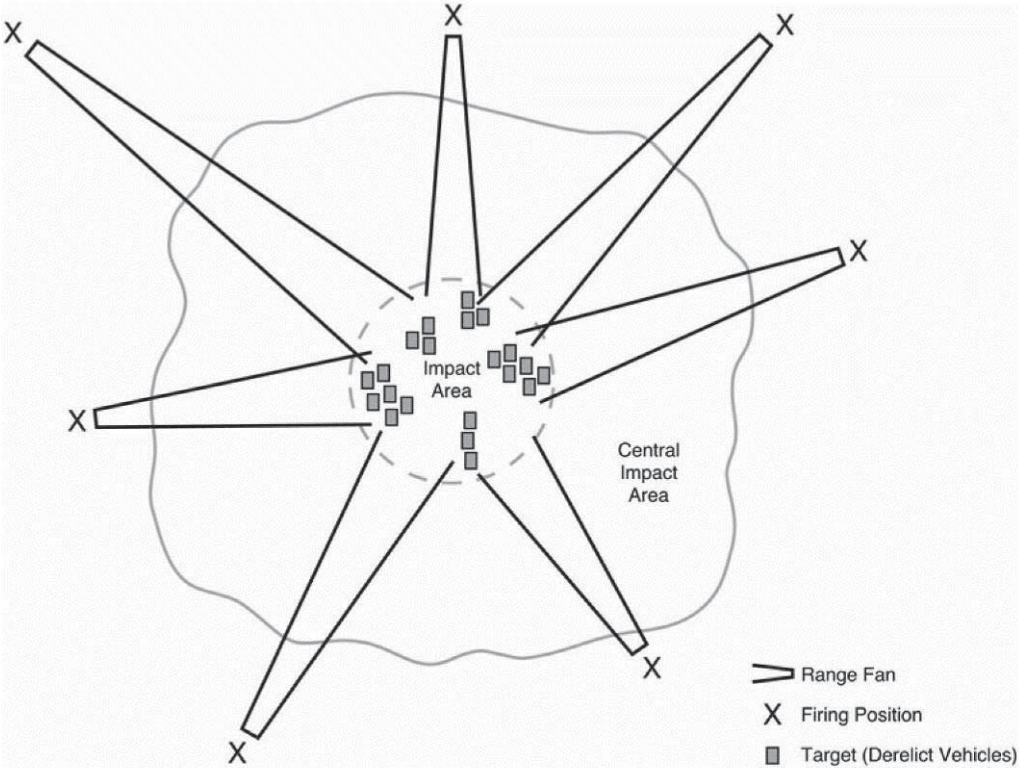


Figure 15. Schematic diagram of an artillery range showing firing points, range safety fan, and impact areas.

to as the safety fan where only a very few rounds impact. Often, this is the largest area of the range. Once the rounds arrive near targets and detonate upon impact, a crater is formed, the size being a function of the type of round, the fuse setting, and the physical properties of the soil. As described earlier, rounds that detonate high order deposit very little energetic residue (the masses of residues deposited has been estimated and is presented in Table 9). For example, three of the six MIS collected in an area 100 by 100 m that had over 600 impact craters present had TNT concentrations less than the detection limit, and the other three ranged from 0.2 to 0.8 mg/kg (Hewitt et al. 2005b). Occasionally a round will impact without detonating, resulting in either a surface or subsurface UXO. On ranges where the soil is rocky or very hard, many of these UXO items can be seen on the surface. In a relatively small number of cases, a round will partially detonate or become breached upon impact, resulting in a low-order detonation (Lewis et al. 2009). A surface UXO can also be partially detonated or cracked open by a nearby high-order detonation. In these cases, none or only a portion of the explosive fill may be consumed, which sometimes leaves a substantial fraction of the explosive fill in or near the ruptured casing (Taylor et al. 2004).

Many artillery ranges have been used for training for decades. The munitions that have been fired into these ranges include ordnance currently in the inventory as well as ordnance used pre- and post-World War 2, during the Korean Conflict and in Vietnam. UXO of a wide array of munitions are present on these ranges and many are still live.

The most common munitions fired into these ranges are artillery rounds and mortars; also used are a variety of rockets, missiles, and Air Force and Navy bombs. Currently the major systems being fired into these ranges include 155- and 105-mm howitzers, 120-mm main tank guns, and 81-, 60-, and 120-mm mortars. Other munitions such as 90-mm recoilless rifle rounds, 4.2-in mortar rounds, 8-in artillery rounds, bombs of various sizes, 40-mm grenades, 106-mm high-explosive plastic (HEP) rounds, 2.75-in LAW rockets, and TOW missiles have also been fired into some of these ranges, as well as some foreign ordnance. These munitions are delivered using single-, double-, and triple-base gun propellants, as well as rocket and missile propellants. The energetic component of single-base gun propellant is composed of NC that contains 2,4-DNT, double-base propellant is composed of NC and NG, and triple-base propellant is composed of NC, NG and NQ. The high explosives used in artillery and mortar warheads are generally either TNT or Composition B, although some older rounds also contained tetryl. Some smoke-generating munitions contain WP. Bombs that have been dropped in some of these ranges contain TNT, Tritonal (TNT and aluminum), or H-6 (RDX, TNT, aluminum), 40-mm grenades contain RDX, and LAW and AT4 rockets contain octol (HMX and TNT).

Artillery and tank range firing points

A number of firing points at various artillery ranges including firing areas for 105- and 155-mm howitzers, various mortars, and 120-mm tank guns have been sampled. The highest concentrations of 2,4-DNT are found at 105-mm firing points. When the concentration of 2,4-DNT in a sample was above 3 mg/kg, 2,6-DNT was sometimes detected at much lower concentrations as well. The compound 2,6-DNT is an impurity in military-grade 2,4-DNT. Soil profile samples indicate most of the propellant residue is present on the soil surface (M.E. Walsh et al. 2004, 2005). Microscopic analysis of the residues indicated that the residues consisted of unburned and partially burned propellant fibers with fiber lengths ranging from 0.4 to 7.5 mm (M.E. Walsh et al. 2007a).

In another example, surface soil was collected at a multi-purpose range complex in front of a fixed firing point for 120-mm tank guns. Both 2,4-DNT and NG were detected at 75 m, the farthest distance sampled from the firing point. Soil samples collected at 155-mm firing points, however, had much lower residue concentrations, often below analytical detection limits.

Artillery ranges away from impact areas and firing points

At several installations, the U.S. Army Environmental Command (AEC) and the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) conducted Regional Range Studies to assess the overall environmental impacts of residues from firing activities on artillery ranges (USACHPPM 2001, 2003, 2004, 2005). Extensive studies have also been conducted at MMR (Clausen et al. 2006). Similar studies were conducted by the Defence Research Establishment-Valcartier (Thiboutot et al. 2003, 2004). Because target areas represent only a small fraction of the total area of artillery ranges, many of the areas sampled were quite a distance from any recognizable target. Most of these samples did not contain detectable energetic residues indicating that most of the total area at these ranges is probably uncontaminated.

Artillery and mortar range target/impact areas

Because target areas receive the largest number of detonations, sampling has been preferentially performed around targets at a number of artillery ranges. These targets are generally derelict trucks, tanks, and armored personnel carriers; many have sustained enormous damage after years of target practice. Because of the danger of encountering buried UXO items, and the fact that most detonations scatter residue on the surface, most of the soil samples were collected from the near surface.

Overall, the concentrations of energetic compounds near artillery targets are low and a defined concentration gradient away from the target is not apparent, unlike that found for antitank range target areas. Surface soil samples from some targets can have concentrations in excess of one mg/kg, but the concentrations at most targets are less, sometimes below the detection limits of the analytical methods used. This makes sense based on results of deposition studies showing that very little residue is deposited from rounds that detonate high order, as designed.

Artillery ranges near low-order (partial) detonations and detonation craters

By far the highest concentrations of energetic residues encountered at artillery ranges were associated with rounds that had undergone a low-order detonation (Jenkins et al. 2005c). In most cases, chunks of pure explosive were observed on the soil surface near these items and concentrations of energetic compounds in the surface soil (particles <2 mm) were up to percent levels. Although areas influenced by these low-order detonations were explored in several cases, no generalizations with regard to the sizes of areas contaminated by these events are currently possible; this remains an important research topic. Samples were also collected within impact craters and around their perimeter to determine the residual concentrations of energetic compounds. Overall, areas in and near detonation craters and intact UXO items are not heavily contaminated (Hewitt et al. 2005a). However, destruction of UXO items with C4 demolition explosive can result in a substantial increase of energetic compound concentrations in the near vicinity of the detonations, particularly when they result in a low-order detonation of the item being destroyed.

Bombing ranges

Air Force bombing ranges are very large, generally hundreds of square km in size, but the areas currently used for training with bombs containing high explosives (HE) is much smaller, generally only tens of hectares. Samples have been collected at two live-fire bombing ranges (Ampleman et al. 2003b, 2004, Jenkins et al. 2006b) and several artillery ranges where bombing with HE-containing bombs had occurred (Ch. 2 in Pennington et al. 2002, Jenkins et al. 2004a).

The high explosive present in U.S. and Canadian Air Force bombs is usually Tritonal (TNT, aluminum powder). While no one has sampled residue deposited when a bomb detonates as designed, experimental results for large artillery rounds indicate that large mass HE detonations are very efficient, dispersing only microgram to milligram quantities of energetic residue when they detonate high order. As with other munitions, low-order detonations are undoubtedly the major source of residues from bombs. Communication with range personnel indicates that low-order bomb detonations generally occur several times per year. A low-order bomb can deposit kg quantities of residues as chunks and soil-size particles. Several low-order bombs have been observed during range studies.

Results for soil samples collected at Air Force bombing ranges indicates that high concentrations of TNT (hundreds of mg/kg) are found in the immediate vicinity of low-order bombs that contain Tritonal, but soils concentrations elsewhere are much lower (Fig. 16). The mono amino transformation products of TNT (2AmDNT and 4AmDNT) are also found but at much lower concentrations. RDX has been detected at low concentrations (generally less than 0.1 mg/kg) and its presence may be due to the C4 demolition explosive (91% RDX) used to destroy duds.

Navy and Marine Corps bombs contain H-6 as the main explosive charge. This charge is used because it is composed of RDX, TNT and aluminum, a mixture considered safer for on-ship

Figure 16. Bombing range at Holloman AFB, New Mexico.

storage. Hewitt et al. (2005a) sampled a range where H-6 bombs were dropped. At least one bomb had apparently undergone a low-order detonation. In this area, H-6 chunks were observed and the mean concentrations of RDX, TNT, and HMX in a 100 × 100-m area just down slope of where the largest mass of explosive was located were 9.4, 1.4, and 1.3 mg/kg, respectively.

Open Burn/Open Detonation (OB/OD) Ranges

Military EOD technicians use OB/OD ranges at active DoD training facilities to destroy duds of various munitions that are considered acceptable to move. Sometimes chunks of high explosive or unused propellants are also destroyed at these ranges either by detonation or burning. OB/OD ranges are generally only a few hectares in size and sparsely vegetated near detonation craters. Detonation craters are often used many times before being filled in. At active installations, C4 explosive is placed on the item and detonated using a blasting cap, eliminating any detonation hazards from these items. At some Air Force and Navy demolition ranges, C4 explosive is used to blow a hole in practice bombs to ensure they contain no high explosives before they can be removed from the range for recycling. One such area was sampled and RDX and HMX concentrations in the surface soil from the C4 explosive ranged from approximately one to 30 mg/kg (Jenkins et al. 2006b).

RDX and HMX were generally found in surface soils at the ranges sampled, presumably from the use of C4 demolition explosive (Jenkins et al. 2005c). For example, soil concentrations of RDX and HMX were found to be 11.7 and 2.0 mg/kg, respectively, at a Fort Richardson, AK demolition range (Hewitt et al. 2009). Pieces of C4 are often observed on the surface at these ranges; unlike other ranges, they 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 MMR were the highest found at the installation (Clausen et al. 2004). RDX has also been observed in groundwater near OB/OD ranges at Camp Bonneville, WA, Camp Grayling, MI, CFB Petawawa, ON, and SUBASE Bangor, WA.

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. NG and 2,4-DNT are often present at these ranges.

Small arms ranges

Propellant residues at firing points

A variety of small arms ranges are present at many Army, Navy, Marine Corps, and Air Force installations. These include certification ranges for rifle and pistol as well as ranges for machine gun and vehicle-mounted weapons. At some installations, ranges are also available for use with private sports weapons including pistol, shotgun and rifle. The sizes of small arms ranges vary considerably. On the smaller end are pistol ranges with a bullet catching berm that can be less than 20 m in length; conversely, rifle ranges can be several hundred m in length and as wide as a hundred m. A diagram of a typical small arms range is shown in Figure 17.

In the past, the major environmental concern at these ranges was the accumulation of lead, and more recently tungsten, generally at backstops and berms (see section “Metals and other potential contaminants of concern”). Beginning in 2006, ranges at several installations were sampled to assess the propellant concentrations in soil near firing points for rifle, pistol, and machine gun training locations (Jenkins et al. 2007, 2008).

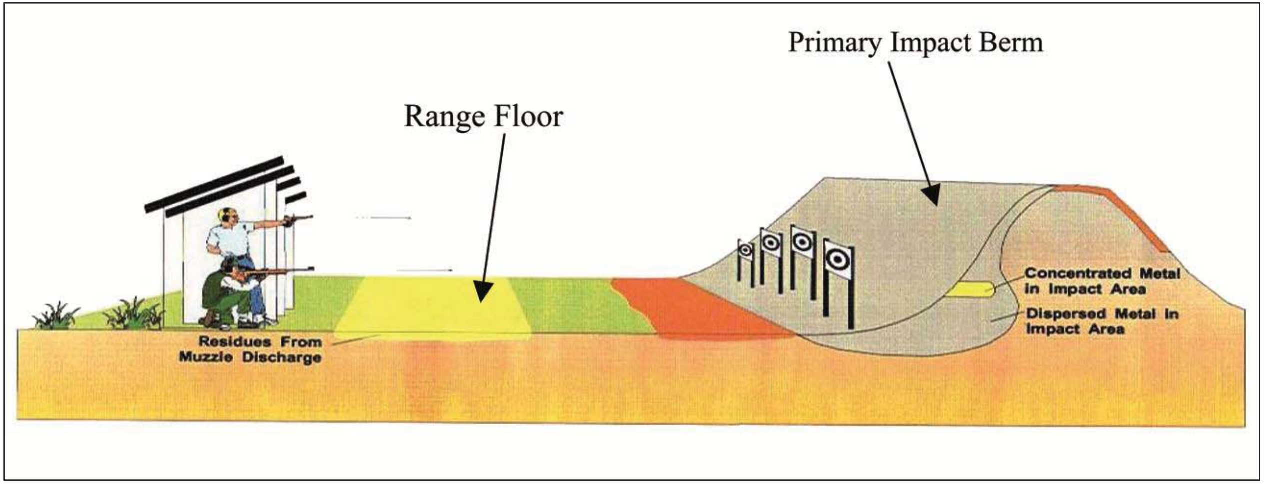


Figure 17. Cross section of a typical static rifle and handgun range (from ITRC 2003).

Table 14 lists the composition of the propellants used for a variety of small arms used by the United States military (M.R. Walsh et al. 2007a). The major component of these propellants is NC, which presents little environmental concern because it is a polymeric material with little or no water solubility and has not been shown to have any environmental toxicity, but may retain ignitable characteristics. Analytical methods for the analysis of NC in soil have been adapted from the method developed by M. E. Walsh (personal communication), but data for NC in soil at ranges is scarce. One study did measure NC in soil along with NG (Chapter 3 in Jenkins et al. 2007). They found that the ratio of NC/NG for soil samples at the various small arms ranges varied substantially from 2.1 to 6.8.

The ratio of NC/NG for soils at firing points should increase over time, as the NG is dissolved from the NC matrix by rainfall and transported or degraded (Martel et al. 2009a). Nitroglycerin is the second most abundant component in military small arms propellant, ranging from 9.7 to 12.5 % for the propellant formulations shown in Table 14. NG is deposited on small arms ranges as a component of NC particles. These particles can have any diameter not exceeding that of the original propellant grain. Generally the residues are smaller because the propellant grain has burned. If burned completely only ash remains, if the grain was barely heated it will look almost identical to an unfired propellant grain (Fig. 18, Taylor et al. Ch. 2 in Jenkins et al. 2008). These particles remain at the surface, and NG slowly leaches from this polymeric matrix into precipitation and soil solution. Estimates of the rate of leaching have been made by controlled drip tests. These tests show rapid initial dissolution of the energetic compounds from all unfired propellants and fired residues tested to date followed by much slower dissolution (Taylor et al. Chapter 2 in Jenkins et al. 2008, Taylor personal communication).

Table 14. Mass of various components in small arms rounds (taken from M.R. Walsh et al. 2007a Appendix Table A2).

		Composition (%)				
Munition	Propellant	NC	NG	DNT	DB*	DP**
9-mm Pistol	WPR289	79.1	12.5			0.9
M-16 Rifle						
5.56 mm (ball)	WC844	66.9	9.9		6.0	1.5
5.56 mm (tracer)	WC844	69.4	10.1		4.8	
M-14 Rifle (7.62 mm)	WC846	80.5	10.0	0.1	5.2	1.1
50 cal Machine gun	WC860	78.9	9.7		8.0	1.1
50 cal Machine gun	WC857	68.5	10.8		5.9	1.2

* DB – Dibutyl phthalate

**DP – Diphenyl amine

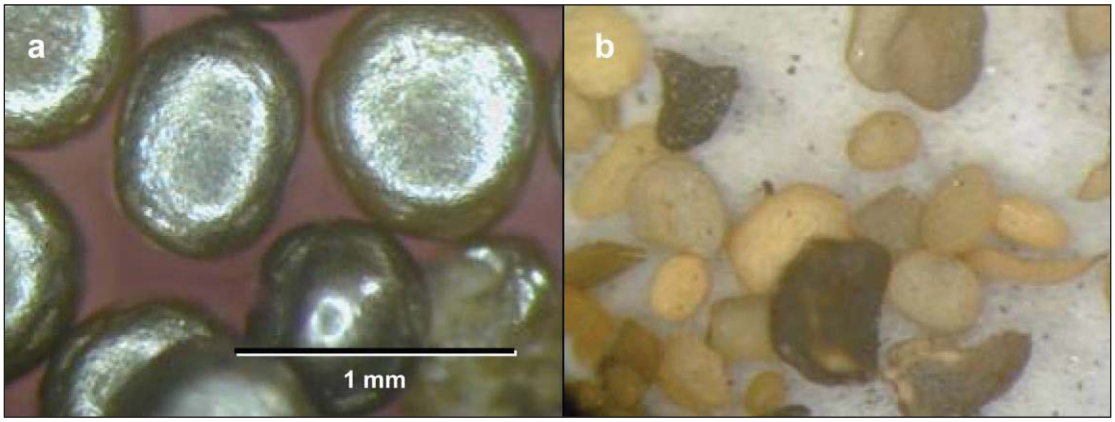


Figure 18 Unfired grains (a) and fired residues (b) from a 0.50 Caliber machine gun photographed at the same scale.

A series of experiments have been conducted at a variety of small arms ranges in the United States and Canada to estimate the distances downrange where residues are deposited. These studies include collection of surface soil in front of the firing positions at a variety of small arms ranges (Table 15), and controlled firing studies where residues were deposited into pans placed on the surface at various distances downrange (Figures 19 to 21).

The concentration of NG in surface soils from 0 to 5 m downrange of the firing line ranged from 8.6 to 413 mg/kg (Table 15). The amount of accumulation is clearly a function of the number of rounds fired at the various ranges. In some cases, 2,4-DNT was also detected in surface soils, but it was generally at two orders of magnitude less than NG. Low concentrations of 2,4-DNT can be present in some small arms propellant.

From these analyses it also appears that most of the propellant residue is deposited within 10 m of the firing line (Fig. 19 to 21). Some minor deposition appears occurred as far as 35 m away from the firing line at the Ft. Richardson Sport Fire range. These distances are somewhat larger than estimated from depositional studies by M.R. Walsh et al. (Chapter 3 in Jenkins et al. 2008). It appears that in general, 99% of the total propellant deposition and accumulation on small arms ranges will be from the firing line to a distance of 20 m downrange, except perhaps for sports fire ranges where some deposition appears to occur beyond 20 m.

Soil depth profile samples were collected at the Ft. Richardson Sport Fire Range and at a 29 Palms rifle range, each at a distance of 2 m ahead of the firing line, and at three ranges at Camp Edwards, MA (Table 16). (Chapter 8 in Jenkins et al. 2008). NG and 2,4-DNT were detected as deep as 6-8 cm in samples collected by digging a pit and carefully sampling from the sidewall at Ft. Richardson. At 29 Palms, NG residues were found as deep as 14 to 18 cm, but 2,4-DNT was

Table 15. Concentration of nitroglycerin in surface soils for various distances downrange at small arms ranges in the United States and Canada.

Location/Range	Type of Use	Samples analyzed	NG Concentration (mg/kg) at Downrange Distance (m) 0–5m	5–10	10–15	15–20	20–25	25–30	30–35
Yakima Training Center, WA [1]	Mixed	1	85						
Ft. Lewis, WA[1]	Mixed MG*	5	8.6	2.1	1.2				
	M-16	10	413	252					
CFB/ASU Wainwright, AB [2]	M-9 pistol	3	21						
	M-16	3	13						
CFB-Petawawa, Ontario [2]	M-16	8	15						
29 Palms, CA[2]	MG	3	93	89	15	6.8	2.5		
	M-9 pistol	4	110						
	M-16	10	25	2.9	4.6				
Ft. Richardson, AK [2]	Mixed MG	10	357	336	9.4	4.6	13		
	Mixed Sports	10	113	199	9.1	6.9	12	15	24
Camp Edwards, MA [3]									
Juliet Range	M-9 pistol & M-16	2	3						
Echo Range		2	0.4						
Kilo Range		2	56						

* MG – machine gun

[1] Jenkins et al. 2007; [2] Jenkins et al. 2008; [3] Clausen et al. 2010b

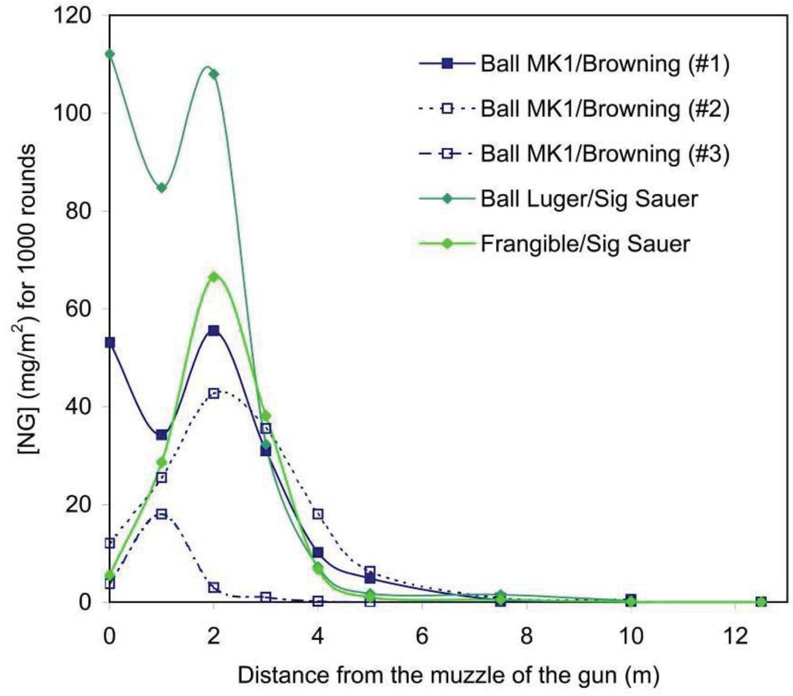


Figure 19. Dispersion of NG on the ground for the 9-mm caliber after 1000 rounds.#1, #2, and #3 are triplicates of Ball MK1/Browning (from Faucher et al. Ch 5 in Jenkins et al. 2008).

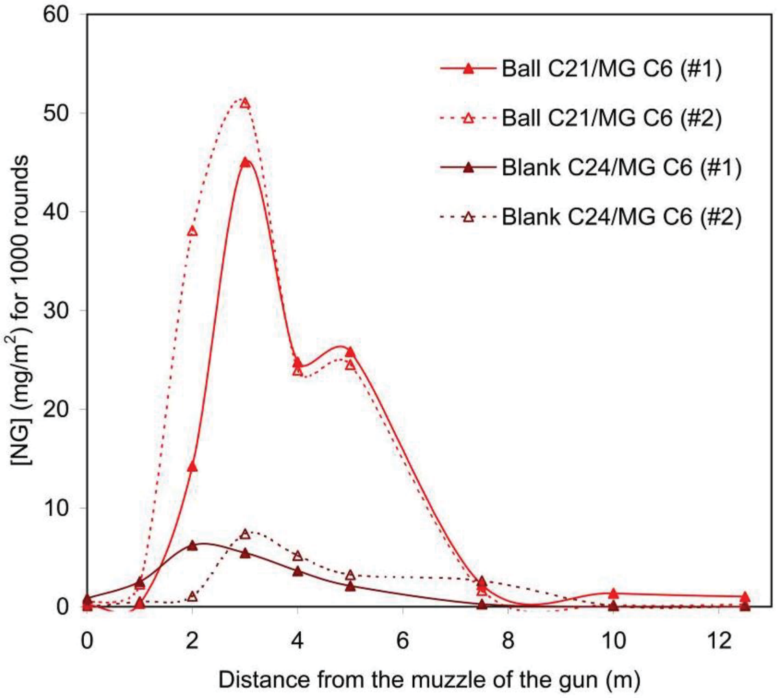


Figure 20. Dispersion of NG on the ground for the 7.62-mm caliber after 1000 rounds. #1 and #2 are duplicates (from Faucher et al. Ch 5 in Jenkins et al. 2008).

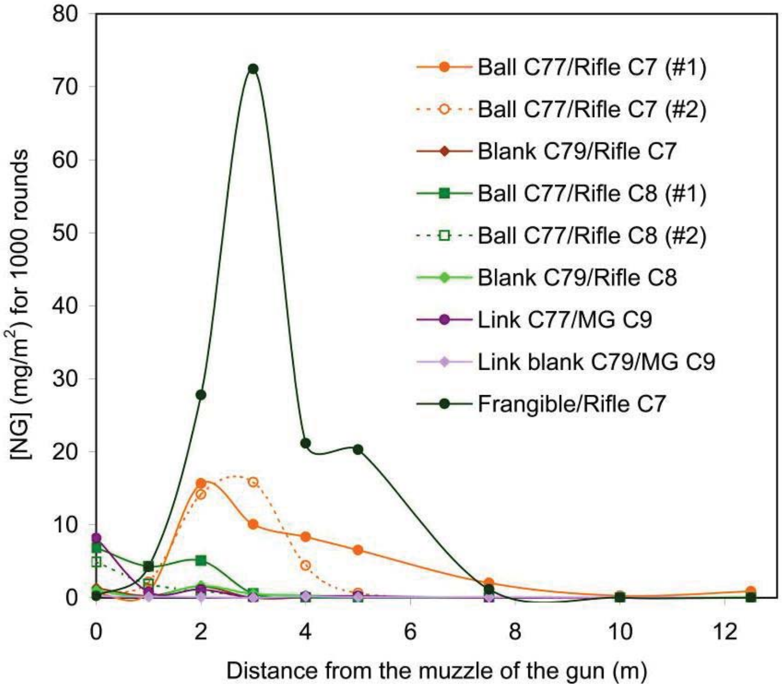


Figure 21. Dispersion of NG on the ground for the 5.56-mm caliber after 1000 rounds. #1 and #2 are duplicates (from Faucher et al. Ch 5 in Jenkins et al. 2008).

Table 16. Concentrations of NG and 2,4-DNT in soil depth profile samples from the Sport Fire Range at Ft. Richardson, AK, a rifle range at 29 Palms, CA (Jenkins et al. 2008) and mixed use ranges (M-9 pistol and M-16 rifle) at Camp Edwards, MA (Clausen et al. 2010a).

	Mean Concentration (mg/kg)									
	Ft. Richardson, AK		29 Palms, CA		Camp Edwards, MA					
	Sport Fire Range		Rifle Range		Juliette Range		Echo Range		Kilo Range	
Depth (cm)	NG	2,4-DNT	NG	2,4-DNT	NG	2,4-DNT	NG	2,4-DNT	NG	2,4-DNT
0–2, 0–8	85.9	1.66	42.3	< 0.04	3.0	0.085	0.4	<0.014	91	1.3
2–4, 2–6	15.7	0.48	9.88	< 0.04						
4–6, 6–10	9.8	0.26	0.64	< 0.04						
6–8, 10–14	6.3	0.16	0.11	< 0.04						
8–10, 14–18	<0.05	<0.04	0.12	< 0.04						
10–15, 18–22	<0.05	<0.04	1.30	< 0.04						
15–20	<0.05	<0.04								
20–25	<0.05	<0.04								
25–30,23–30	<0.05	<0.04			3.4	0.11	0.06	<0.014	1.4	0.05
30–35	<0.05	<0.04								
35–40	<0.05	<0.04								
45–61					0.21	<0.014	< 0.02	<0.014	0.69	<0.014
76–91					0.13	<0.014	< 0.02	<0.014	0.67	<0.014

not detected in any of these samples. These results suggest about 90% of the total NG accumulation and about 88% of the 2,4-DNT accumulation is present in the top 5 cm of the soil profile at Ft. Richardson, and 96% of the NG accumulation is within the top 6 cm at 29 Palms.

Site characterization

Soil sampling studies

Several experiments have been conducted by the Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL) of the U. S. Army Corps of Engineers for the purposes of (1) evaluating alternative strategies for collection of representative samples to characterize exposure areas at training range firing points and impact areas and (2) assessing laboratory sample processing and analysis protocols for accurate and precise determination of residue concentrations in these soil samples.

Site characterization 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, the size of each being a function of the total area to be assessed and the future land use envisioned. Within each sampling unit, one (or sometimes several) discrete sample(s) is collected and shipped to an offsite contractor laboratory where samples are processed and analyzed. The results of these analyses are assumed to be representative of concentrations within the sampling unit and the concentrations of the individual samples are generally assumed to be normally distributed. The assumption that these discrete samples are "representative" of analyte concentrations within the sampling unit is generally not tested, although the concentrations determined for discrete samples collected from within the same unit often do not agree. The results from these discrete samples are then used to calculate the mean concentration for that sampling unit.

Results from discrete sampling at ranges

Because earlier research had indicated that explosive concentrations in discrete samples can vary substantially even over short distances (Jenkins et al. 1997a,b; 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 average concentrations in soil at firing points and impact areas. To test just how diverse individual discrete samples might be from within these areas, experiments were conducted at firing points and impact areas at several different military training ranges. In most cases, a 10 × 10-m sampling unit was established and subdivided into one hundred 1 × 1-m cells. A discrete sample was collected from each cell and analyzed for energetic compounds according to established protocols (SW846 Methods 8330 or 8330B).

The major analyte detected in seven different sampling units at six different installations varied from 2,4-DNT and NG at firing point areas to RDX, TNT and HMX at impact areas (Table 17). 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 samplings units as small as 10 × 10 m. In fact, the maximum and minimum concentrations among nine discrete samples collected within a single 1×1-m cell varied by two orders of magni-

Table 17. Variability of soil concentrations among 100 discrete samples collected within 10-m x 10-m sampling units at various training range impact areas.

				Concentration (mg/kg)				
Installation	Area*	Range type	Analyte	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)[2]	FP	Antitank rocket	NG	2.94	0.02	0.281	0.451	0.494
CFB-Valcartier (QC)[2]	IA	Antitank rocket	HMX	1150	5.8	197	292	290
Holloman AFB (NM)[3]	IA	Bombing	TNT	778	0.15	6.36	31.8	87.0
Ft. Polk (LA)[4]	IA	Mortar	RDX	2390	0.037	1.7	71.5	315
Cold Lake (AB)[5]	IA	Bombing	TNT	289	0.38	6.57	16.2	32.3
Ft. Richardson (AK)[6]	IA	Artillery	RDX	172	<0.04	<0.04	5.46	24.8
Ft. Richardson (AK)[7]	IA	Mortar	RDX	4450	<0.04	<0.04	—**	—

* Firing point (FP) or Impact Area (IA). [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. 2007b. [7] Hewitt et al. 2009 (Note: results from 200 discretes).
** — Not computed

tude, demonstrating the magnitude of short-range heterogeneity in these areas (Jenkins et al. 2006b). This extreme heterogeneity is due to the presence of particles of energetic residues. Median values for the hundred discrete samples within each data set were always less than the mean, indicating most discrete samples underestimated 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 a mean based on just a few discrete samples will result in a mean value that is biased low.

Results from MULTI-INCREMENT samples at ranges

Another approach investigated to estimate mean concentrations within a sampling unit was use of *MULTI-INCREMENT*® samples (MIS®). 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 as the decision unit or the sampling grid. 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-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 (Fig. 22).

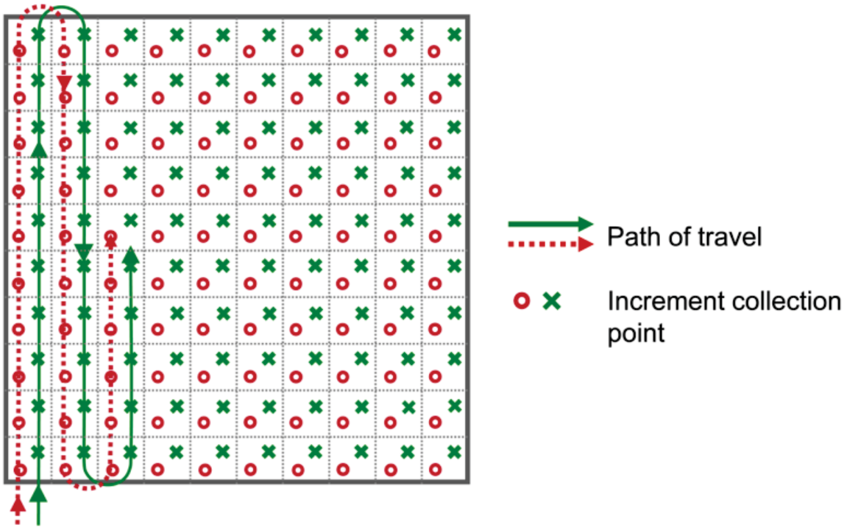


Figure 22. Illustration of *MULTI INCREMENT* sampling using a systematic-random sampling design for collecting two separate 100-increment samples.

® *MULTI INCREMENT* is a registered trademark of EnviroStat, Inc. of Fort Collins, CO, for a comprehensive sampling methodology. More information is available at www.envirostat.org

In several comparative sampling studies, the variability among replicate MIS was much lower than for discrete samples taken within the same sampling units (Table 18). For example, 2,4-DNT concentrations in discrete samples collected within a 10 × 10-m firing point sampling unit at Donnelly Training Area ranged over almost four orders of magnitude, whereas concentrations among the ten replicate MIS from this sampling unit varied by less than a factor of three. Similarly, the range in RDX concentrations for discrete samples from a 10 × 10-m sampling unit at a Ft. 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 Ft. 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 (Fig. 22).

Sampling units up to 100 × 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. 2005b). Triplicate samples varied from 3.9 to 9.4 mg/kg for RDX for soil samples from an impact area at 29 Palms, CA (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 (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 (Fig. 22). 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

Table 18. Variability of soil concentrations among replicate multi-increment samples (MIS) collected within sampling units at various ranges.

Installation	Area*	Range type	Increments/ 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
Ft. 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

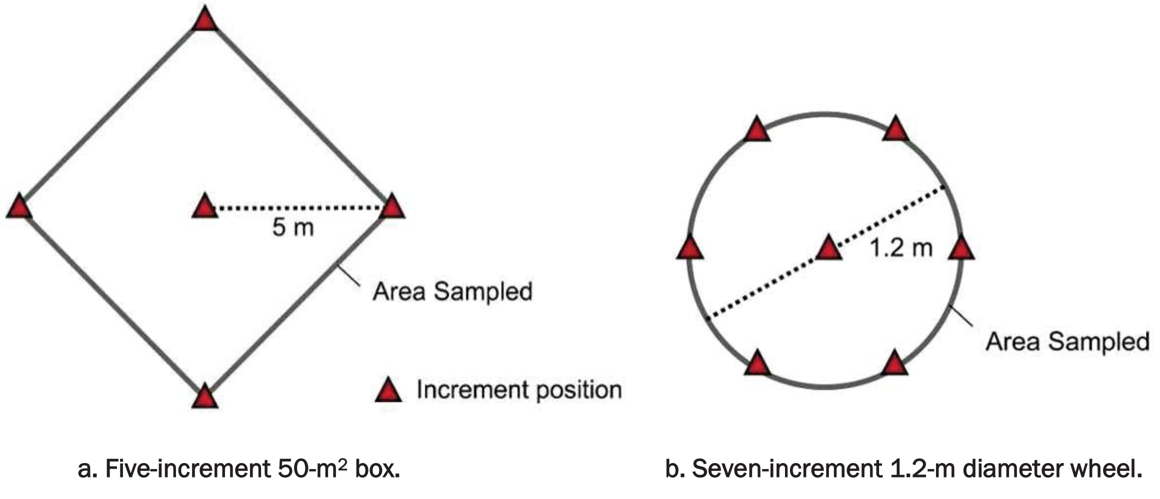
* Firing point (FP), Impact Area (IA), or Thermal Treatment Area (TTA). [1] M.E. Walsh et al. 2004, [2] Jenkins et al. 2006b, [3] Jenkins et al, 2004a, [4] Hewitt et al. 2005a, [5] Nieman 2007

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. For areas where solid pieces of the energetic compound are present on the surface, replicate MIS samples will often not be normally distributed.

Comparison of discrete, wheel, box, and MIS approaches at impact areas and firing points

Two other approaches have been used to estimate mean explosive concentrations for sampling units at training ranges. The first is a “box” sampling design in which a five-increment sample is obtained from a 7 × 7-m sampling unit with increments collected from the center point and the four corners as shown in Figure 23a (USACHPPM 2001, 2003, 2004, 2005). The second, shown in Figure 23b, uses a “wheel” sampling design with a seven-increment sample collected with six increments from the periphery of a 1.2-m diameter circle and the seventh from the center. These two approaches were compared with the collection of discrete samples and 100-increment MIS samples in a study conducted by Roote (2010). Four replicate samples were collected using each design and the results were compared. This was done at a bombing range impact area where TNT was the major contaminant, and at an antitank firing point where NG was the contaminant of interest (Tables 19 and 20).

In both cases, the relative standard deviation (RSD) was much lower for MIS than for the discrete, box, or wheel sampling approaches and thus provides a much more reliable estimate of the mean concentration for the sampling unit.



a. Five-increment 50-m² box. b. Seven-increment 1.2-m diameter wheel.

Figure 23. Two conventional sampling designs evaluated.

Table 19. Concentration of TNT (mg/kg) in soil samples from Holloman AFB, NM bombing range impact area, comparison of different sample collection strategies (from Roote 2010).

	TNT Concentration (mg/kg)						
Sample Type	*Rep. 1**	*Rep. 2*	*Rep. 3*	*Rep. 4*	Mean	Std Dev	% RSD
Discrete	1900	11	37	200	537	913	170
Box	1100	160	6400	3700	2840	2810	99
Wheel	0.6	21000	42	90	5280	10,500	198
MIS**	1500	2100	1000	1700	1580	457	29
* Rep. – Replicate ** 100 increments for each MIS							

Table 20. Concentration of NG (mg/kg) in soil samples from antitank rocket firing range at Ft. Lewis, Washington, comparison of different sample collection strategies (from Roote 2010).

	NG Concentration (mg/kg)						
Sample Type	*Rep.1**	*Rep.2*	*Rep.3*	*Rep.4*	Mean	Std Dev	% RSD
Discrete	2300	1900	1550	6360	3050	2230	73
Box	5320	1520	4200	5120	4040	1750	43
Wheel	2470	3490	1800	2400	2540	701	28
MIS	1630	1890	1990	1950	1870	162	9
* Rep. – Replicate							

Sampling depth

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 UXO is blown-in-place on impact ranges. Figure 24 shows two examples of unconsumed particles: one photograph shows TNT particles collected after the blow-in-place of a 155-mm howitzer round with a block of C4; the other shows fibers that accumulated on snow in front of a gun where the M1 propellant was used to accelerate 105-mm howitzer projectiles downrange.

The chemicals in these energetic particles have low vapor pressures. Therefore, the principal mechanisms that determine the fate of these chemicals include dissolution, transformation, and for some, chemical mineralization. Figure 25 shows concentration profiles of energetic residues obtained directly beneath chunks (> 2 cm) of explosives found on the surface. Concentrations in the surface soil immediately beneath the chunks were a consequence of small (< 1 mm) particles washed off or abraded from the surface. With increasing depth, the concentration results from the migration of dissolved energetic analytes. The inherently lower concentrations of energetic chemicals in the subsurface result from a combination of limited solubility, limited volumetric

Figure 24. Examples of energetic material particles: TNT particles (<1 mm, fraction) from a blow-in-place detonation (left), 105-mm howitzer propellant fibers from a collection tray 3 m from muzzle (right, 1-mm scale).

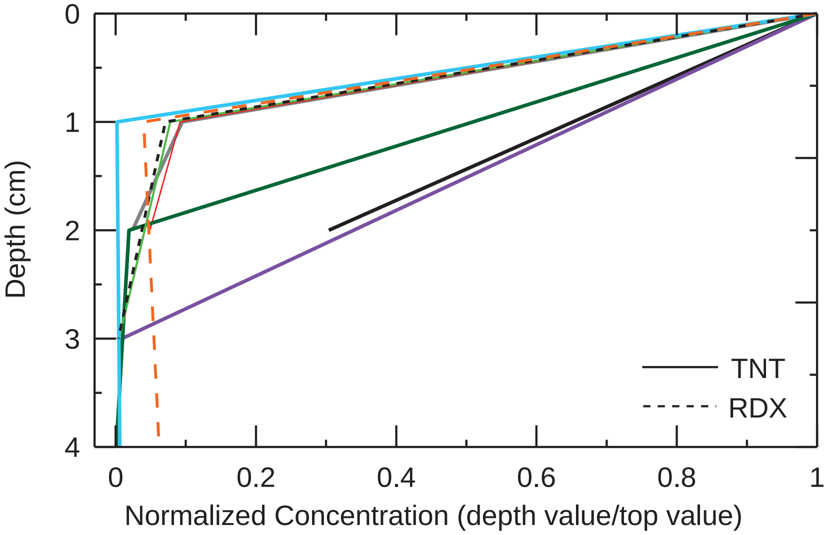


Figure 25. Normalized profile showing decreasing concentration in energetic compounds with depth directly beneath seven TNT chunks (> 2 cm) found on the surface at Fort Bliss and two chunks of Composition H-6 at 29 Palms. Equivalent samples are shown in the same color.

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 is in the top 2.5 cm. Once the energetic residue particles have been completely dissolved, it is unlikely their presence will remain detectable in surface soils for more than a couple years. That is, once energetic residues no longer are present in the solid form, they degrade or migrate away from the original source area. In arid regions, however, dissolution can take many decades.

Vegetation

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. Figure 26 shows examples of vegetation at a firing point and surrounding a crater where an 81-mm mortar had low-ordered on an artillery impact range. If vegetation is removed or patches of vegetation are avoided, energetic residues trapped within this portion of the surface matrix will not be included in the sample and the analyzed amount of energetic residue is likely to be underestimated. Use of specially designed (Fig. 27, M.R. Walsh 2004) or commercially available coring tools at vegetated sites aids

Figure 26. Examples of surface vegetation at a firing point (inset) and in and around a crater of an 81-mm mortar low-order detonation crater on an artillery impact range.

Figure 27. Coring tool designed specifically for collecting cohesive multi-increment soil samples.

in the collection of surface samples with minimal surface disturbance and human effort. Most importantly, use of coring tools helps avoid biased sampling, i.e., sampling only the exposed soil surfaces. In addition, this type of sampling tool enhances surface area, depth, and increment volume precision. With the exception of very thick vegetative mats, vegetation from the surface interface included with a soil sample typically makes up less than a percent of the total dry sample weight.

Sampling Design

Sampling Theory

Representative sampling should be a major project objective (USEPA 2002, 2003; D.M. Crumbling personal communication). To do so, the sampling strategy must address the compositional and distribution heterogeneity of the constituents of concern (Pitard 1993). Compositional heterogeneity is due to the fact that not all soil-sized particles within the population have the same concentration of target analytes. This heterogeneity is at a maximum when a portion of the target analytes is present as discrete particles. Error due to compositional heterogeneity is called the fundamental error and is inversely related to the sample mass. A more thorough discussion of fundamental error is provided in Appendix B. Distributional heterogeneity is due to contaminant particles being scattered across the site unevenly, sometimes with a systematic component as well as a short-range random component. Error associated with distributional heterogeneity is inversely related to the number of individual increments used to build the sample. This type of error is at a maximum when a single discrete sample is used to estimate the mean for a larger sampling unit (sampling unit – population, area of concern, ecological habitat, etc). To reduce the influence of distributional heterogeneity in the estimate of the mean concentration for a sampling unit, the collection of 30 or more evenly spaced increments to form an individual soil sample has been recommended (Jenkins et al. 2004a,b, 2005c, 2006a; M.E. Walsh et al. 2005; Hewitt et al. 2005a). The objective of this MIS strategy and systematic random design is to obtain a single sample that contains all constituents, including energetic residue particles of every composition as well as non-energetic particles, in exactly the same proportion as they are present in the entire sampling unit.

In the past, the estimate of mean concentration for a sampling unit has often been derived from the collection and analysis of one or several discrete samples. Studies comparing discrete and MIS sampling strategies for the characterization of military training activities, discussed earlier, have shown that the distribution of data obtained from discrete samples is always non-Gaussian and positively skewed, whereas that from a multi-increment data set is often normally distributed (Jenkins et al. 2004a,b, 2005c, 2006a; M.E. Walsh et al. 2005), a result consistent with the central limit theorem of statistics. Moreover, a single discrete sample or small set of discrete samples almost always results in a lower estimate of the mean concentration than the multi-increment sampling strategy. As the number of discrete samples collected approaches the number of increments in a single multi-increment sample, the differences between the estimates of mean concentrations resulting from these two strategies converge. However, each replicate MIS is an independent estimate of the mean and collection of multiple replicate MIS provides an estimate of the error in the mean concentration estimate, something that is never done with discrete sampling strategies.

Uncertainty

The total measurement error includes contributions from sample collection, sample processing, and analytical determination. The best way to estimate the total measurement error, or uncertainty of the mean concentration of contaminants in a sampling unit, is to collect and analyze replicate field samples. It must be emphasized that these are not field splits, but rather independently collected samples from within the sampling unit. If it is important to compute a 95% upper confidence limit (UCL) for the mean concentration within a sampling unit, then this can be done by collecting triplicate MIS. The standard deviation computed from the triplicate results can be used for the 95% UCL computation. A percentage of the total multi-increment samples collected for a given characterization activity should be done in triplicate, the actual percentage being determined on a site-specific basis depending on the data quality objectives.

The ability to achieve low sampling error depends on the sampling strategy and the military training activity under investigation. In general, the more repetitious a given activity, e.g., projectiles fired or detonations occurring in the same general location, the more likely the distribution of energetic residues will become more pronounced (heavier accumulation) and less heterogeneously distributed. As a consequence, sampling uncertainty is likely to be lower at sites such as a fixed firing position, near a direct line-of-sight target, and at a disposal range than at sites around a target or former target on an indirect fire impact range. Studies at firing points and within impact ranges have supported this anticipated trend and have shown that analyte variability is much greater for a large set of discrete samples (n=30) than for a small set (n=3) of replicate 30-increment samples (Jenkins et al. 2004a,b, 2005c, 2006a; M.E. Walsh et al. 2005). This is a common characteristic of analytes that are heterogeneously distributed as particles. For many environmental programs, this source of uncertainty (i.e., determining if the sampling strategy results in representative samples as inferred from the ability to reproduce the sampling results) has often been ignored. This is particularly alarming in light of studies showing sampling error to be the largest portion of the total characterization uncertainty for energetic residues on military training sites (Jenkins et al. 1997a,b, 1999). Therefore, both scientific (data quality) and economic advantages can be realized through the processing and analysis of multi-increment samples (Hewitt et al. 2009).

Sampling unit size

The sampling unit size needs to vary depending on the manner in which the deposition has occurred. For example, at an artillery range firing point the residue is dispersed over a fairly large (e.g. 10,000 m^2) area from a single training exercise. Near a low order detonation, the size of the impacted 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 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, b, c, 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. A practical guide for the setting up sampling units and collection of MIS is provided in Appendix C.

Visual observation of low order detonations and field screening

Chunk residues (pieces of energetic materials > 2 mm) often are present within and around ruptured (low-ordered or breached) munitions and in areas where OB/OD of off-specification, obsolete, or excess energetic materials has been performed. Special precautions should be taken when sampling around low-order detonations and ruptured munitions, both of which often fall under the classification of munition and explosives of concern (MEC). First, the size of the sampling unit should at least encompass the area with visible residues. Delineating this area covered with visible pieces of energetic residues will result in high energetic residue soil concentrations, a possible source zone for surface and ground water contamination. Field analytical screening techniques should be used to identify chunks of energetic residues. Methods approved by the EPA include colorimetric SW-846 Methods 8510 and 8515. Immunoassay Methods 4050 and 4051 (US EPA 2000; US EPA 1996a, b, c) are no longer commercially available. Other screening techniques, such as use of the Expray™ kit, can identify explosives (Plexus Scientific, Silver Spring, MD; Bjella 2005). Once identified, chunks of energetic materials should be gathered, weighed (if not adhering to a munitions casing), and removed by EOD personnel or UXO technicians prior to sampling. Additional information regarding residue identification and the safety concerns are presented in Method 8330B (US EPA 2006).

Systematic random sampling

A systematic-random sampling design is recommended when collecting individual increments to build each MIS (Hewitt et al. 2005b, 2007b). This sampling design is analogous to systematic grid sampling (US EPA 2002), in which an initial position is chosen and the remaining sampling locations are laid out in a regular pattern (Cressie 1993). In the systematic random design, the sampler begins at a randomly chosen point on the edge of the area to be characterized and collects an increment of surface soil after a predetermined number of steps, while walking back and forth in a systemic manner across the area of interest. Figures 22 and 28 show examples of the path a sampler would take using this sampling design for square and circular areas. This provides an unbiased spatial coverage and ensures that the distance between any two increments is minimized. The proper number of increments needed in order to obtain a representative (reproducible) sample is a function of the distributional heterogeneity. The total mass of each increment and total mass of the sample is a function of the compositional heterogeneity. The number of increments and size of the sampling units cited for the range-sampling activities described below have often produced replicate samples with similar analyte concentrations. Generally, samples must contain a minimum of 30 increments to produce replicates that are normally distributed (Jenkins et al. 2004a). The assumption is that the distribution of energetic residues is similar between military facilities with ranges designed for the same activity is the basis for the recommended sizes of sampling units and number of increments. Because increments are being combined to create a single sample, cleaning the sampling tool between collecting increments of a given sample is unnecessary. A clean sampling tool is necessary for each new sampling unit.

Sample Processing

Multi-increment samples collected with the sampling designs described above and in the following sections are typically 1 kg or greater. Laboratory analysis is conducted on a small portion of the sample, referred to as a subsample. Method 8330B Appendix A (US EPA 2006) provides guidance on how to process soil samples so they can be representatively subsampled in preparation for analysis. Several studies cited in the revised method have shown that in order to determine representative analyte concentrations in soils containing energetic residues, they must either be

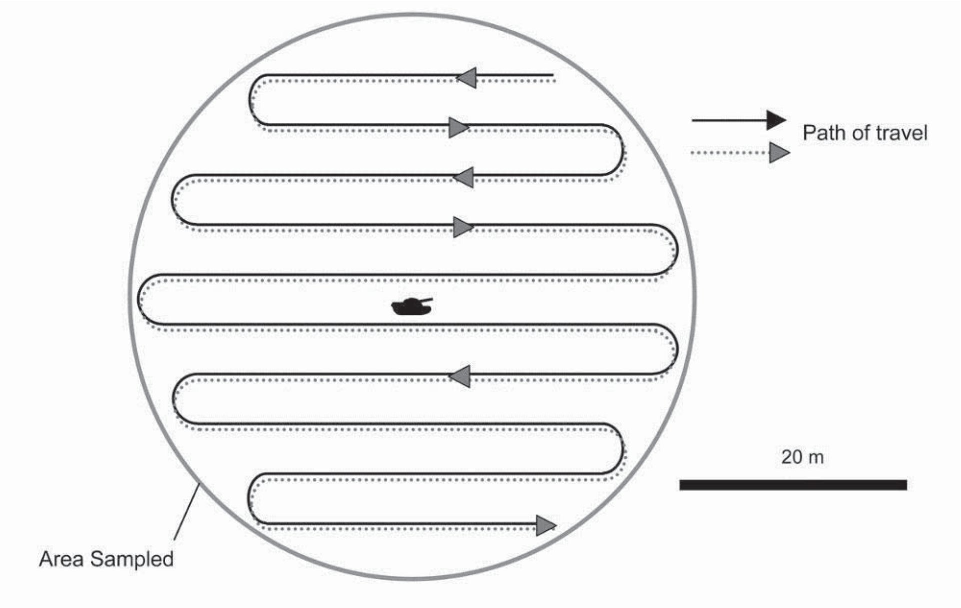


Figure 28. Systematic-random multi-increment sampling design surrounding a tank target at the impact area of an anti-tank range.

ground before subsampling or the entire sample must be extracted. Following the guidance in Method 8330B, the results for laboratory replicate subsamples have been shown to be both reproducible and experimentally accurate (method established accuracy), since in a few cases, the remaining sample was extracted in its entirety and analyzed to obtain an estimate of the true sample mean concentration subject only to analytical uncertainty, and thus eliminating all error due to sample processing and subsampling.

Multi-increment Sampling

Multi-increment sampling using a systematic-random sampling design is recommended for estimating mean concentrations of energetic compounds at all the military training ranges addressed in this document. In addition, collecting triplicate multi-increment samples is strongly recommended for at least one sampling unit on each type of training range under investigation. To aid in the collection of multi-increment samples with a targeted weight of approximately 1 kg, special sampling tools may need to be acquired so as to obtain the appropriate incremental mass relative to the recommended number of increments and sampling depth (Appendix C). The coring tools, shown in Figure 27, are made with 2- and 3-cm inner diameters to help meet these needs. Oakfield corers or similar push tube devices are soil sampling tools available in several different core barrel widths and lengths. These soil-coring tools are easy to operate in cohesive soils. However, they are not practical for some cobbled and non-cohesive soils. Metal or hardened plastic scoops and trowels are more suited for use in cobble-rich and non-cohesive (sandy) soils. Both of these soil-sampling tools are available from equipment vendors such as AMS (http://www.ams-samplers.com/), Forestry Suppliers, Inc. (http://www.forestry-suppliers.com/), Enviro-

Tech (http://www.envirotechonline.com/), and Ben Meadows Company (http://www.benmeadows.com/).

It also should be noted that the guidance provided herein also applies to the surfaces of other ranges not specifically addressed in this document that are operationally similar. For example, on direct line-of-sight ranges, the areas anticipated to have the highest accumulation of munitions constituents would be at the firing point and around targets.

Recommended sampling protocols

Hand grenade ranges

At hand grenade ranges, the sampling area should be an area between 5 and 40 m in front of the throwing bay and the width of the impact zone. For grenade courts that are not separated by barriers, the entire impact range can be characterized as a single sampling unit. When walls or other features separate the impact zone into several distinct areas, at least one MIS should be taken for each impact zone.

Individual increments for multi-increment samples should be collected from the soil surface to a depth of 10 cm. If the surface area to be characterized is less than 100 m^2, the sample collected should include 30 or more increments. For larger areas, samples consisting of 50 or 100 increments are recommended. In both cases, the sample collection pattern should be as shown in Figure 22.

Profile sampling is recommended for those ranges where the surface has been disturbed and, as a consequence, particles may be present in the subsurface. Within the area with the highest crater density, at least five depth profiles should be collected in 10-cm intervals down to a depth of at least 30 cm. Sample increments from the same 10-cm depth interval (0–10 cm, 10–20 cm, and 20–30 cm) should be combined to produce a single five-increment sample (Fig. 29). Because of the limited number of increments, this sampling strategy is best suited for determining the depth to which residues have been mixed into the soil profile and not to estimate the average concentration for a subsurface layer over a large horizontal cross-sectional area. To achieve this second objective, 30 to100 increments should be collected. For depths below 30 cm, a surface geophysical survey may not be sensitive enough to detect grenades; therefore, down-hole clearance should be performed.

If a ruptured grenade with energetic residues on its interior surfaces or a grenade surrounded by chunk residues is encountered, an area that encompasses the visibly affected surface should be sampled as a separate sampling unit. Prior to sampling, all visible pieces of energetic residues (i.e., energetic residues present as MECs) should be removed. A 30-increment sample should be collected from the sampling unit.

Anti-tank rocket ranges

Targets

Studies of anti-tank rocket range impact areas indicate that most the residues are within a 25-m radius of targets (Jenkins et al. 1997b, 2004b; Thiboutot et al. 1998). To estimate the mass of residues on these ranges, multi-increment samples collected within a 25-m radius around each target is recommended (Fig. 28). Because the area represented by each sample will be about 2000 m^2, 100 increments of the top 5 cm are recommended. In general, more increments are required to adequately characterize larger sampling units; otherwise the distance between increments may be inadequate to capture residues from individual events.

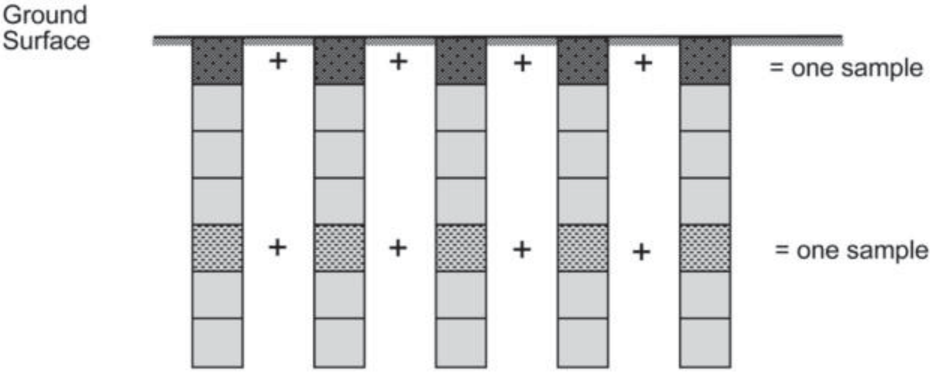


Figure 29. Schematic of procedure to collect multiple-increment profile samples where transport and deposition of energetic materials is suspected.

If a more detailed characterization is required, a segmented halo design is recommended (Jenkins et al. 2004b, Pennington et al. 2004). In this design, as shown in Figure 30, concentric rings are established at distances of 5, 15 and 25 m from the target, the rings are segmented, and multi-increment samples are collected within each segment. Because the surface area within a segment is relatively small, each sample should be built from 30 increments.

Profile sampling at anti-tank ranges can be conducted to look for subsurface migration of dissolved energetic residues. Unlike hand grenade ranges, particles remain on the soil surface at anti-tank impact ranges and only the dissolved compounds will be transported downward. Any sampling for this purpose should be done immediately in front of the heaviest impacted target, where surface concentrations will likely be very high. Since the area in front of the target is relatively small, this can be performed as a single sampling unit encompassing at least five profiles with at least five sampling intervals within the top 60 cm (Fig. 29).

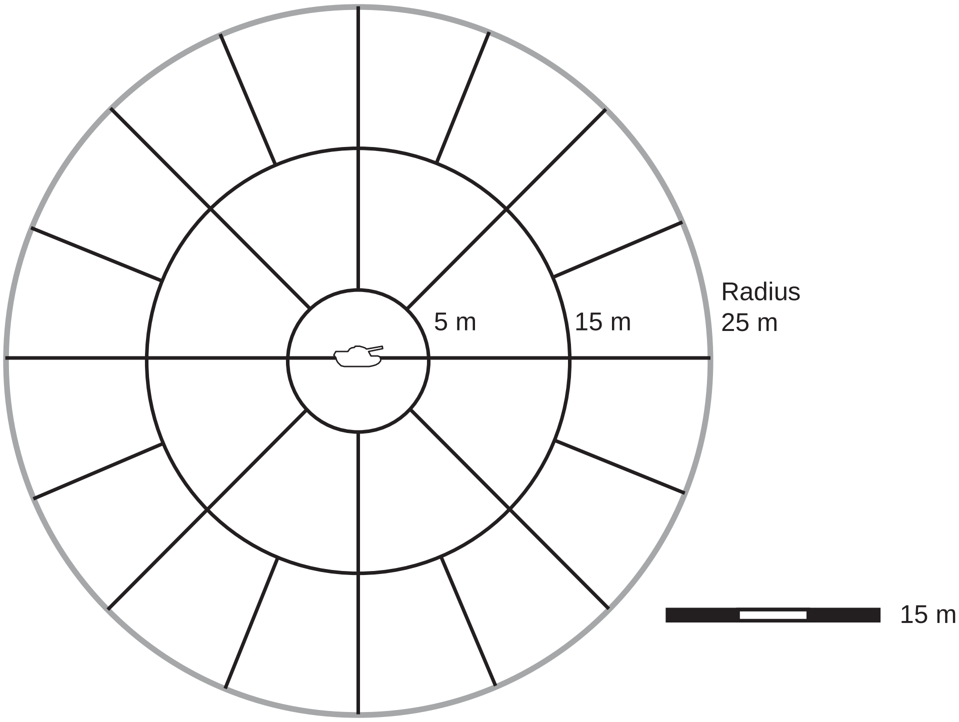


Figure 30. Segmented halo sampling pattern surrounding a tank target at a live-fire bombing range impact area.

Firing points

The highest concentration of the propellant residues at anti-tank ranges is behind the firing line. To estimate the total mass of residue in this area, a single 100-increment sample is recommended in a rectangle 30 m wide and running the entire length of the firing line (Fig. 31a). This same design can be used just in front of the firing line. If a more detailed characterization is desired, divide the area behind and in front of the firing line into three 10-m-wide rectangles along the entire length of the firing line and collect a 30-increment sample within each area (Fig. 31b). Because residues are deposited at the surface and little surface disruption occurs, it is recommended that firing point samples be taken from the top 2.5 cm.

To assess whether subsurface migration of dissolved propellant-related compounds has occurred, the same strategy as presented in the hand grenade range is recommended. Sampling locations should be 5–10 m behind the firing line at the most heavily used firing position.

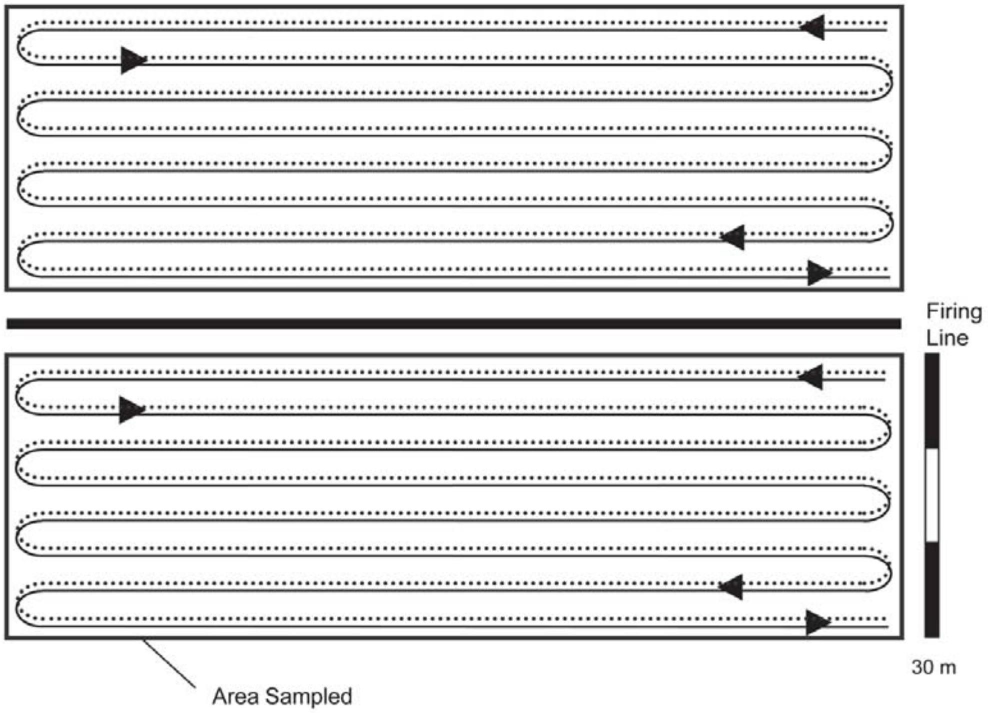
Artillery Ranges

Away from firing points and targeted areas

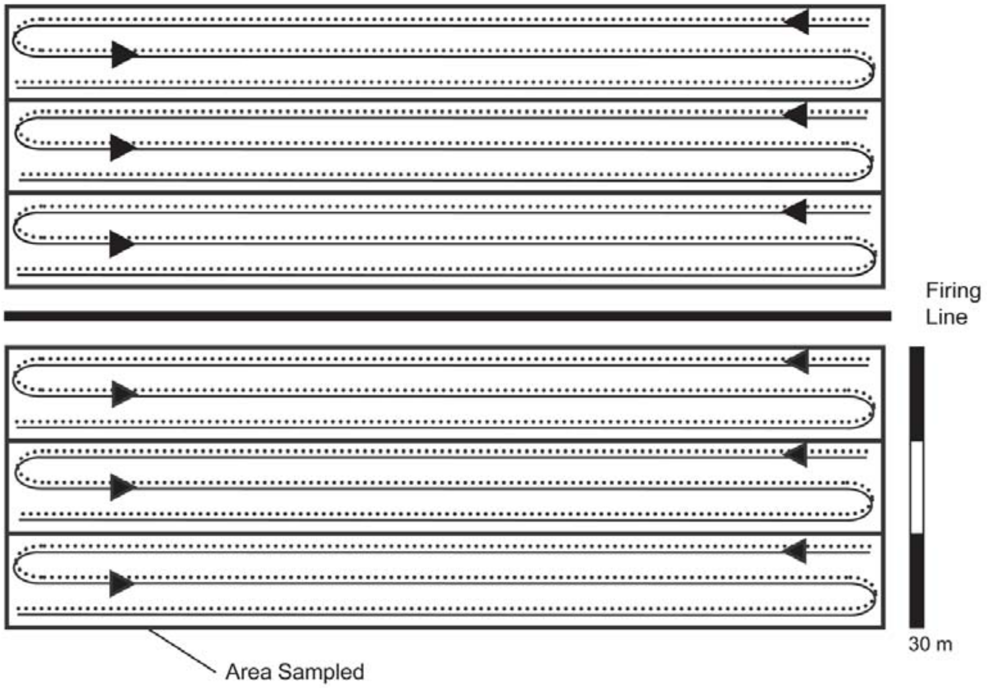
Sampling studies performed in the region 100 m from an established firing position to within 500 m of targets or heavily cratered areas have generally not found any measurable concentrations of energetic compounds (Ampleman et al. 2003a; Thiboutot et al. 2003, 2004; USACHPPM 2001, 2003, 2004, 2005; ME. Walsh et al. 2001). Thus, it is not recommended that sampling be conducted in this area. If it is decided that this area needs to be sampled, a square sampling unit sized 50 × 50 m or larger should be chosen if no surface anomalies are observed, and a 100-increment sample should be collected from the top 5 cm. Alternatively, if the sampling plan requests that a qualitative reconnaissance (visual inspection) be performed in this area, it is recommend that a MIS strategy with widely distributed collection points accompany this activity. When sampling large areas (> 10,000 m^2), global positioning systems could be used to help locate evenly spaced positions where individual increments will be collected. This is particularly important in adverse terrain with large changes in elevation and/or dense vegetation.

Impact areas

For areas with a defined target (or target debris), it is recommended to take a 100-increment sample from the top 5 cm of a 50- × 50-m square area centered on each target using the systematic-random design (Fig. 22). If rounds have undergone low-order detonation or chunks of energetic residues are visible and identified by field screening methods, mark a 10- × 10-m sampling unit or smaller sampling unit centered on each of these areas (Fig. 32). Then, qualified personnel should remove all visible pieces of MEC. In some cases, a UXO that cannot be moved may also be present in the sampling unit. This item and any other magnetic anomalies should be avoided. Once these tasks have been completed, a 30-increment sample from the top 5 cm of soil should be collected.



a. Pattern to collect two multi-increment samples in a single 30-m wide sampling unit.



b. Pattern to collect multi-increment samples in three 10-m-wide sampling units.

Figure 31. Strategies for collecting multi-increment samples in rectangular sampling units behind or in front of a firing line at an anti-tank range.

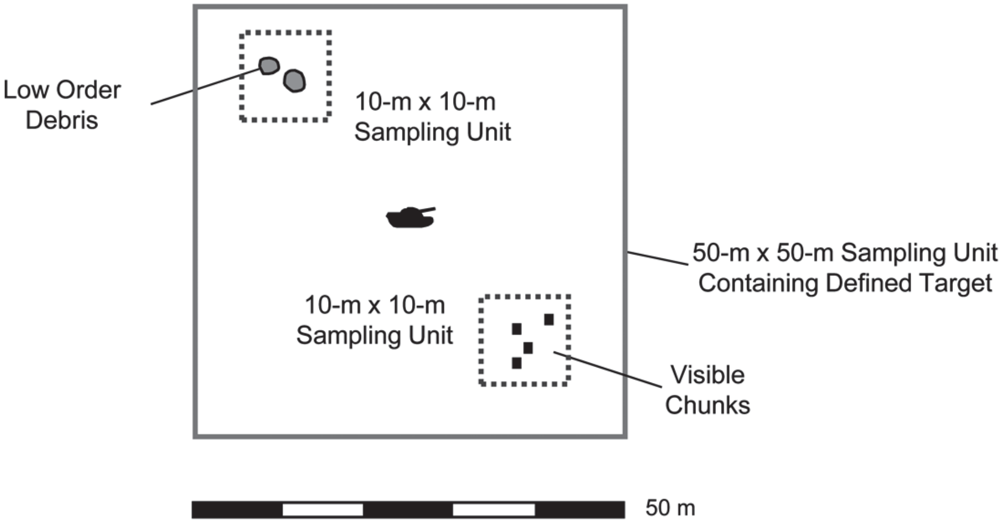


Figure 32. Sampling unit for collecting multi-increment sample surrounding a defined target at the impact area of an artillery range.

For heavily cratered areas, the area of concern should encompass at least 95% of the craters and a 20-m buffer zone (Fig. 33). These areas can be very large, depending on several factors such as placement of targets, training objectives, and age of the training facility. The recommended size of sampling units within this area is 50 × 50 m (or smaller) and a 100-increment sample from the top 5 cm should be collected in each unit. In the event that a low order detonation is found within a sampling unit, or chunks of energetic residues are visible, then a 10- × 10-m or smaller sampling unit can help identify areas where remediation may be necessary.

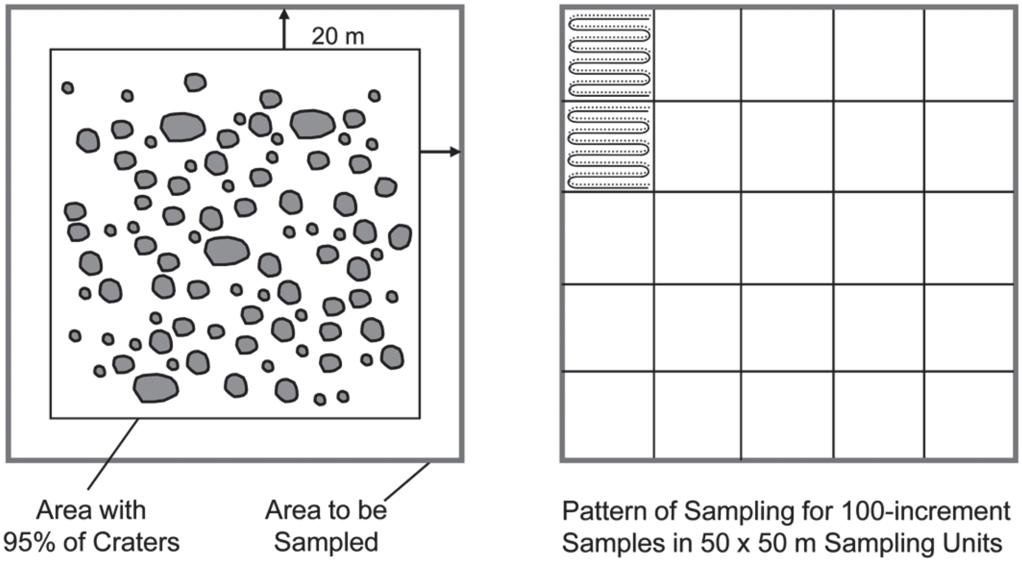


Figure 33. Example of sampling strategy at a crater field section of an artillery-mortar range impact area.

Profile sampling is recommended only in areas where low-order detonations have been found. As before, it is recommended to collect at least five profile samples, then combining the individual depth intervals (0–10 cm, 10–20 cm, and 20–30 cm) to form a single five-increment sample for each of these depths (Fig. 29). These samples establish the depth to which residues have been mixed into the soil profile, not to determine the average concentration for a subsurface layer over a large area. To achieve this second objective, 30–100 increment profile samples are needed, which clearly is unrealistic for profile samples. At the present, there are no established procedures to adequately characterize the subsurface. For depths below 30 cm, a surface geophysical survey may not be sensitive enough to detect UXOs, so down-hole clearance should be performed.

Firing point areas on artillery-mortar ranges

Most of the propellant residue deposition at mortar or artillery firing locations occurs in front of the gun tube. However, residue can accumulate on the surface at detectable levels up to 100 m downrange (Pennington et al. 2002, M.R. Walsh et al. 2006). Within firing areas where a variety of gun arrays are used, gradients in concentrations of energetic residues become obscured. However, they may exist downrange from the edge of the firing area. Within the firing area, sampling units of 50 × 50 m or smaller can be used for collecting 100 increments from the top 2.5 cm (M.E. Walsh et al. 2004, 2005). Therefore, to adequately characterize a firing point, which often covers several acres, multiple sampling areas would need to be defined and sampled.

At an established firing line or along the perimeter of the firing area, samples can be collected in rectangular sampling units to assess the downrange gradient parallel with the direction of fire. For each rectangular sampling unit, a 30-increment sample of the top 2.5 cm should be collected (Fig. 31b).

Sometimes, excess propellants are burned onsite at firing points after training exercises. These areas can be easily identified by the black soot on the ground created by the burned propellant residues. When a location that has been used to burn excess propellant is found, this area should be treated as a separate sampling unit. A 30-increment sample from the top 5 cm should be collected within a 10 × 10-m or smaller area centered on the location to quantify the concentration within this higher source zone. Sometimes, these areas are located within a firing point area and may not be distinguishable. If this is the case, concentrations of energetic compounds in replicate samples may vary substantially.

Profile sampling would only be recommended at a heavily used fixed firing point or directly beneath a location where propellant was burned on the ground surface. At a fixed firing point, profile sampling should be performed using our recommended strategy within 5 m of a mortar firing point and within 10 m of a howitzer firing point.

Bombing ranges

Surface sampling studies were conducted on two bombing ranges. At one range, samples were collected around a fixed target position, and at the other range, in a large (tens of hectares) crater field. Based on these preliminary findings the sampling designs and strategy recommendations for an artillery impact range would also apply here. High-resolution orthophotography, range maps, and LIDAR (Light Detection And Ranging) images can be evaluated as forensic evidence to locate former targets and craters. Using this evidence, sampling units can then be established within the range. Groundwater contamination by explosives may indicate the location of former targets (Bordeleau et al. 2007).

OB/OD ranges

To sample a range where open detonation or open burning is performed, divide it into 10 × 10-m sampling units and collect a 30-increment sample from the top 10 cm of soil from each (Fig. 34). Profile samples should also be collected in areas where the surface has been discolored or where demolition craters had been located in the past. Depth increments from at least five profile samples should be combined in a manner similar to that recommended for other ranges (Fig. 29). In this case, however, the sampling depth should extend below 4 m and perhaps continue to the groundwater table. For depths below 30 cm, down-hole clearance should be performed at 20-cm intervals.

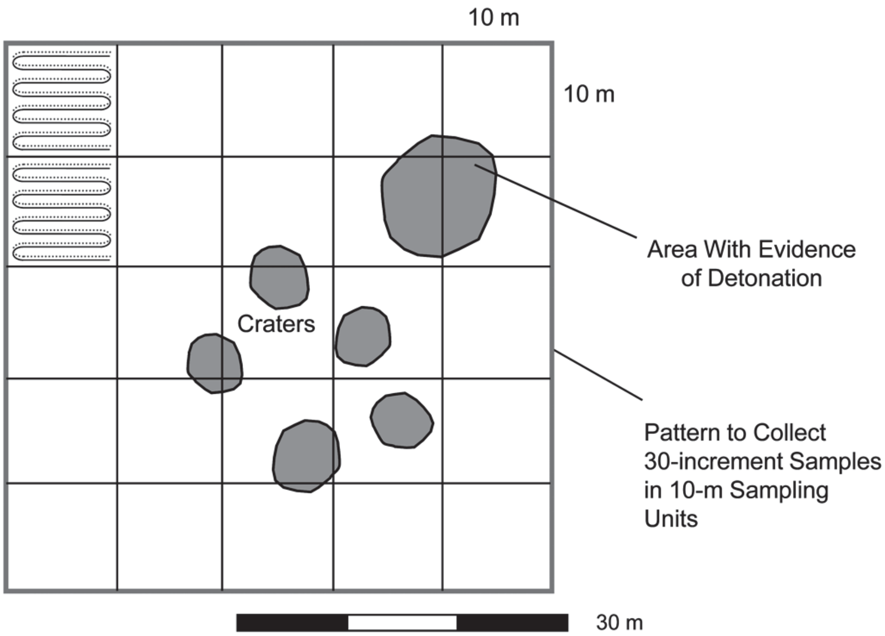


Figure 34. Recommended sampling units for collecting multi-increment samples at a detonation range.

Small arms ranges

Propellant and metal residues at firing points

Results from sampling experiments indicated that almost all of the propellant residues at small arms ranges were deposited within 10 m downrange of the firing line and within the top 5 cm of soil. For machine gun ranges or sport fire ranges, this distance might be extended to 20 m. To sample these ranges, 100 increment MI samples are collected from the firing line to a distance of 10 m (or 20 m for machine gun or sport fire ranges) from the firing line along the full width of the range. The sampling depth should be 5 cm. See Appendix A5 that describes an example site investigation of a small arms range using MI sampling techniques.

Metal residues at berm

Previous work has demonstrated that the entire berm face can be considered a sampling unit. Typically, the berm face is several meters high and several hundred meters long. To sample these ranges, 100 increment MI samples are collected from the berm face in a manner similar to Figure 31b. The sampling depth should be 5 cm.

Sample splitting in the field

Hewitt et al. (2009) evaluated if samples could be split in the field to minimize the mass of sample shipped to the laboratory without loss of sample integrity. Samples from five different ranges were placed in stainless steel bowls, the contents stirred with a stainless spoon to mix the contents as well as possible in the field, and divided into 5 or 7 equal splits. The entire < 2-mm fraction of each split was extracted and analyzed. There were 10 samples studied; within those samples, 20 split values were compared to the total analyte concentration. The median RSD value among replicate splits was about 40%; maximum values were in excess of 100%. Thus field splitting introduces unacceptable error and is not recommended. The entire sample should be shipped to the laboratory for processing and analysis. If regulators want to split samples for QA purposes, the samples should be split at the laboratory after the entire sample has been processed (Hewitt et al. 2009).

Laboratory sample processing for soils to be analyzed for energetic constituents

After soil samples are collected, they are generally sent to a commercial analytical laboratory to determine the concentrations of energetics 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 chromatography, usually using SW-846 Method 8330 (US EPA 1994). 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 has been to remove a small portion of the soil sample from the top of the jar. The remainder of the sample (often greater than 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 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 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. If the subsample contains the particle, the concentration 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 energetics determinations for replicate subsamples from 5 and 7 sample composites. 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, three replicate subsamples from 5-increment and 7-increment soil samples were obtained in a fashion similar to that used at commercial laboratories, i.e. a single scoop off the top. There were 37 possible comparisons, but in six cases, analysis of at least one of the subsamples failed to result in a measurable concentration above analytical detections limits. In the worst case, TNT concentrations among the three replicates varied from < 0.035 to 262 mg/kg. Among the 31 triplicates without non-detect results, the 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. This could be explained by settling of the energetic particles to the bottom of the jar during shipment and storage. Clearly, subsampling by taking a scoop off the top of a sample does not yield an accurate average concentration of the soil sample.

M.E. Walsh et al. (2002) studied the variability of subsampling after samples had been air dried and ground with a mortar and pestle as specified in SW846 Methods 8330 and 8095. 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 effectively homogenize the soil, even when large subsamples (50 g) are used. 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. Subsequent research by Walsh and co-workers found that grinding for 60 to 90 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 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. 2007, Hewitt et al. 2007a). In both cases, a 10-g subsample built from 30 increments of the ground material should be extracted with 20 mL of acetonitrile.

These changes to the way samples are collected and processed have been described in SW846 Method 8330B (US EPA 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. (2007) 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.

Analytical determination

Method 8330 (US EPA 1994) specifies using HPLC-UV (HPLC with an ultraviolet 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 (US EPA 1999) that employs the same sample-processing steps as Method 8330, but uses 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 CHPPM and laboratories working for them (Bishop et al. 2003). 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. However, the instrumentation is more expensive, and is thus a more costly approach than HPLC-UV. As a part of the study conducted by Roote (2010), a direct comparison of determinations for the same extracts from soil samples from two training ranges were analyzed by HPLC-UV and HPLC-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 provide similar detection for the target analytes. HPLC-UV and HPLC-MS-MS are both included within SW846 Method 8330B.

Overall recommendation for sampling and analysis

It is recommended that soil samples from training ranges be collected and analyzed according to the procedures specified in SW846 Method 8330B. MIS is a robust method for collecting representative samples from a sampling unit that yields reproducible and unbiased estimates for energetic compounds. Often replicates collected in this fashion will be normally distributed allowing the use of simple statistics to obtain estimates of the remaining uncertainty in mean concentration estimates for exposure areas.

The entire sample collected in the field should be shipped to the laboratory. The laboratory should air dry and process the entire sample before subsampling. The dried sample should be passed through a 2-mm sieve to remove over-sized particles and the material less than 2-mm should be mechanically ground using a ring mill to reduce particle sizes of soil and energetic compounds. If larger pieces of explosive or propellant are observed, they should be weighed and noted. Subsampling should be conducted on the ground material using the MIS approach as well to build a 10-g subsample that should be extracted with 20 mL of acetonitrile. The resulting extracts should be determined using the method outlined in SW846 Method 8330B, using either HPLC-UV or HPLC-MS-MS. If HPLC-UV is used, identification of target analytes must be confirmed using the second column as specified in the method.

Metals and other potential contaminants of concern

Other chemicals besides energetic compounds and lead are potentially present at military ranges. The only extensive study conducted looking for constituents other than energetic compounds is the work at MMR (Clausen 2005, Clausen et al. 2004). The MMR studies have included the sampling of soil, surface water, sediment, and groundwater. The areas investigated were artillery/mortar firing points and an impact range, anti-tank rocket firing points and targets, WWII era grenade courts, OB/OD areas, maneuver training areas, and contractor test ranges. In addition to the analysis for the common energetic compounds, an expanded list of metabolites of RDX such as hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) have been targeted (Table 21). Also, non-energetic constituents were looked for such as MTBE, EDB, dioxin, furans, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), herbicides, pesticides, dyes, metals, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOC). VOC and SVOC samples analyzed by GC/MS were intensely scrutinized for tentatively identified compounds (TICs) (Clausen et al. 2004).

Table 21. Target analyte list for MMR.

Target Analytes		
volatile organic compounds (VOCs)	polychlorinated biphenyls (PCBs)	nitrate/nitrite-nitrogen
methyl tert-butyl ether (MTBE)	dioxins	ammonia-nitrogen
ethylene dibromide (EDB)	furans	total organic carbon
semi-volatile organic compounds (SVOCs) including polyaromatic hydrocarbons (PAH)	polychlorinated naphthalenes (PCNs)	Dye Disperse Red 9 (methylaminoanthraquinone)
herbicides	white phosphorous	Dye Disperse Violet 1 (1.4- diaminodihydroanthraquinone)
pesticides	perchlorate	Yellow Dye (benzanthrone)
standard metals as well as antimony, molybdenum, and titanium	cyanide	Dye Vat Yellow 4 (dibenzochrysenedione)
radionuclides	phosphate-phosphorous	Dye Solvent Green 3 (1,4-di-o-toluidine-9,10-anthraquinone

Samples were also analyzed by GC/MS and lists of tentatively identified compounds (TICs) from VOC (volatile organic compounds) and SVOC determination (semi-volatile organic compounds) were intensely scrutinized (Clausen et al. 2004).

Compounds detected at MMR by media type and range usage varied (Table 22). An extensive discussion of the potential contaminants of concern for both soil and groundwater at MMR, as well as the materials fate-and-transport properties, are presented in Clausen et al. (2007).

Artillery and mortar firing positions

Artillery and mortar propellants contain a number of chemicals in addition to 2,4-DNT including di-n-butylphthalate, diphenylamine, and ethylcentralite, each ranging from 0 to 10 percent depending on the mixture specifications. Barium nitrate, potassium nitrate, potassium sulfate, and graphite, at 0–1.5 %, also are present in some propellant mixtures. Diphenylamine is present is some propellants and can be transformed to N-nitrosodiphenylamine in storage and perhaps during combustion (Stine 1991, Espinoza and Thornton 1994). At MMR 2,4-DNT and 2,6-DNT, diethyl phthalate, di-n-butyl phthalate and N-nitrosodiphenylamine were consistently detected in surface soil at the 37 artillery and mortar firing positions sampled (Clausen et al. 2007, Table 23). Although metals have been observed in surface soils, neither they nor any of the identified constituents listed above, other than the DNTs, were detected in the 20 monitoring wells installed at eight locations within the firing position or in downgradient locations.

Table 22. List of compounds detected in soils and groundwater at the MMR ranges.

Compound Class	Detected Constituent	Potential Contaminant of Concern	
		Surface Soil	Groundwater
Explosives	Yes	Yes	Yes (RDX, HMX, ADNT, DNTs)
Propellant energetics	Yes	Yes	No
VOCs	No	No	No
SVOCs	Yes (OB/OD & Firing Points)	Yes	No
Metals	Yes (SAR berms)	Yes	No
Radionuclides (DU)	No	No	No
Pesticide/Herbicides/PCBs	No	No	No
Dioxin/Furan	Yes (OB/OD)	Yes	No
PCN	Yes (Impact Area)	Yes	No
WP	Yes (limited)	Yes (anoxic environments)	No
Perchlorate	(Firing points, Impact Areas & OB/OD)	No	Yes
Dyes	Yes (Maneuver Areas & OB/OD)	No	No

DU = depleted uranium; SAR = small arms range

Artillery and mortar impact area

As previously discussed, energetic compounds are found in the impact area surface soils near targets and low-order detonations as well as sometimes in groundwater. Three additional constituents (perchlorate, PCNs, and metals) warrant a brief discussion.

Perchlorate is used in the spotting charge for artillery ordnance when a HE warhead is not utilized. Low-levels of perchlorate, < 50 µg/kg, have been detected in surface soils as well as in groundwater at MMR (Table 23). As discussed in Clausen et al. (2007) perchlorate is rapidly dissolved, does not sorb to soil components, is largely recalcitrant, and thus it is highly mobile. The high solubility and ease of dissolution prevents persistent build-up in soil, but can potentially produce groundwater contamination.

Some inert artillery and mortar projectiles also contain a wax filler, referred to as Halowax (Falandyz 1998), in the warhead as a weight replacement for HE. Halowax contains polychlorinated napthalene (PCN) compounds and these were detected in a number of surface soil samples from the Impact Area and contractor test ranges at MMR. The fate-and-transport properties of

Table 23. Analytes identified in various media at MMR by range activity.

Range Activity/Location	Media	Analytes Identified
Artillery and Mortar Firing Points	Soil	DNT, phthalates, N-nitrosodiphenylamine
	Groundwater	None
Artillery and Mortar Impact Area – Away from Targets	Soil	None
	Groundwater	None
Artillery and Mortar Impact Area – Near Targets	Soil	RDX, HMX, TNT, metals, perchlorate, PCNs
	Groundwater	RDX, HMX, perchlorate
Anti-Tank Rocket Range Firing Point	Soil	NG
	Groundwater	None
Anti-Tank Rocket Targets	Soil	RDX, TNT, metals
	Groundwater	None
OB/OD and EOD Demolition Areas	Soil	RDX, HMX, TNT, DNT, aDNT, perchlorate, metals, dioxins, furans
	Groundwater	RDX, HMX, TNT, aDNT, perchlorate,
Maneuver Training Areas	Soil	None
	Groundwater	None
Small Arms Ranges Firing Points	Soil	NG, 2,4-DNT
	Groundwater	None
Small Arms Range – Range Floor	Soil	None

	Groundwater	None
Small Arms Ranges Impact Berm	Soil	Metals (Cu, Pb, Sb, W, Zn)
	Groundwater	None
Note: In the case of metals identification refers to detection at a concentration above background values.		

PCNs indicate that they are not likely to be mobile and they were not detected in groundwater at MMR (Clausen et al. 2007).

Metals were also detected in all soil samples collected from the Impact Area at MMR (AMEC 2001a, b). However, it is difficult to determine whether the metals detected were from military activities, were anthropogenic metals derived from atmospheric fallout, or were from natural metals even when comparisons are possible with background samples. Most of the metals detected in the Impact Area were at concentration levels on par with background levels. In a few cases, elevated metals concentrations above background seemed to be the result of military activity. The metals falling into this category include aluminum, iron, molybdenum and possibly manganese and nickel. However, when the spatial distribution of the metal concentrations were mapped in relation to the target locations, there were no obvious patterns (AMEC 2001b).

Depleted uranium may have been used at a few military sites in the USA, but it has not been investigated and will not be discussed in this document.

Anti-tank rocket ranges

As discussed previously, NG is often found in surface soil at anti-tank firing points, sometimes at rather high concentrations. However, NG has not been detected in groundwater at MMR (Ogden 2000). Besides NG, no other compounds were observed in surface soil at the firing points other than metals, which were also observed at the target locations (Table 23). However, the metals concentrations in soil at the anti-tank range appear to be consistent with background levels (Ogden 2000).

OB/OD and EOD Detonation Areas

In addition to the energetic compounds previously noted at OB/OD sites, a wide variety of other constituents have been detected in surface soils at Demolition Area 1 at MMR. These constituents include low-levels of perchlorate, which were noted in the soil as well as groundwater (Table 23). Perchlorate is likely the result of burning of pyrotechnics, including fireworks. Other compounds identified in the surface soil include metals, dioxins, and furans. The dioxin and furans are presumably due to the burning of materials. Although metals were detected in groundwater, the concentrations were consistent with background levels and did not indicate the migration from surface soil. The dioxin and furans were not detected in groundwater.

Small arms ranges

As previously discussed, the energetic compounds NG and 2,4-DNT are often detected in surface soil at small arms range firing positions, and they were detected in soil at these ranges at MMR. Other than metals no other munitions-related constituents were detected in soils at small arms firing positions at MMR (Table 23). On the range floor, metal constituents such as antimony, lead, copper, tungsten, and zinc were slightly elevated and increased in concentration when approaching the berm face (Clausen et al. 2007). In contrast, at the berm face elevated concentrations of the metals antimony, copper lead, tungsten, and zinc have been observed (Clausen and Korte 2009) with concentrations in the 100s to 10,000s mg/kg.

Metals at other ranges

The casing materials for most artillery and mortar projectiles primarily consist of the metals iron and manganese, including copper and zinc in the rotating bands of artillery projectiles. The predominant metal in anti-tank rockets is aluminum. Metals have been observed in artillery and mortar impact areas and anti-tank rocket ranges near targets (Clausen et al. 2004). The observed concentrations were lower than the levels observed at small arms ranges.

Given the presence of elevated concentrations of metals at small arms ranges the focus of this section is on such ranges. A question exists on whether methodologies developed for energetics, Method 8330B, should be adopted and applied for metals constituents introduced to the environment as metal particulates. Similar to the energetic compounds, the metals are being deposited as solids so the same distributional issues applying to energetics may be relevant to the metals. Recently, research has been undertaken at CRREL to address this question.

MI Sampling Necessity

The first issue explored is the question of whether MIS is necessary when sampling for metals and, if so, how the sampling units should be configured. A study was undertaken where a small arms range berm was considered as a single sampling unit and sampled using a systematic random MIS design, a systematic random discrete sample design, a biased discrete sample design, and a biased large volume design (a portion of the berm is shown in Fig. 35). The sampling unit consisted of surface soils to a depth of 5 cm over an entire small arms berm face approximately 100 m long and 3 m high.

Data for seven discrete samples collected in a systematic random manner from the berm face shows elevated relative standard deviations (RSDs) for all metals with a low of 16% for iron to a high of 180% for copper (Table 24). Five metals (arsenic, chromium, molybdenum, nickel, and vanadium) were not detected at a detection limit of 15 mg/kg. Analyses of laboratory triplicates from sample B8 (B8-A, B8-B, and B8-C; Table 25) show that error (variability) attributable to

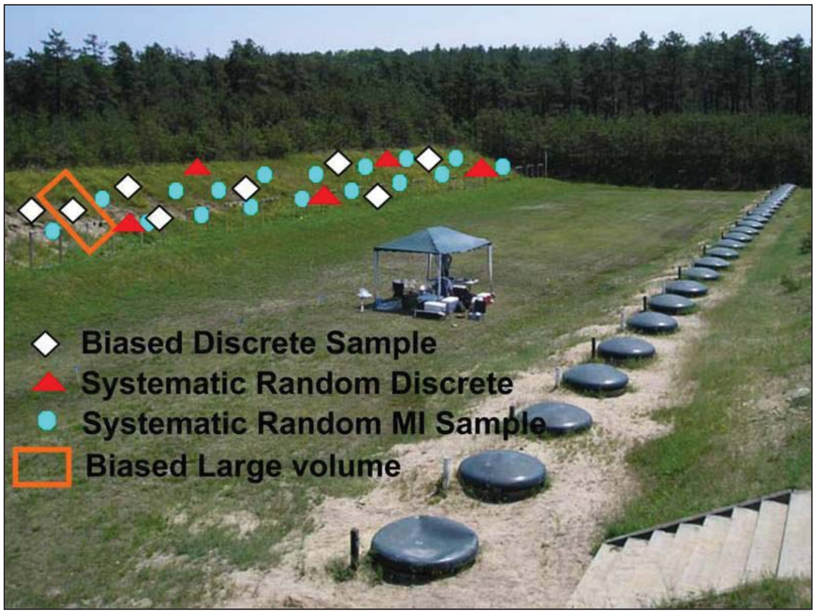


Figure 35. Schematic showing comparison of different sampling designs for a portion of a small arms range berm. Blue dots represent approximate locations where increments were collected to build MI sample. White and red symbols represent approximate locations of discrete samples.

Table 24. Systematic random discrete sample metal results (mg/kg) for samples B8-A through B14.

	Concentration (mg/kg)									
Element	B8-A	B9	B10	B11	B12	B13	B14	Mean (mg/kg)	Std. Dev. (mg/kg)	% RSD
Al	4,323	4,202	5,390	4,983	4,339	3,605	5,938	4,676	801	17
Ca	11,905	23,876	26,968	22,218	20,708	20,835	21,972	21,214	4,629	22
Cu	84	257	430	2316	29	24	109	462	830	180
Fe	5,691	5,630	6,811	6,646	5,628	4,866	7,774	6,116	999	16
Mg	602	793	962	974	733	723	1,065	839	162	19
Mn	41	38	54	54	39	42	90	51	19	37
Pb	277	345	590	549	264	720	370	445	175	39
Sb	16.4	<15	16.0	16.2	<15	16.6	<15	NA	NA	NA
Se	<15	<15	17.78	15.10	<15	<15	<15	NA	NA	NA
W	429	625	1,054	1,374	292	142	777	666	439	66
Zn	24.8	41.7	46.6	61.0	<15	16.5	35.4	37.7	15.9	42

NA – not applicable

Table 25. Precision of laboratory replicates of sample B8-A.

Element	Concentration (mg/kg)			Mean (mg/kg)	Std. Dev. (mg/kg)	% RSD
	B8-A	B8-B	B8-C			
Al	4,323	4,483	4,011	4,272	240	5.6
Ca	11,905	12,431	11,427	11,921	502	4.2
Cu	84	60	61	69	14	19.8
Fe	5,691	5,608	5,066	5,455	339	6.2
Mg	602	717	547	622	87	13.9
Mn	41	43	35	40	4.3	10.9
Pb	277	303	248	276	28	10.0
Sb	16.4	<15	<15	NA	NA	NA
Se	<15	<15	<15	NA	NA	NA
W	429	392	359	393	35	9.0
Zn	24.8	26.6	22.9	24.8	1.9	7.5
NA – not applicable						

laboratory subsampling, processing, and instrument variability is generally significantly less that the variability between the individual discrete field samples (Table 24). The variability between laboratory replicates in Table 25 reflects the combined error due to aliquot selection, sample preparation, and analytical (instrument) error (i.e. TEL + AE in eqn 2 of Appendix B, this document), and reveals the general magnitude of field sampling variability (TEF) in the total error.

Table 26 compares the mean results for the biased discrete, systematic random discrete, biased large volume, and multi-increment samples. The RSDs among replicates are presented in Table 27. In general, the mean concentrations of the discrete metal results are consistently higher than the MI sample results. Further, the RSDs for the biased discrete samples are lower than systematic random discrete samples. However, the RSDs for the MI samples are even lower than the discrete samples and little difference was evident between the 50- and 100-increment MIS.

Table 26. Comparison of mean metal concentrations for the different sampling methods.

Sample Type	Discrete		Large-volume Discrete	Multi-increment		
Sample Design	Systematic Random	Biased	Biased	Biased	Systematic Random	Systematic Random
Element	Concentration (mg/kg)					
Increments per sample	1	1	1	15	100	50
Al	4676	7147	4025	4377	4368	4473

As	<15	<15	<15	<15	<15	<15
Ca	21,214	23,385	12,969	20,166	13,230	13,150
Cr	<15	184	74	75	78	76
Cu	462	1,555	569	984	643	709
Fe	6,116	10,646	6,686	7,423	7,392	7,233
Mg	839	1134	691	822	720	720
Mn	51	79	43	51	46	46
Mo	<15	<15	<15	<15	<15	<15
Ni	<15	<15	<15	<15	<15	<15
Pb	445	1,182	952	945	339	357
Sb	16.3	31.4	25.4	23.3	15.8	15.2
Se	16.4	17.2	<15	<15	<15	<15
V	<15	16.2	<15	<15	<15	<15
W	666	1,479	581	1,247	787	783
Zn	38	135	32	41	32	43
Number of samples	8	8	1	1	2	2

Table 27. Comparison of relative standard deviations (RSD) or relative percent difference (RPD) for the different sampling methods.

Sample Type	Discrete		Multi-increment	
Approach	Systematic Random	Biased	Systematic Random	Systematic Random
Element	% RSD	% RSD	% RPD	% RPD
Increments per sample	1	1	100	50
Al	17	9	4	6
Ca	22	2	13	9
Cr	--	7	8	4
Cu	180	71	7	38
Fe	16	4	3	4
Mg	19	5	9	9
Mn	37	8	9	10
Pb	39	25	4	5
Sb	2.0	13.3	2	2
Se	11.5	7.6	NA	NA
W	66	5	14	13
Zn	42	89	21	0.3

Number of samples	8	8	2	2
NA = not applicable, RPD = relative percent difference				

The discrete systematic random and biased discrete are sample designs routinely used for sampling in the environmental industry. As these results indicate, a discrete sample yields results that are not reproducible and thus not representative of site conditions. In contrast, the systematic random MI sampling approach yielded results with significantly lower RPDs. Consequently, this sampling design will yield more reproducible results. Therefore, it is clear that MIS field sampling is necessary to reduce the sampling error to an acceptable level so that reproducible samples can be collected.

Sampling unit configuration

Small arms ranges consist of a firing point, range floor, berm face, and the back berm area (Fig. 36). A study of the metal distribution on several small arms ranges found differences between different areas (Clausen and Korte 2009, Clausen et al. 2007). Therefore, if the intent is to characterize the entire range, then at a minimum the sampling unit should consist of the firing point, range floor, and berm face, and in general, these should have different sampling units (ITRC 2003). In terms of the berm face, the sampling unit selected is dependent on the data quality objectives and should be determined during project planning. It is entirely feasible to treat the entire berm face as a single sampling unit. On the other hand, if information is desired from a more focused area it is possible to break the berm face up into several individual sampling units. Differences between metal concentrations at bullet pockets versus non-bullet pocket areas, upper, middle, and lower berm face locations, and between the middle of the berm face and lateral areas were evident (Clausen and Korte 2009, Clausen et al. 2007). There is no right or wrong way in configuring the sampling unit. Rather, the configuration is dependent on the study needs.

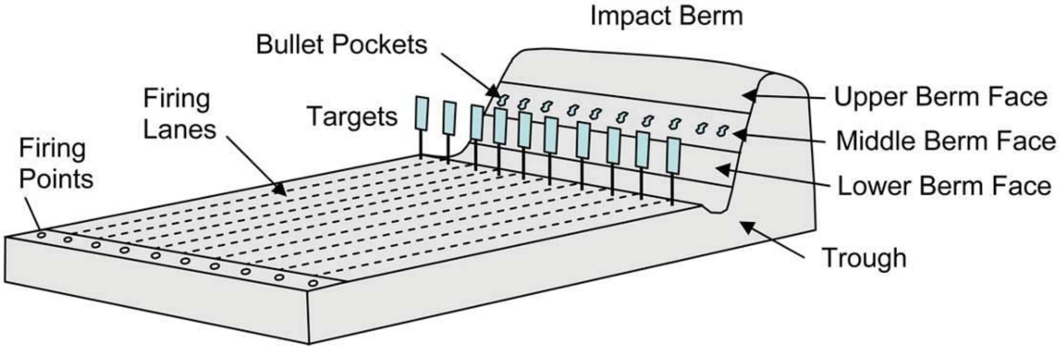


Figure 36. Typical configuration of a small arms range.

Sieving

Method 8330B for analysis of samples for energetic compounds calls for sieving of the soil sample to separate the sample into > 2 mm and < 2 mm size fractions. Analysis is performed on the < 2-mm fraction whereas the > 2mm fraction is not typically analyzed, since this material is not considered to be soil. At present, it is not known if the 2-mm size cutoff is appropriate for metals or if a different sieve size cutoff is appropriate. In the absence of data, the present EPA Method 3050B use of a #10 sieve, yielding a < 2-mm sample seems appropriate.

Previous work established differences in metal concentrations between < 2-mm and > 2-mm soil fractions collected from small arms ranges (Clausen et al. 2007). This was primarily due to the presence of intact bullets, bullet fragments, and metallic debris in the oversize fraction. In the case of a small arms range where tungsten projectiles were used, tungsten mass in the >2-mm sample varied significantly from sample to sample and represented anywhere between 20 to 80% of the total tungsten metal mass. So, in some cases, the < 2-mm fraction contained the bulk of the tungsten mass and in other samples the bulk of the tungsten was in the > 2 mm size fraction. However, the issue of whether the metal mass in the > 2-mm size fraction is environmentally important remains a research question.

Sample Pulverization

The next question that arises is whether the compositional heterogeneity of metal concentrations in soil is sufficiently variable to warrant pulverization of the soil through grinding. Results presented by Clausen et al. (2010a) for a sandy soil suggest if a RSD of 30% or less is acceptable then grinding may not be necessary. However, other preliminary data for samples from other ranges suggests grinding may be warranted. One of the important factors in whether particle size reduction is necessary in the preparation of samples containing particulate metals is the concentration of the metal of interest in the material being sampled. Because Fundamental Error and %RSD are inversely proportional to concentration, error tends to become very large when working with samples of low or moderate concentration, such as when approaching a regulatory decision limit or action level of a few hundred mg/kg or less (e.g. residential soil screening levels for lead). Achieving acceptable precision at such concentrations for analytical subsamples having mass of only a few grams requires particle size reduction (see Appendix B, Fundamental Error, Example C). An overarching determination on the necessity of grinding samples for metals analysis is not warranted at this time. However, if low metal concentrations are anticipated or levels close to a regulatory value then sample pulverization should be considered. It should be noted that an optimum grinding interval and identification of appropriate grinding equipment has not be completed. Another issue to consider when using metallic grinding apparatus is the possibility of the introduction of metal into the sample from the grinding equipment. This is discussed for one study in Appendix A5. Preliminary studies suggest this may be an important issue to consider if chromium, iron, manganese, or tungsten are constituents of interest. Research into this topic is ongoing and includes the degree of grinding necessary, comparison of different grinders, and grinding cross-contamination issues.

If trap and skeet small arms ranges are being sampled PAHs are possible contaminant of concern. Preliminary studies suggest this type of training activity results in particulate PAH deposition. Sample pulverization may be necessary for samples containing PAHs. However, the state of research on the optimum procedures for this class of compounds is less advanced than the research with metals. Given, the physical similarity between PAHs and propellant compounds it is suggested that the procedures developed for sample preparation of soils containing propellants be followed for samples containing PAHs.

Sample Digestion

The present EPA Method 3050B calls for digestion of 1 to 2 g of sample. Studies are ongoing at CRREL to assess whether this digestion mass is appropriate or whether a larger digestion mass is necessary for samples from military ranges. As discussed earlier, in the case of energetics, a larger extracted soil mass yielded a more representative and reproducible result.

Another research question related to sample digestion is whether different digestate solutions are warranted to improve metals recoveries. Method 3050B requires use of nitric acid to recovery the environmentally available metals and hydrogen peroxide to remove organics. Clausen et al. (2010c) found the addition of phosphoric acid to the Method 3050B digestate protocol was necessary to keep tungsten in solution. Low tungsten recoveries were observed when using only nitric acid. Consequently, digestion following Method 3050B was compared against digestion using stronger acids for the metals of interest at small arms range (Clausen and Korte 2009). Although, metal recovery increased with increasing digestion solution aggressiveness, the difference in results was not significant to change the interpretation of results. Therefore, Clausen and Korte (2009) recommended no changes to EPA Method 3050B for digestion. Only in the case where tungsten is expected and information is desired on the concentration and distribution should Method 3050B be altered by adding phosphoric acid to the digestate to improve tungsten recoveries. Additional work may be necessary for antimony and thallium due to poor recoveries using the existing methodology for Method 3050B.

Other Constituents

In regards to other constituents such as PCNs, SVOCs, dioxins, furans observed at some types of military ranges, the question remains whether MI sampling and sample processing protocols developed for energetic compounds need modification. MIS sampling and the sample processing in Method 8330B have been successfully used at an OB/OD site at Hill AFB for analysis of perchlorate (see Appendix A2). At present, research studies for other constituents have not been undertaken so the existing sampling and sample preparation procedures should be followed.

A case study in which MIS sampling was used to evaluate deposition of perchlorate by a Multiple Launch Rocket System is given in Appendix A4.

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Appendix A1. Case Study: Incremental Sampling of Sediments Contaminated with White Phosphorus

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Background Information

Eagle River Flats (ERF) is an Alaskan salt marsh that serves as a staging area for migrating waterfowl. The marsh, located in the upper Cook Inlet of Fort Richardson (Fig. A1-1), has also served as a U.S. Army artillery impact range into which howitzer, mortar, and rocket rounds have been fired since around 1950. In the early 1980s, high numbers of waterfowl carcasses were found at ERF by a U.S. Army biologist. Subsequent studies in the 1980s documented the extent of the mortality but did not reveal the cause. In 1989, use of ERF as an impact area was suspended due to the suspicion that residues from high explosives were the cause of the waterfowl deaths.

Figure A1-1. Aerial view of the 865-ha Eagle River Flats, with the Knik Arm of Cook Inlet in the background.

In 1990, we sampled ERF for high explosives (HE) residues, specifically RDX and TNT. Because dabbling ducks were the principal victims, we surmised that the poison resided as solid discrete particles in the sediments of shallow ponds where the ducks forage for food. Also, only a small portion of ducks that fed at ERF was poisoned, indicating that the poison was sporadically distributed. These conditions required that we collect many more samples than were collected by previous investigators. Our sampling did not reveal the presence of RDX or TNT; however, one sediment sample that gave off a vapor cloud and garlic-like odor indicated the presence of another munition that had been fired into ERF: white phosphorus (WP) (Racine et al. 1992). WP is used as an obscurant and was fired into ERF from mortars and howitzers.

During the initial investigations at ERF to determine the spatial extent of the contamination, surface sediment samples were collected at approximately 25-m intervals along transects through ponds in the marsh where ducks were observed to actively feed. This spacing was based on the radius of the area estimated to contain most of the fallout from the kinds of smoke projectiles that were commonly fired into ERF during training exercises (Shinn et al. 1985). At each sample location, several increments of surface sediment were collected from within a 1-m diameter area. Most of the samples from these transects contained low or undetectable concentrations of WP. Along transects where WP was detected frequently, concentrations varied widely, with relatively few samples having high concentrations (over 100 μg/g). When samples were taken at close intervals (1 to 5 m) around sample points with high WP concentrations, we again observed extreme heterogeneity, with non-detectable concentrations within a few meters of high concentration samples. This pattern of contamination led us to believe that most of the WP was located at the points of impact of WP projectiles.

Microscopic examination of high concentration samples revealed the presence of solid WP particles, most of which were 0.5 to 2 mm long, with some up to 6 mm long and weighing over 100 mg. These particles are much larger than the fine-grained silts and clays (95% finer than 0.02 mm) that make up the salt marsh sediment and could easily be selected by dabbling ducks searching for food or grit. The very low concentrations (less then 1 μg/g) detected in most samples were probably due to colloidal, dissolved, or molecular WP sorbed to sediment surfaces.

During the early 1990s, we determined the distribution and persistence of WP at ERF. These studies were followed by investigations of potential remediation and monitoring methods. Because WP readily oxidizes to phosphates when exposed to air, the sampling in 1998 was to use temporary pond draining by pumping because it was the most effective and least destructive remedial option. The plan was to pump water from contaminated ponds each summer until WP concentrations fell below 1 μg/g.

Incremental Sampling Methodology Development

The remediation objective was to remove WP from the surface sediments. The objective of sediment sampling was to estimate the mass of WP in the surface sediment of the ponds remediated by drying. If the WP had been evenly dispersed as fine particles over each pond, a set of discrete samples may have been sufficient to estimate the mass of WP over the treated area. However, the nature and distribution of the WP was much more complex.

Results from close-interval sampling at ERF and observations of impact points of 81-mm WP mortars at an upland site (Walsh and Collins 1993) indicated that the bulk of the WP available to feeding waterfowl (particles) was confined to very small areas (1 to 2 m diameter) punctuating much larger areas with little or no contamination. Subsequent studies at ERF indicated that these high concentration areas corresponded to the point of impact of WP projectiles, and that WP was not detectable or barely detectable outside of a 2- to 3-m radius.

Dabbling ducks were successful at finding WP, so we designed two sampling strategies that mimic feeding waterfowl. Dabbling ducks take numerous sediment increments as they feed in a pond. The poisoned ducks were those that dabbled within the very small diameter areas that contained milligram-size white phosphorus particles.

Grid multi-increment sampling method

The first method (grid multi-increment sampling) was developed in 1996 (Walsh et al. 1997) as an alternative to using penned sentinel ducks to determine if sufficient WP mass to poison waterfowl was present in a defined area. In this method, grid multi-increment samples are formed by combining sediment aliquots collected using an Oakfield corer (2 cm diameter) to a depth of 10 cm at the nodes of a 1.82-m-square grid. Spacing of the increments is designed to detect 2-m diameter hotspots (Gilbert 1987). A quadrat is used to maintain relatively precise subsample spacing (Fig. A1-2). Sampling unit grid size is generally 5.46 x 20 m, yielding 48 increments per multi-increment sample that combine to a final mass of 1–4 kg. A 200-g subsample of this field sample is later analyzed for white phosphorus. Based on the method detection limit for the analytical method (0.0002 µg/g), a single sediment increment with a white phosphorus concentration of 0.01 µg/g will yield a detectable white phosphorus concentration in the multi-increment sample. Lethal white phosphorus particles are generally associated with much higher concentrations (1 µg/g). Placement of the sampling unit grids is tailored to the area to be sampled. To sample small ponds, sampling unit grids are placed to maximize coverage of open water; to sample marsh areas that contains many small pools, sampling unit grids are placed at intervals (e.g., 30-m) (Fig. A1-3). When WP was detected within the marsh, then individual pools within and near the positive grids were sampled.

Figure A1-2. Sampling for white phosphorus in sediment using a 1.82-m square quadrat.

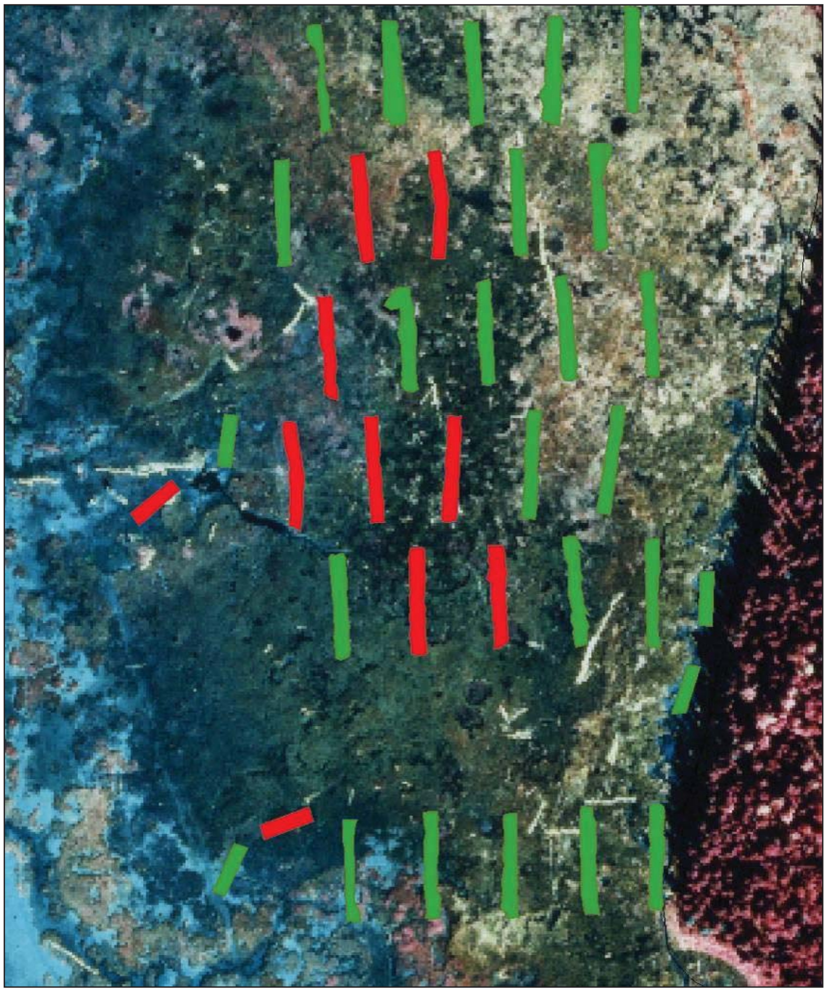

Figure A1-3. Rectangular incremental sampling areas spaced at 30 m intervals along transects across a bulrush marsh. Areas colored in red designate the presence of mg or greater quantities of white phosphorus.

Sieved multi-increment sampling method

The sieved multi-increment method is used in water-covered areas to sample large areas (entire ponds) or to intensively sample smaller areas by taking increments at least every half meter and placing them in a sieve bucket (0.59-mm mesh) (Fig. A1-4). The sediment is stirred and sieved underwater to remove the fine grain sediment. The mesh is sufficiently fine to also retain the ecologically relevant white phosphorus particles that, if present, would pose significant hazard to waterfowl.

Laboratory analysis of sediments for white phosphorus residues

All samples were stored at 4°C in the dark and were tightly sealed to prevent loss of moisture. Samples were analyzed using procedures described in EPA SW-846 Method 7580 [White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography] (US EPA 1995). Each whole sediment multi-increment sample (1–4 kg) is thoroughly mixed by stirring. The wet sample is spread to a thickness of 1 cm, and a minimum of 30 small aliquots are taken to form a 200-g subsample. Sufficient water is added to form a slurry. Sieved multi-increment samples were not subsampled. Instead, the entire sample was transferred to a sufficiently large glass jar and enough water added to cover the sample.

The presence of white phosphorus is determined using solid-phase micro-extraction and gas chromatography. If white phosphorus was detected, the white phosphorus concentration is estimated by extracting the white phosphorus from the sample with solvent (isooctane) and analyzing the extract by gas chromatography (nitrogen–phosphorus detector). The gas chromatograph was calibrated daily using freshly prepared standards in the range of 1.8 to 88 µg/L. A linear calibration model was used to calculate the WP concentrations in the sediment extracts. If needed, extracts were diluted with isooctane to be within the calibration range.

a.) In a channel (May 2006)

b.) Close-up of sieve bucket (August 2006)

Figure A1-4. Collecting sieved multi-increment samples.

Two Examples of Results

Table A1-1 shows the results for replicate samples obtained and processed using the grid multi-increment sampling method for five, 5.46 × 40-m sampling areas that stretched across a shallow pond (Walsh et al. 2000). Based on a sample mass of 4 kg and the lowest value established for the sampling area at the 100-m interval (18 µg/kg), a 1.6 mg particle of white phosphorus could have been present if only one increment among the 92 was from a hot spot. Using this logic one could make the assumption that at least one hot spot (location where a phosphorus round had incompletely detonated) was present in this pond, and particles large enough to cause water fowl mortality existed. This logic was used as a criterion to select which ponds needed to be drained with the aid of a semi-autonomous pump system (Walsh M.R. et al. 2000, 2006). Once drained, the surface sediments desaturated, which caused WP to sublime, a very effective and non-invasive remediation strategy for this hazardous compound in a fragile wetlands.

This particular pond was drained for several consecutive years and the sampling area with the highest average concentrations of white phosphorus was monitored by sampling annually (Table A1-2). After only a couple of drying seasons, the concentrations of white phosphorus in the top 10 cm of the sediments declined and remained below lethal levels for dabbling ducks.

Table A1-1. White phosphorus concentrations (µg/kg) in replicate samples along a transect bisecting a pond at 50 m intervals. Samples obtained in June, 1997.

Replicate	0 m*	50 m	100 m	150 m	200 m
1	< 0.2	0.32	18	2.7	0.37
2	< 0.2	0.49	61	3.5	0.42
3	< 0.2	0.61	69	4.0	0.47
4	< 0.2	0.70	73	4.1	0.67
5	< 0.2	0.76	85	4.9	0.83

* 92 increments per sample

Table A1-2. White phosphorus concentrations found in grid multi-increment samples collected from 100-m sampling area in the middle of a pond. Data are shown for all field replicates.

Date	WP Conc. (µg/kg)
4 June 1997	18, 61, 69, 73, 85
4 September 1997	5.4, 6.3, 6.3, 6.5, 10
22 August 1998	5.4, 6.1, 7.4, 8.4, 44
15 September 1999	1.1, 2.1
16 August 2000	0.42, 0.67
11 September 2001	<0.2, 0.2
15 September 2003	<0.2, <0.2
25 August 2008	<0.2, <0.2
16 September 2009	<0.2, <0.2

Table A1-3 shows the results of sieved multi-increment samples collected within 5 m segments of water-filled channels. This sampling activity identified several locations where hot spots existed. Because the water in these channels could not be easily drained and the sediment dried, geotextile overlain with coarse gravel was used to cover these hot spots (Fig. A1-5). This barrier was added in the winter when this wetland was ice covered, using GPS coordinates

Table A1-3. Mass of white phosphorus in sieved incremental samples from drainage ditches. Samples were collected to define the horizontal distribution of white phosphorus in the channels.

Channel Segment #	Distance (m)	WP Mass (mg)
Segment 1	0 to 5	not detected
	5 to 10	0.0001
	10 to 15	not detected
	15 to 20	not detected
	20 to 25	not detected
	25 to 30*	122
	30 to 35	0.009
	35 to 40	0.005
	40 to 45	not detected
	45 to 50	not detected
	50 to 55	0.07
	55 to 59	not detected
	59 to 63	not detected
Segment 3	0 to 5	not detected
	5 to 10	not detected
	10 to 15	not detected
	15 to 20	0.00006
	20 to 24.25*	11.5
	24.25 to 28.5	1.9
Segment 5	0 to 5	2.3
	5 to 10	0.5
	10 to 15*	3.2
	15 to 20	not detected
	20 to 25	0.005
	25 to 30	not detected
	30 to 35	not detected
	35 to 40	not detected
	40 to 46.8	not detected
Segment 7W	0 to 5	not detected
	5 to 10	1.0
	10 to 15	1.8
	15 to 20	8.6
	20 to 25	168
	25 to 28.75	0.53
	28.75 to 32.5	0.002

* WP ordnance scrap was found within these intervals.

Figure. A1-5 Mounds of gravel covering hot spots of white phosphorus particles found in drainage channels and small ponds.

obtained when the ponds were ice-free. Multi-increment samples were collected over the next couple of years in a 0.5-m annulus around the perimeter of the gravel mounds to check that no ≥1 mg particles of white phosphorus particles were present (Bigl and Collins 2009). If white phosphorus was detected, more gravel was added to the mound, or the covered area was spread out, or both.

Summary

Today, firing of white phosphorus rounds into wetlands is prohibited by the U.S. and many foreign militaries (U.S. Army 2009). Members of the Fort Richardson Integrated Training Area Management team are writing an Environmental Impact Statement (EIS) to evaluate the return to year-round training activities, with a concerted effort towards avoiding areas containing white phosphorus. Independent of the EIS, the impact range has been decreased in size to avoid the disturbance of sediments in areas where white phosphorus is likely to remain buried deep within the sediments. To offset this constraint, the ERF program helped to establish new target arrays outside the treatment areas. Equally important, this area is no longer an imminent risk to migrating ducks and shorebirds; less than 10 white-phosphorus-related fatalities were reported for 2008, compared with about 1,000 in 1996 (CH2M Hill 1998). MIS was instrumental in mapping the distribution of WP and helping to remediate the hazard to waterfowl while continuing military training. Without this technique, it would have taken a couple more decades to reach these current levels of training sustainability and ecological remediation.

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Appendix A2. Case Study: Implementation of Method 8330B for Explosives Residue Characterization at the Utah Test and Training Range

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Introduction

The Utah Test and Training Range (UTTR) Thermal Treatment Unit is located approximately 50 miles west of Salt Lake City, UT. It is operated for the Ogden Air Logistics Center, Hill Air Force Base, Utah, by the 75 Civil Engineer Group, Explosive Ordnance Disposal Division. The facility covers an area of approximately 1500 acres and is permitted by the State of Utah through a State issued RCRA Part B Permit. Figure A2-1 shows the site layout with detonation and burn pads indicated. Treatment of most DoD owned reactive wastes or munitions are permitted at the facility, but the primary workload involves treatment of large rocket motors from 10,000 to 84,000 pounds net explosive weight (NEW) including C4 and D5 Trident, Minuteman, and Sprint solid rocket motors. Permitted operational limits are 320,000 lbs NEW for OB and 149,000 lbs NEW for OD for any single event. The Title V air permit limits OD operations to 84,000 lbs NEW/day and 6,552,000 pounds NEW/year. Items are detonated or burned above ground on specified pads that are constructed and maintained to facilitate the disposal operations.

Although the facility has operated for over 30 years, annual soil sampling has only been required since the RCRA Permit was issued in 2003. Prior to 2003, discrete sampling of soil occurred in 1989, 1991, and 2002. Discrete sampling was again conducted in 2004. The data from the soil sampling events are intended to support both the Human Health and Ecological Risk Assessments for the facility; however the large area and long and varied history of the site made characterization for these purposes challenging. Method 8330B techniques using *MULTI INCREMENT*® sample collection and pre-analysis sample preparation were first implemented in 2005 and have been used at the site through the 2009 sampling event.

Sampling Methodology

To characterize the site for surface contamination, the area was gridded into 100 m square grids as shown in Figure A2-1. Each grid cell is sampled by taking 100 incremental samples

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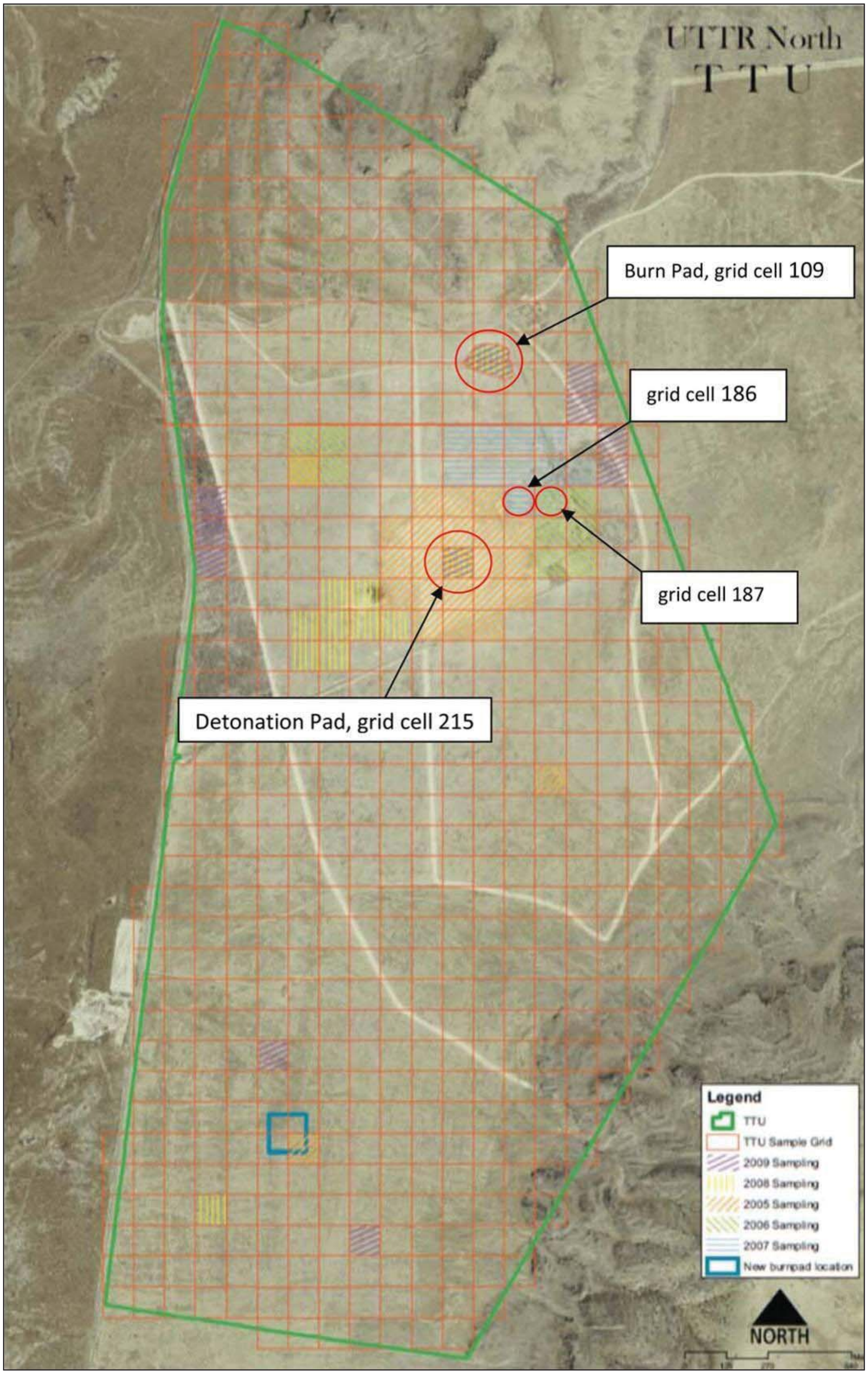


Figure A2-1. Utah Test and Training Range Thermal Treatment Unit with sampling grid and operational areas indicated.

in a systematic random sub-grid with an approximate spacing of 10 m between samples. Individual increments of approximately 20 grams are collected from the top 1-2 cm of the soil surface with pre-cleaned soil scoops and consolidated into a clean polyethylene bag. Samples are collected by teams of two people. Grids are pre-marked with stakes prior to the sampling event and each stake has an area location map attached to it so sampling teams do not need GIS support in the field. Samples collected in areas with excessive gravel are passed through a #10 sieve in the field to avoid collection of material greater than 2.0 mm.

Collected samples are shipped to the Hill Air Force Base Analytical Laboratory for pre-analysis sample preparation in accordance with Method 8330B. Air-dried samples are sieved through a #10 sieve and ground in a puck mill in 500-g batches. Sample grinding time has been reduced from five minutes (five, one minute grinds) to one minute to reduce metal (primarily chromium) contamination from the grinder. Chromium was detected in the 2005 samples. Ground samples are re-combined in their collection bags and then laid out on aluminum foil where 10-g samples are prepared from approximately 30 incremental scoops for analysis as specified in Method 8330B. Samples for metals (Methods 6010B, 6020 and 7471) and perchlorate (Method 6860) are prepared in a similar manner. Grinding and preparation of samples taken in 2005 and 2006 were conducted by the US Army Cold Regions Research and Engineering Laboratory (CRREL).

Results

Data from the 2005 to 2008 sampling events indicate that the 8330B methodology provides repeatable data applicable to human health and ecological risk assessments at the UTTR Thermal Treatment Unit (TTU). Analysis of soil samples has shown that the primary contaminants of concern at the site are perchlorate, HMX, and RDX. Distributions of these three contaminants at the TTU are shown in Figures A2-2, -3, and -4. All concentrations were below the site specific risk based concentrations of 713 mg/kg for perchlorate, 30,700 mg/kg for HMX, and 16 mg/kg for RDX.

Field triplicates or duplicates were collected and analyzed for selected areas each year. Some areas including grid cell 215, the center of the detonation pad, and grid cell 109, the primary burn pad, were sampled each year to evaluate year-to-year repeatability. These results are presented in Table A2-1. Within year repeatability was generally good with percent relative standard deviation (%RSD) values ranging from 3.7 for HMX on the detonation pad to 36.9 for perchlorate on the burn pad. Relative percent difference (RPD) values for field duplicates ranged from 0.0 for perchlorate duplicates on the burn pad in 2006 to 55.6 for perchlorate duplicates in grid cell 186, an area of infrequent mixed use between the detonation and burn pads, in 2007.

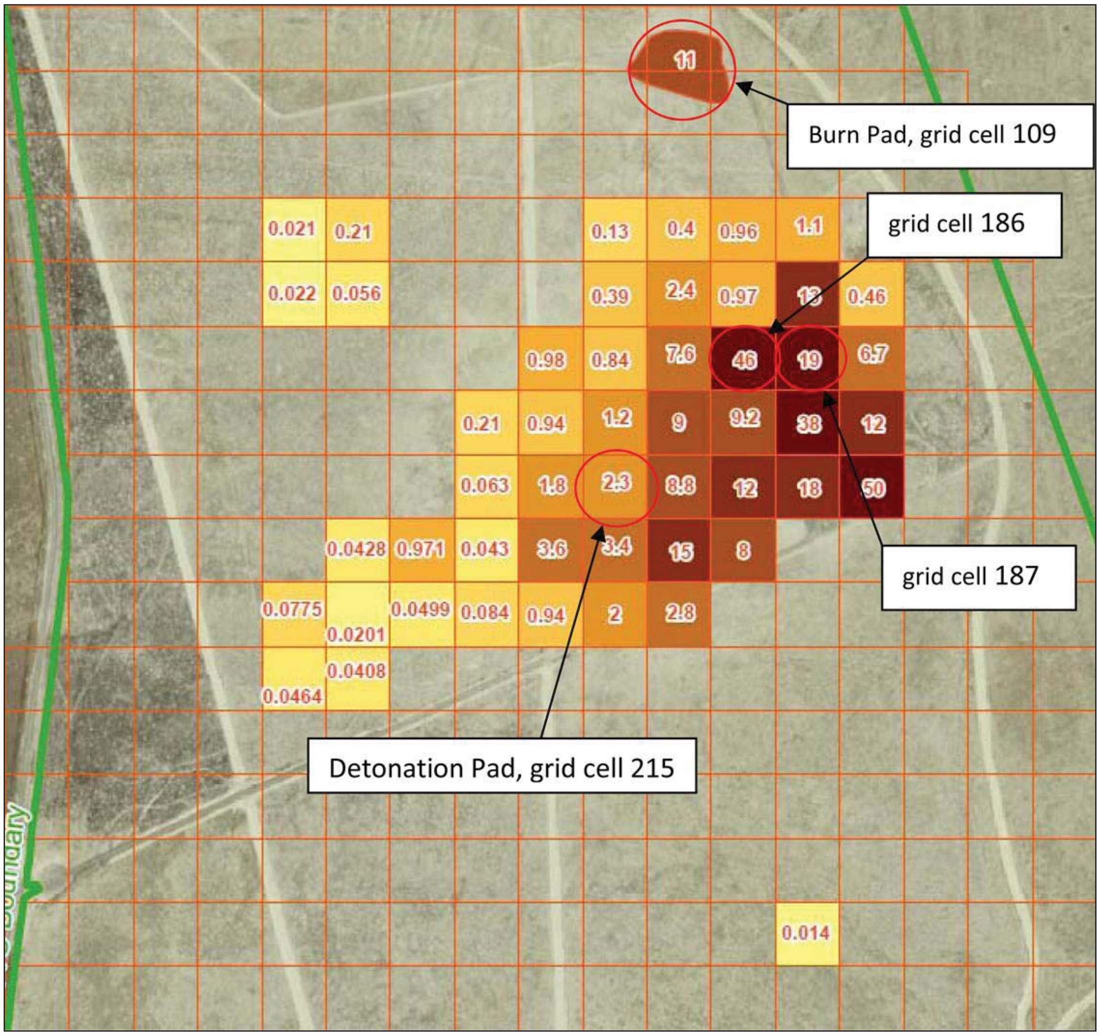


Figure A2-2. Perchlorate distribution at the TTU. Concentrations are given in mg/kg. For areas with repeated samples, values shown are for the first year's sampling event (with the exception of the Burn Pad, which was sampled as one unit for the first time in 2006).

Year to year repeatability (see Table A2-1) was also generally very good, given the fact that the area is an active disposal facility. Apparent exceptions include the jump in perchlorate concentrations on the detonation pad (grid cell 215) from 2005 to 2006 and a decrease in perchlorate concentrations on the burn pad (grid cell 109) from 2007 to 2008. If discrete samples had been collected, these variations would likely have been explained as inherent site variability, however because of the good within year repeatability that had been observed, further explanations were sought regarding site operations that may have contributed to these observed differences. It was discovered that a deflagration event had likely contaminated the detonation pad with perchlorate

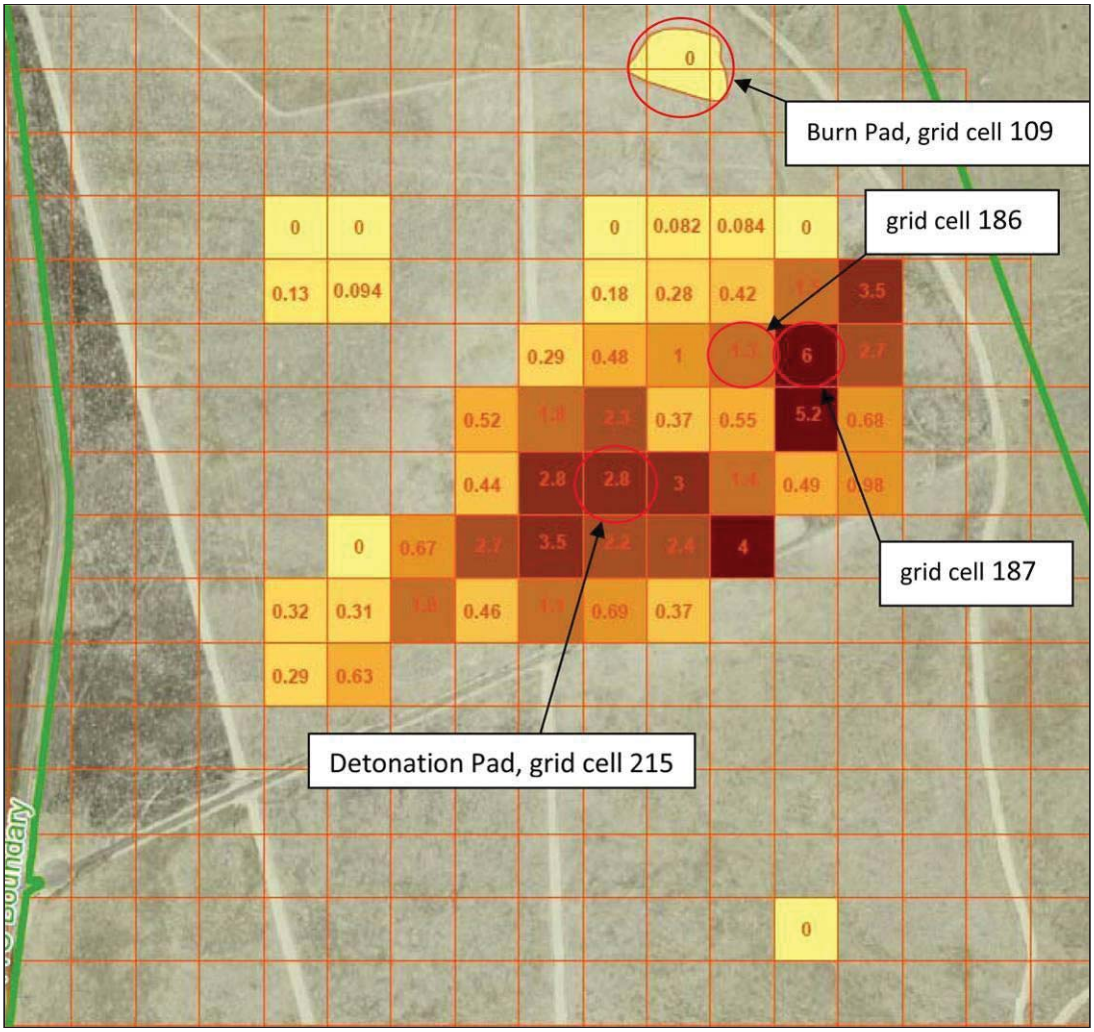


Figure A2-3. HMX distribution at the TTU. Concentrations are given in mg/kg. For areas with repeated samples, values shown are for the first year's sampling event (with the exception of the Burn Pad, which was sampled as one unit for the first time in 2006).

in 2006 causing elevated levels of perchlorate in 2006 and 2007 and the decrease in perchlorate concentrations on the burn pad is likely the result of decreased open burn operations during 2008. Repeated samples from grid cell 187 in 2006 and 2007 also showed fairly good agreement for all three contaminants.

In addition to field duplicates and year-to-year replication, laboratory replicates were also analyzed for HMX by independent laboratories, Severn Trent Laboratory (Denver) and CRREL, in 2005 and 2006. The samples were both prepared at CRREL prior to analysis. As indicated in Table A2-1, results from the two labs were found to be in agreement in both 2005 and 2006.

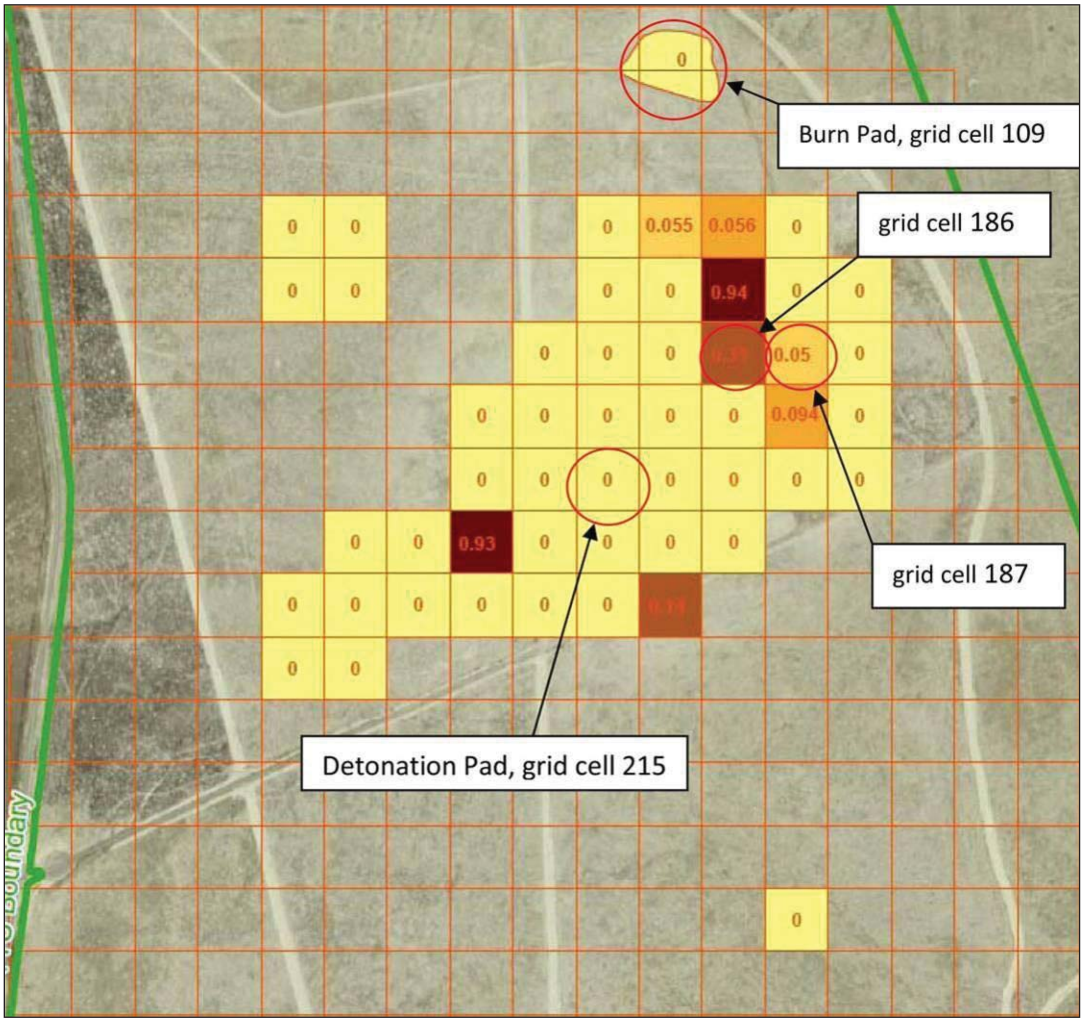


Figure A2-4. RDX distribution at the TTU. Concentrations are given in mg/kg. For areas with repeated samples, values shown are for the first year's sampling event (with the exception of the Burn Pad, which was sampled as one unit for the first time in 2006).

Sampling Costs

Annual costs of TTU soil sampling are shown in Table A2-2. These costs include preparation of sampling and analysis plans, sample collection, sample preparation (grinding), chemical analysis, and reporting. The elevated annual costs for 2008 were partially because dioxin/furan analysis was conducted on some samples. Average annual costs from 2005 to 2009 were \$0.28/m^2 if all duplicate and triplicate field samples are counted separately giving a total of 95 samples that have been collected and analyzed. If costs are calculated based on the total area that has been characterized, 78 grid cells or 780,000 m^2, then the average cost is \$0.34/m^2. This cost would be a conservative estimate for a similar program with the same level of quality assurance/quality control sampling.

Table A2-1. Results of replicate sampling at the UTTR. All Results are reported in mg/kg. Percent relative standard deviation (%RSD) is reported for triplicate samples and relative percent difference (RPD) is reported for duplicates.

Cell# [Area]	Contaminant of Concern	Repetition	Year			
			2005	2006	2007	2008
215 [det pad]	Perchlorate	1	2.3	68	61	9.4
		2	2.2	62	52	6.9
		3	2.1	86		
		%RSD or {RPD}	**4.5**	**17.3**	**{15.9}**	**{30.7}**
	HMX*	1	3.9 [4.3]	2.2 [2.3]	2.1	1.6
		2	3.4 [4.0]	2.2 [2.2]	1.6	1.5
		3	3.7 [4.2]	2.8 [2.9]		
		%RSD or {RPD}	**6.9 [3.7]**	**14.4 [15.3]**	**{27.0}**	**{6.5}**
109 [burn pad] †	Perchlorate	1	16	11	22	1.57
		2	16	11		1.5
		3	29			
		%RSD or {RPD}	**36.9**	**{0.0}**		**{4.6}**
186 [NE of det pad]	Perchlorate	1			46	
		2			26	
		RPD			**55.6**	
	HMX	1			1.3	
		2			0.79	
		RPD			**48.8**	
	RDX	1			0.31	
		2			0.40	
		RPD			**25.4**	
187 [NE of det pad]	perchlorate	1		19	28	
	HMX	1		6.0	6.0	
	RDX	1		0.11	0.05	

* In 2005 and 2006, split samples were analyzed for HMX by Severn Trent Laboratory, Denver (shown without brackets) and the US Army Cold Regions Research and Engineering Laboratory (in square brackets).

†The primary burn pad was divided into quarters for the 2005 sampling. 2005 values are for triplicate sampling of one of these quarters. Values for subsequent years represent the entire pad area.

Table A2-2. Costs of TTU soil sampling from 2005 to 2009.

Year	Cost*	# of cells**	cost/cell	cost/1000 m^2	cost/m^2
2005	$104,000	39	$2,667	$267	$0.27
2006	$43,000	15	$2,867	$287	$0.29
2007	$34,000	15	$2,267	$227	$0.23
2008	$46,000	13	$3,538	$354	$0.35
2009	$36,000	13	$2,769	$277	$0.28
Total/Average	$263,000	95	$2,822	$282	$0.28
Cost/cell excluding QA/QC samples (78 cells):			$3,372	$337	$0.34

* Total cost including plan preparation, sample collection, sample preparations, analytical, and reporting

**Total number of 100-m x100-m grid cells sampled including QA/QC samples

Conclusion

Method 8330B has been an effective method for soil characterization at the Utah Test and Training Range Thermal Treatment Unit. Discrete sampling used previously did not provide sufficient data to delineate the spatial extent of site contamination or to be effectively used in human health and ecological risk assessments. The MIS data has successfully delineated the areas of contamination and shown that exposure levels are far below the risk based levels of concern for the site. Method 8330B will continue to be used at the site to ensure for safe and sustainable operations.

Appendix A3. Case Study: Arnhem Antitank Rocket Range, Canadian Force Base Valcartier, Quebec

THOMAS JENKINS, BOWHEAD, RICHARD MARTEL, UNIVERSITY OF QUEBEC

The following is a summary of a series of studies conducted at the Arnhem antitank rocket range, located 35 km north of Quebec City at Canadian Force Base Valcartier, Canada. This range has been used continuously for target practice with antitank rockets since the 1970s. Site investigations have been conducted from May 1995 through 2006; they include soil sampling to assess the concentrations of energetic compounds in near surface soils and installation of ground water wells and groundwater sampling activities. Methods for sample collection, sample processing, and analysis employed at Arnhem have evolved as knowledge of the nature of energetic contamination has improved.

Site description

The Arnhem training range is situated on the north side of an east-west valley bounded by two mountains. The northern part of the range contains several target vehicles located on a steep, sloping boulder field. Several additional target vehicles are located at the base of the slope on a sand terrace. A hydrostratigraphic section of the region where the Arnhem range is located is shown in Figure A3-1. A regional aquifer underlies the site. While surface runoff flows to the west, the deeper ground water flows eastward.

Because of the difficulty in accessing the steep sloping region of the range related to UXO, all characterization has been conducted in the flat sand terrace area. In this area there are several target vehicles located approximately 100 m from the firing line where shoulder-fired rockets are launched (Fig. A3-2). The depth to ground water within this flat portion of the range varies from about 26 to 34 m below ground surface. An annual average of 135 cm of precipitation falls at Arnhem. However, 40 % of the precipitation (54 cm) recharges the aquifer.

Description of the munition fired at Arnhem

The munition fired at Arnhem for most of the lifetime of this range has been the M72 66-mm Light Anti-Armor Weapon (LAW rocket). The warhead of this weapon contains 300 g of octol, which is composed of 70/30 HMX/TNT melt cast explosive. The propellant charge is 163 g of M7 double-base propellant, containing 54.6% nitrocellulose (NC), 35.5% nitroglycerin (NG), 7.8% potassium perchlorate, 0.9 % ethyl centralite, and 1.2% carbon black (Fig. A3-3). There is

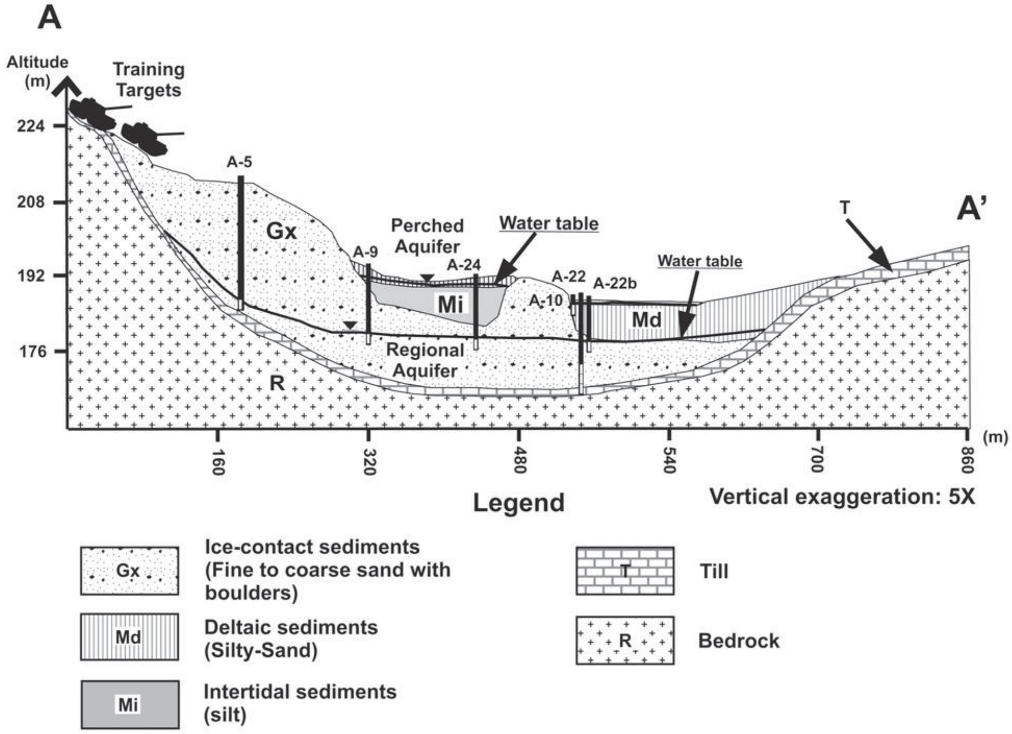


Figure A3-1. Hydrostratigraphic section along a north to south profile within the Arnhem Range area (from Martel et al. 2009).

Figure A3-2. View of Arnhem range targets from firing line position during soil sampling.

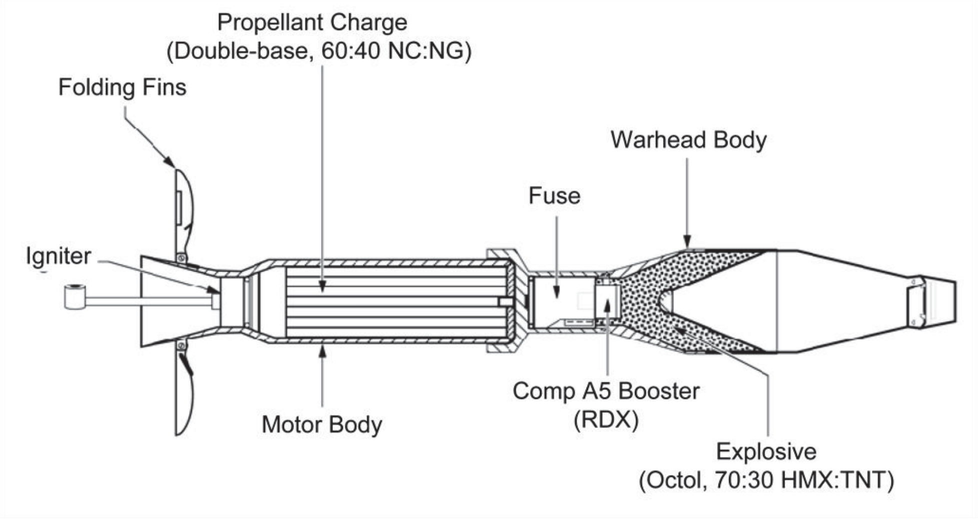


Figure A3-3. M72 Light Anti-Armor Weapon, also known as the LAW rocket.

a small amount of RDX in the booster of this weapon, and C4 block (91% RDX) has been used to detonate unexploded rockets found on the surface at Arnhem. The mass of residues of energetic compounds remaining in the impact area is due largely to ruptured M-72 rockets that did not detonate, but were ripped open by side impacts with the ground surface, spreading their undetonated explosive charge over the surface.

Soil characterization for energetic contamination

A preliminary characterization of explosives contamination in soil at Arnhem impact area was conducted in 1995 by Thiboutot et al. (1998). Analysis of these initial soil samples indicated that HMX was the major explosive contaminant present, with lesser amounts of RDX and TNT. Profile samples indicated that greater than 90% of the explosives residue was present in the top 15 cm of soil.

In 1996, a more extensive surface soil characterization was conducted in the impact area (Jenkins et al. 1997, 1999). Composite soil samples were collected within a series of grids located around one target vehicle and between it and a second target vehicle (Fig. A3-4). Once again, HMX was the predominant residue detected, with the concentrations of TNT only about 1/600th that of HMX. RDX was generally below the detection limit of about 1 mg/kg. The two mono amino transformation products of TNT (4ADNT, 2ADNT) were also detected in a number of these samples.

HMX concentrations in the surface soil (0–2.5 cm) near the targets were generally greater than several hundred mg/kg with a maximum value of 1900 mg/kg. A concentration gradient was present with concentrations dropping to less than 100 mg/kg at a distance of 20 m or so from the target. Several samples were collected from the 0–7.5 cm and 7.5–15 cm depths. For these samples the HMX concentration was about 9 times higher in the 0–7.5 cm depth interval than in the

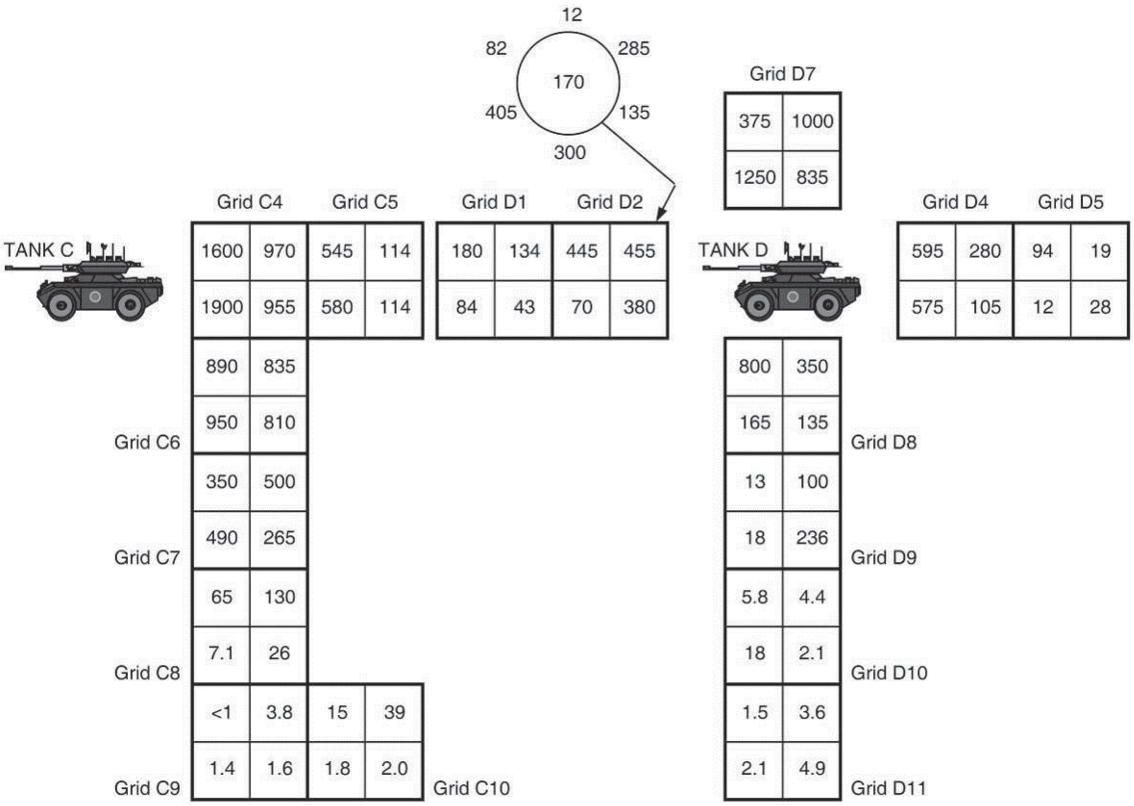


Figure A3-4.HMX concentrations (mg/kg) from commercial laboratory analysis using Method 8330. Larger grids are 6 x 6 m, subgrid size is 3 x 3 m (From Jenkins et al. 1997).

7.5–15 cm depth interval. From these results and some assumptions about unsampled areas, Martel et al. (2009) estimated the mass of HMX and TNT at the impact area to be about 16 kg and 0.1 kg, respectively. One well water sample was analyzed in 1996 and concentrations of HMX, RDX, and TNT were 295, 46 and 3.1 µg/L, respectively.

A decision was made, based on the high HMX concentrations present, its apparent mobility in groundwater, and an interest in evaluating a remediation technology, to remove the top several cm of soil from the impact area and treat it off-site to destroy the energetic residues present. This was done in 1997 using a biopile (Dubois et al. 1999). Martel et al. (2009) estimates that 85% of the HMX present at that time was removed. No characterization of the firing point area was conducted and the soil in that area of the range was not removed or treated.

After the soil removal, M-72 shoulder-fired rockets continued to be used from 1997 to 2003. In 2003, the site was again characterized for both the impact area and, for the first time, the firing point portion of the range (Jenkins et al. 2004). *MULTI-INCREMENT* samples (MIS) were taken from 10 × 10-m grids from the firing line to the center target vehicle, from segmented halos within the impact area, and from line samples along the firing line to a distance of 25 meters behind the firing line (Fig. A3-5). These MIS were collected from the 0 to 2.5 cm depth.

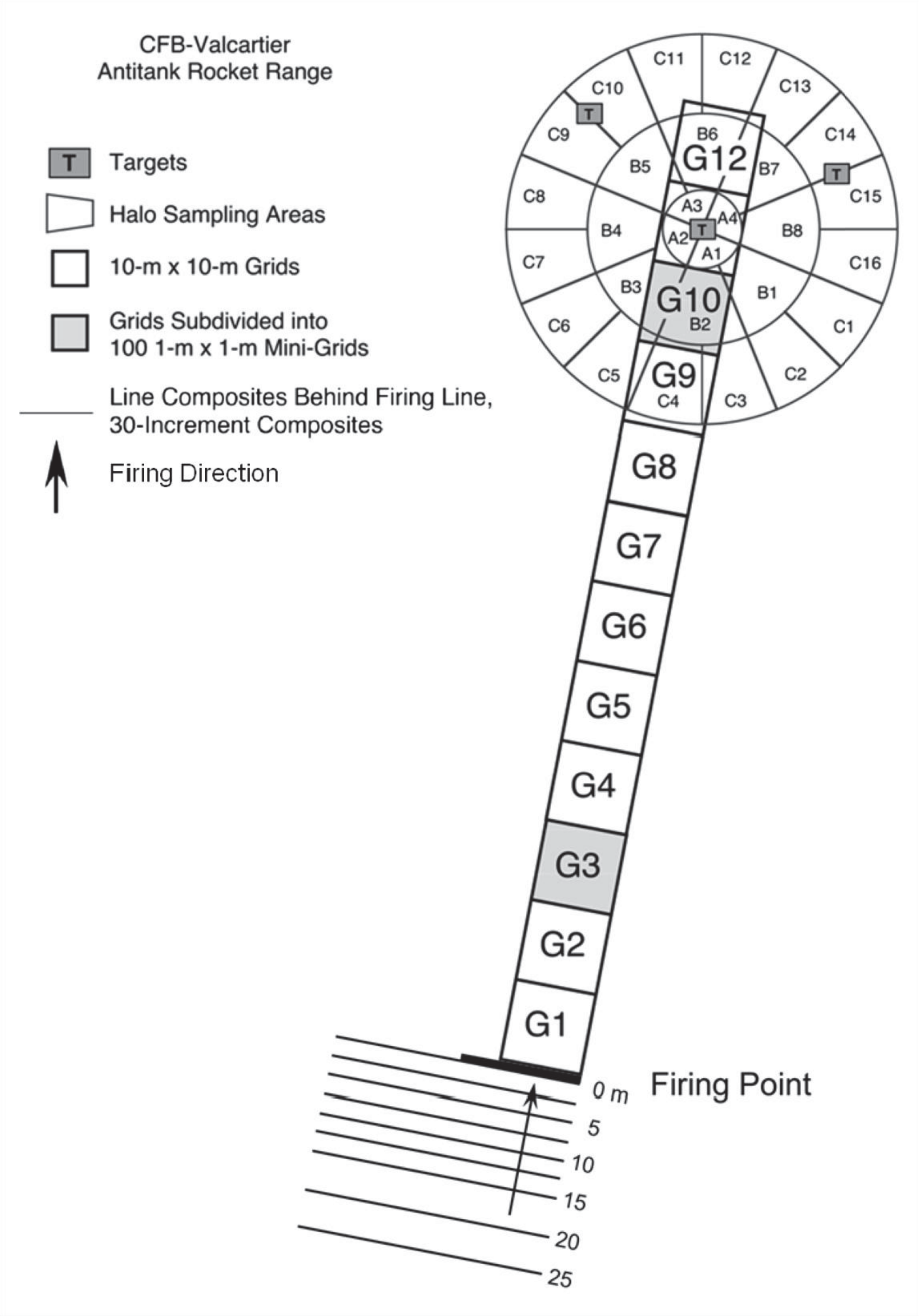


Figure A3-5. Twelve 10-m × 10-m grids located in a direct line from the firing point to and beyond the center target and halo sampling areas around target. Also shown are the positions of lines where composite samples were collected behind the firing line (Jenkins et al. 2004).

The following seven target analytes (in decreasing order of concentration) were detected in the segmented halo samples from the impact area, HMX, NG, TNT, RDX, 4ADNT, 2ADNT, and 2,4-DNT. NG had not been previously determined and it is thought to originate from residual propellant present in the motor body when the rockets detonate, or more likely rupture without detonation. Plots of the HMX and NG concentrations in the impact area in 2003 are shown in Figures A3-6 and A3-7.

Overall the TNT concentrations were only 1/84th of the HMX concentrations. A depth profile sample was collected within grid A1, near the target vehicle. Concentrations of HMX were 1030 mg/kg in the 0–2.5 cm depth interval, 17.1 mg/kg from 2.5–5.0 cm, and 1.9 mg/kg from 5–10 cm. TNT concentrations in these three depth interval samples were 0.94, 0.17, and 0.05 mg/kg, respectively. RDX concentrations were likewise 0.94, 0.06, and 1.2 mg/kg.

In two of the 10 × 10-m grids, one near the firing point (Fig. A3-5, G3) and the other near the target vehicle (G10), 100 discrete samples were also collected to characterize the short-range variability in analyte concentrations. In G3, NG was the energetic compound with the highest concentration, and individual values ranged from 0.02 to 3.37 mg/kg. In G10, HMX was the energetic compound present at highest concentration with values for discrete samples ranging

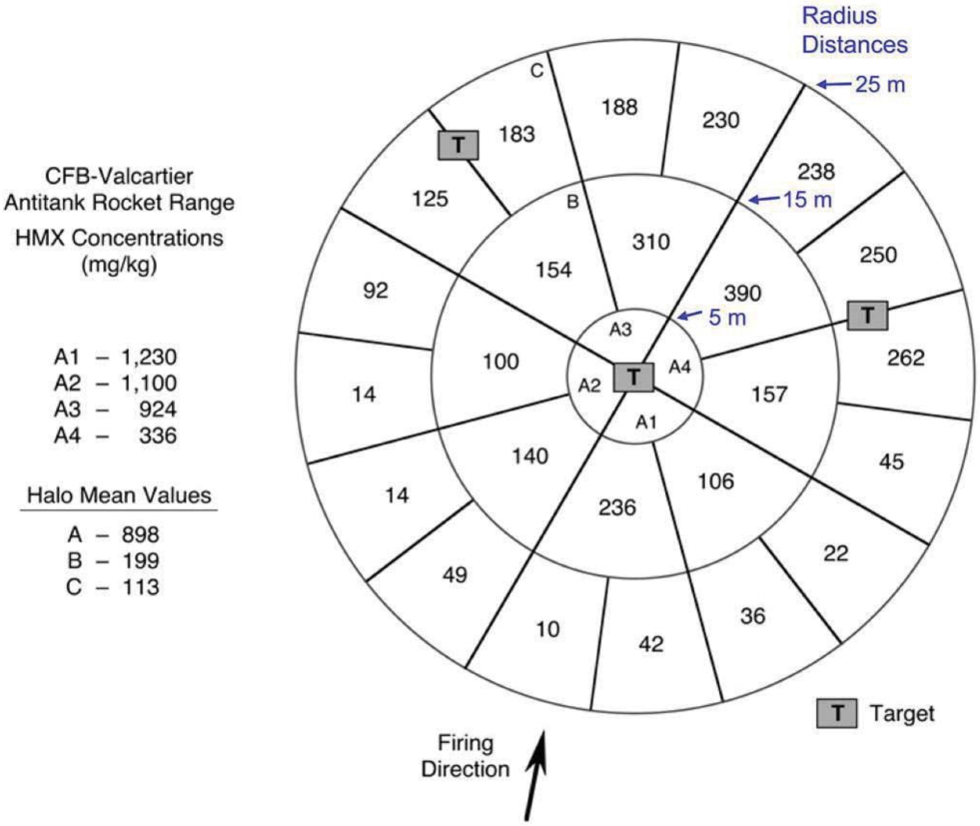


Figure A3-6. Concentration of HMX relative to sample position around targets (Jenkins et al. 2004).

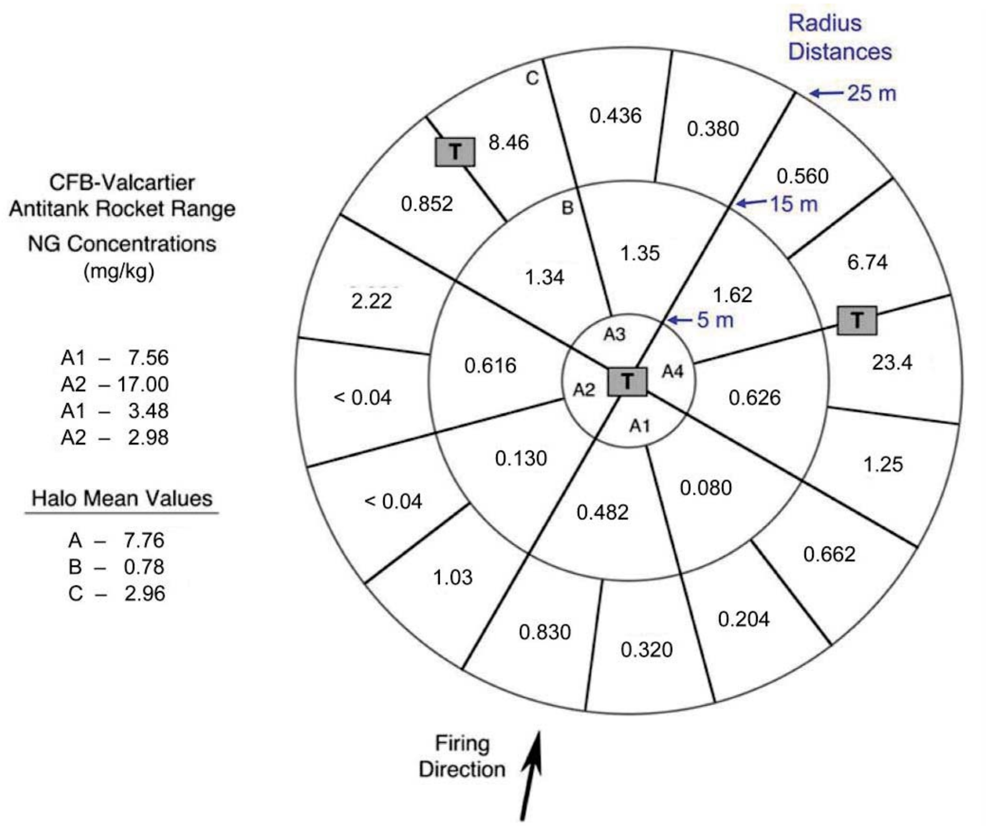


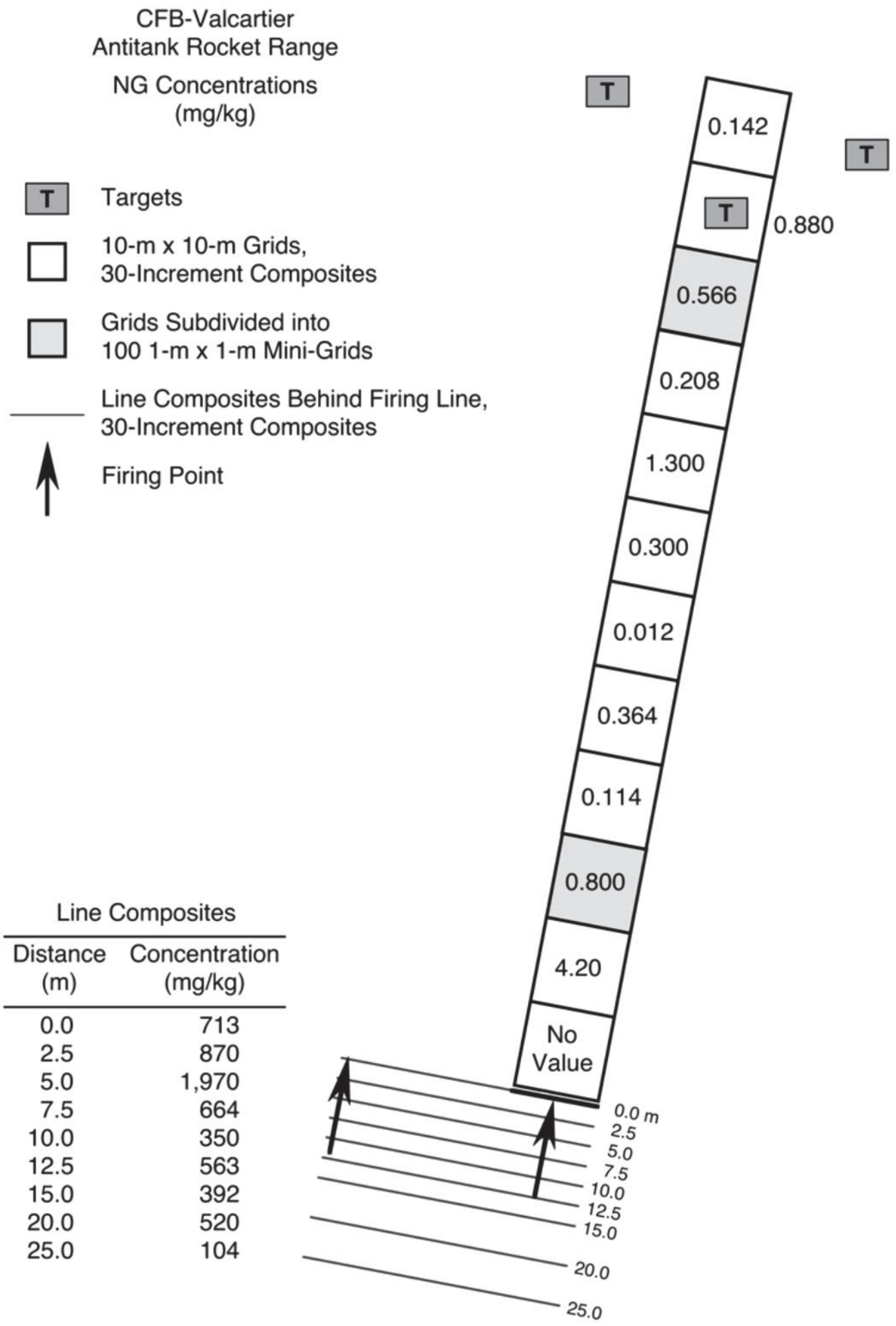
Figure A3-7. Concentration of NG relative to sample position around targets (Jenkins et al. 2004).

from 8.0 to 1920 mg/kg. These results confirm the futility of trying to estimate a mean concentration for an exposure area using a few discrete samples.

Concentrations of NG behind the firing line in the line composite samples were found to exceed those between the firing line and the target by several orders of magnitude (Fig. A3-8). The NG concentration 5 m behind the firing line was 1970 mg/kg dropping to 104 mg/kg at a distance of 25 m behind the firing line. Martel et al. (2009) estimated a mass of NG present on the Arnhem range at 63 kg in 2003.

Ground water sampling

Ground water in the regional aquifer is characterized by low electrical conductivity (about 33 µS cm-1), a high dissolved oxygen concentration (11.6 mg/L) and a pH of about 5.4. A series of ground water wells were established around the Arnhem range within the regional aquifer and were sampled in 1995, 1998, 1999, 2000, and 2005 (Table A3-1). HMX was detected in every sampling campaign; concentrations were found to be variable and related to water table fluctuations (Martel et al. 2009). A diagram of the HMX plume in 1999 is shown in Figure A3-9. In 2005, the highest HMX concentration was 92 µg/L in well A–3. Using well data and results from direct push sampling holes, Martel et al. (2009) estimated a plume length of 115 m, an average



Line Composites

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

Figure A3-8. Concentration of NG in composite soil samples collected in front of and behind the rocket firing line (Jenkins et al. 2004).

Table A3-1. Concentrations of HMX in ground water (1995–2000, A-10 and P-13 in perched aquifer, others in regional aquifer). USEPA guideline for drinking water is 400 µg /L. Most well locations are shown in Figure A3-9 (From Martel et al 2009).

Date	HMX Concentration (µg/L)									
	W-1	A-3	A-4	A-5	A-7	A-9	A-17	A-18	A-19	A-25
May 1995	295	–	–	–	–	–	–	–	–	–
1 July 1998†	–	53	–	67	6	34	–	–	–	–
1 Nov. 1998	–	68	–	47	9	27	–	–	–	–
26 Mar. 1999	–	75	–	71	10.9	42	–	–	–	–
15 Apr. 1999	–	97	–	137	15	46	–	–	–	–
4 May 1999	–	125	–	114	10	32	–	–	–	–
20 May 1999	–	122	–	130	5	45	–	–	–	–
2 June 1999‡	6	56	–	116	3	17	–	–	–	–
14 June 1999§	–	–	–	–	–	–	–	–	–	–
29 June 1999	–	175	–	150	–	–	–	–	–	–
14 July 1999¶	–	–	–	–	3	–	62	21	–	–
25 Oct. 1999#	230	12	–	2.4	3	16	8	15	3	–
12 May 2000	–	140	–	113	18	40	105	39	34	–
20 Sept. 2000	175	36	7	–	<0.05	–	21	13	9	17

† 1 July 1998, <0.05 ppb: A-10, A-11, A-12, P-13.
‡ 2 June 1999, <1 ppb: A-22; <0.05 ppb: A-22B.
§ 14 June 1999, <0.05 ppb: A-11, A-12.
¶ 14 July 1999, <0.05 ppb: A-16.
# 25 Oct. 1999, <1 ppb: A-20, A-21, A-23, A-24.

aquifer thickness of 7.5 m, and an average HMX concentration of 23 µg/L. He estimated the HMX flux into groundwater to be about 3 g/day during the spring of 2005. HMX concentrations (and flux) were lower in other periods of the year, but did not drop to zero. He estimated the yearly flux to be about 0.7 to 1.0 kg, which was about 10% of the mass of HMX on the soil surface within the sand terrace, and 5% on the total range.

TNT and its transformation products (2ADNT and 4ADNT) were only detected in the ground water during sampling in 2000. The maximum TNT and 4 ADNT concentrations were 3.25 and 1.70 µg/L, respectively. TNT was not detected in 2005. In monitoring wells downgradient of the Arnhem range, RDX was detected only in fall 1998, spring 1999, and spring 2000 at a maximum concentration of 2 µg/L (Martel et al. 2009).

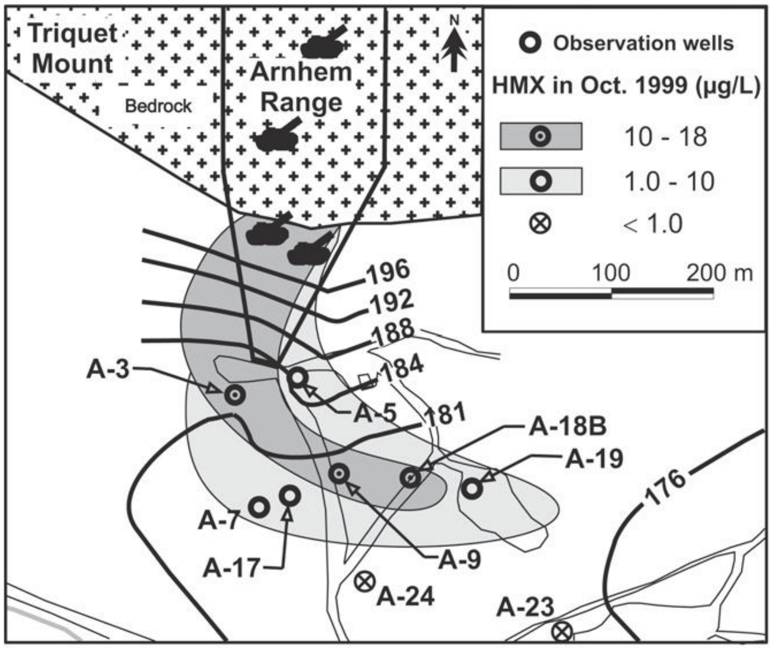


Figure A3-9. Dissolved HMX plume in ground water, fall 1999.
Wells A-20 and A-21 outside of map (<1.0 µg /L).

As noted earlier, the propellant used with the M-72 rockets at the Arnhem range contains 7.8 % potassium perchlorate. Because perchlorate is so soluble in water, and as an anion is not retained in the soil, it can penetrate deep into the soil profile and perhaps become associated with groundwater. Perchlorate was detected in groundwater at the Arnhem site (Fig. A3-10), ranging from a low of about 0.04 µg/L to as high as 14 µg/L (Martel et al. 2009). The areal distribution of perchlorate in groundwater indicated that the highest concentrations were found in the area behind the firing line, the area where most of the propellant residues were deposited.

Fate of Octol particles on the soil surfaces

Octol is a melt cast explosive with crystals of HMX dispersed in a TNT matrix. Simulated rainfall studies with Octol particles conducted by Taylor et al. (2009) indicated that TNT dissolved much faster than HMX, eventually leaving HMX crystals on the surface once the TNT was completely dissolved. This behavior is consistent with the much higher HMX concentrations found in the surface soil at the Arnhem range.

Once dissolved, the two compounds can interact with the soil. At Arnhem, the soil is very sandy and little sorption is expected. A retardation factor of between 4.5 and 6 was estimated for HMX from lysimeter studies for the Arnhem soil (Arel 2004). Soil/water partition coefficients for HMX and TNT are estimated to be within the same order of magnitude for the same soils, but these coefficients are obtained assuming that the TNT lost from solution in these equilibration tests is still intact and has sorbed onto soil. However, TNT is microbiologically (and probably abiotically) transformed under aerobic conditions in soil to 2ADNT and 4ADNT, and these two

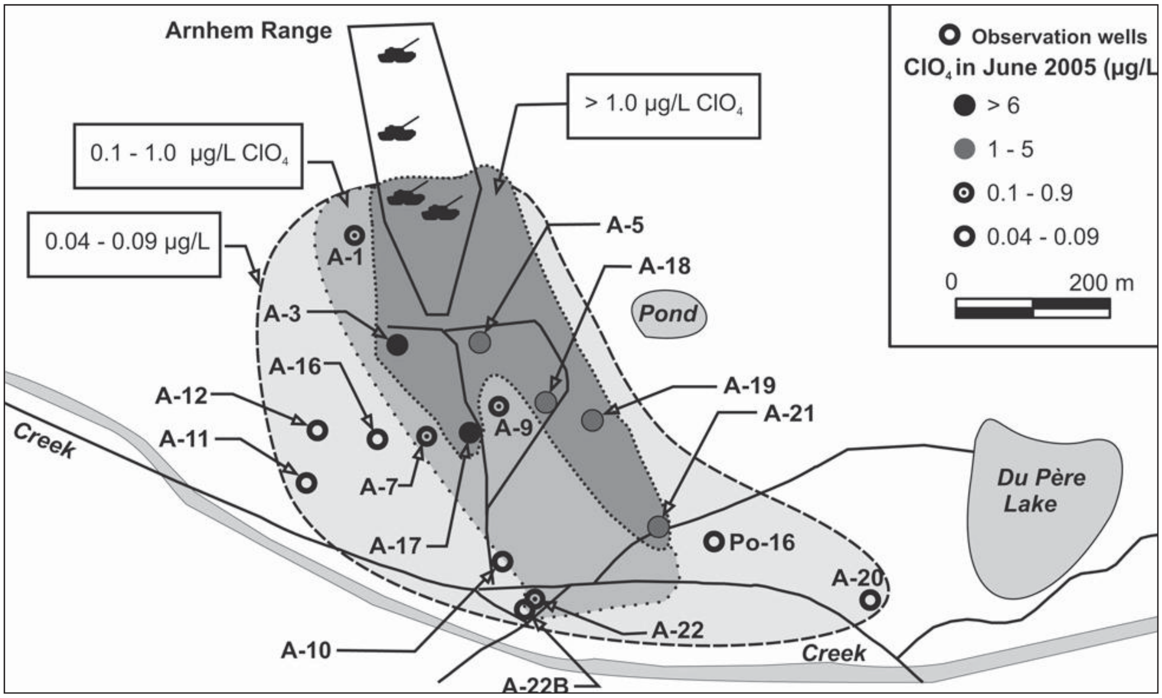


Figure A3-10. Dissolved perchlorate plume in ground water, June 2005. Wells A-11, A-12 and A-16 probably show the contribution from another perchlorate source (from the present three targets, only two have been shown). (from Martel et al. 2009).

compounds can chemisorb to organic matter present in the soil and be irreversibly bound (Thorn et al. 2002). Thus the soil water partition coefficients quoted for TNT are probably too high. HMX is not transformed under aerobic conditions and once it is dissolved, it migrates downward with percolating water. Most of the TNT is transformed into 2ADNT and 4ADNT and retained within the soil profile.

Conceptual site model

Based on the results of this study, conceptual site models for HMX and TNT behavior at the Arnhem range were developed (Fig. A3-11). 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 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 ground water wells located at the range. An HMX plume intercepts the regional aquifer occurs as 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 (see inset Figure A3-11).

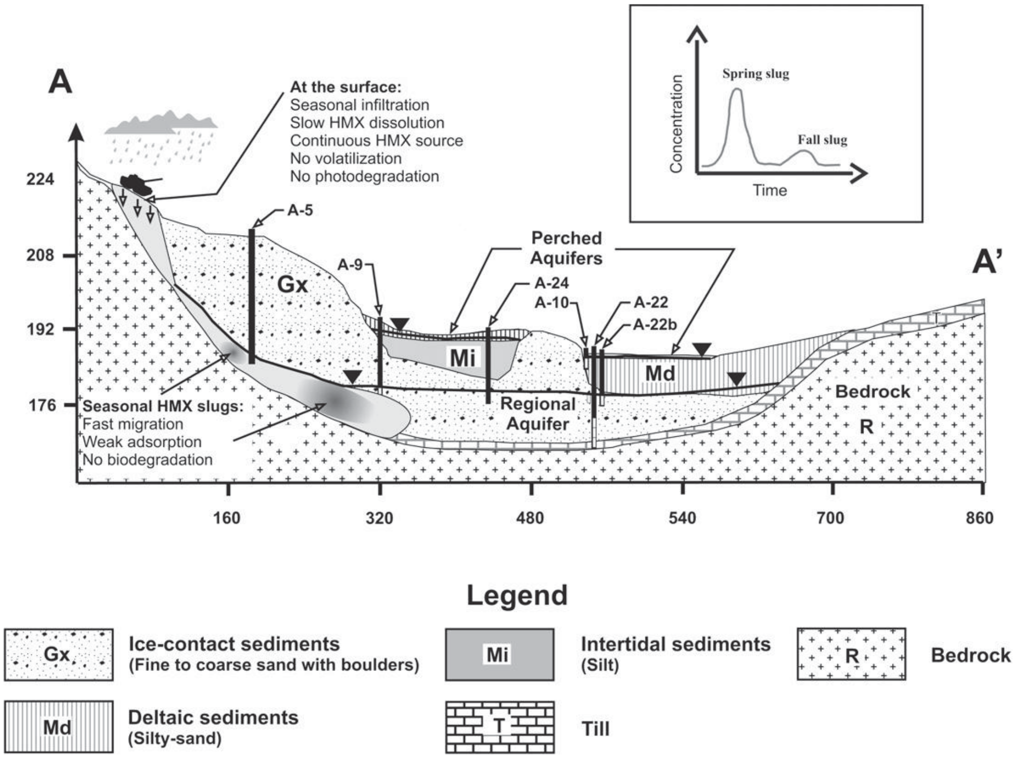


Figure A3-11. Conceptual model of HMX behavior (profile length and altitude in meters).

Conclusions

The high spatial heterogeneity of energetic compounds on the soil around targets anti-tank ranges and its implications for soil sampling has been widely described (e.g., Clausen 2005; Jenkins et al. 2004). MIS provides a reliable way for estimating the mass of EM residues at both the target and firing point portions of the range. Concentrations of energetic compounds also vary in ground water at the Arnhem Anti-Tank Range where concentrations vary in time and space.

This work demonstrates that the flow regime has to be well known when characterizing the ground water contamination related to an anti-tank training range and probably other types of ranges as well. In the case of variable water levels and substantial parts of the aquifer below the training area changing between saturated and unsaturated conditions, sampling periods have to be chosen with great care because observed ground water contamination may vary with the seasons. High infiltration rates cause higher mobility of energetic compounds but may also dilute the concentrations. Snow cover and frozen ground inhibit infiltration for several months, causing an accumulation of contaminants at the ground surface, which may be leached just after snowmelt, causing an extreme peak in the concentration of energetic compounds in groundwater.

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Appendix A4. Case Study: Estimating perchlorate deposition from the firing of a MLRS rocket.

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Introduction

Ammonium and potassium perchlorate are present in a variety of US military items including large rocket motors such as the Multiple Launch Rocket System (MLRS). A study was conducted to assess the deposition of ammonium perchlorate near where this rocket system was fired. The propellant for the MLRS rocket is 98.2 kg (216.5 lb) of Arcadene 360B with 630 g of WC818. The Arcadene 360B is composed of ammonium perchlorate, aluminum powder, HTPB, dioctyl adipate, iron oxide, and less than a percent of several other non-energetic compounds. The rocket motor contains 67.8 kg of ammonium perchlorate or 57.4 kg of perchlorate. WC818 is composed of mostly NC, with smaller amounts of NG, dibutylphthalate, calcium carbonate, and less than a percent of several other non-energetic compounds.

Under normal firing conditions, the residue would be deposited over a very large area as the rocket ascends. In this study, the rocket propelled a sled along a rail that is approximately 1 m above the ground, and residues are deposited over a much smaller surface area near the sled track.

Methods

A diagram of the sampling design at the sled track is shown in Figure A4-1. Forty-six surface soil samples were collected up to 50 m behind the firing line and along the first 274 m (900 ft) of the sled track. Along the track, samples were collected on both sides of the track in 45.6-m (150-ft) intervals, at a distance of 0 to 10 m from the edge of the track. Half of the samples were collected the day prior to firing the MLRS rocket and the other half were collected within three hours after the MLRS rocket was fired. At this facility, the rocket sled is propelled along the 610-m (2000-ft) sled track. Based on information provided by the test site engineer, the rocket motor was operational along the entire portion of the track that was sampled. No rain occurred throughout the two days we sampled.

Multi-increment soil samples were collected behind the firing point and along a sled track before and after launching a single Multiple Launch Rocket System (MLRS) rocket. In all cases, surface soil samples were collected with either a 3-cm-diameter corer (M.R. Walsh 2004) or a stainless-steel scoop. The choice of which tool to use depended on the hardness of the surface

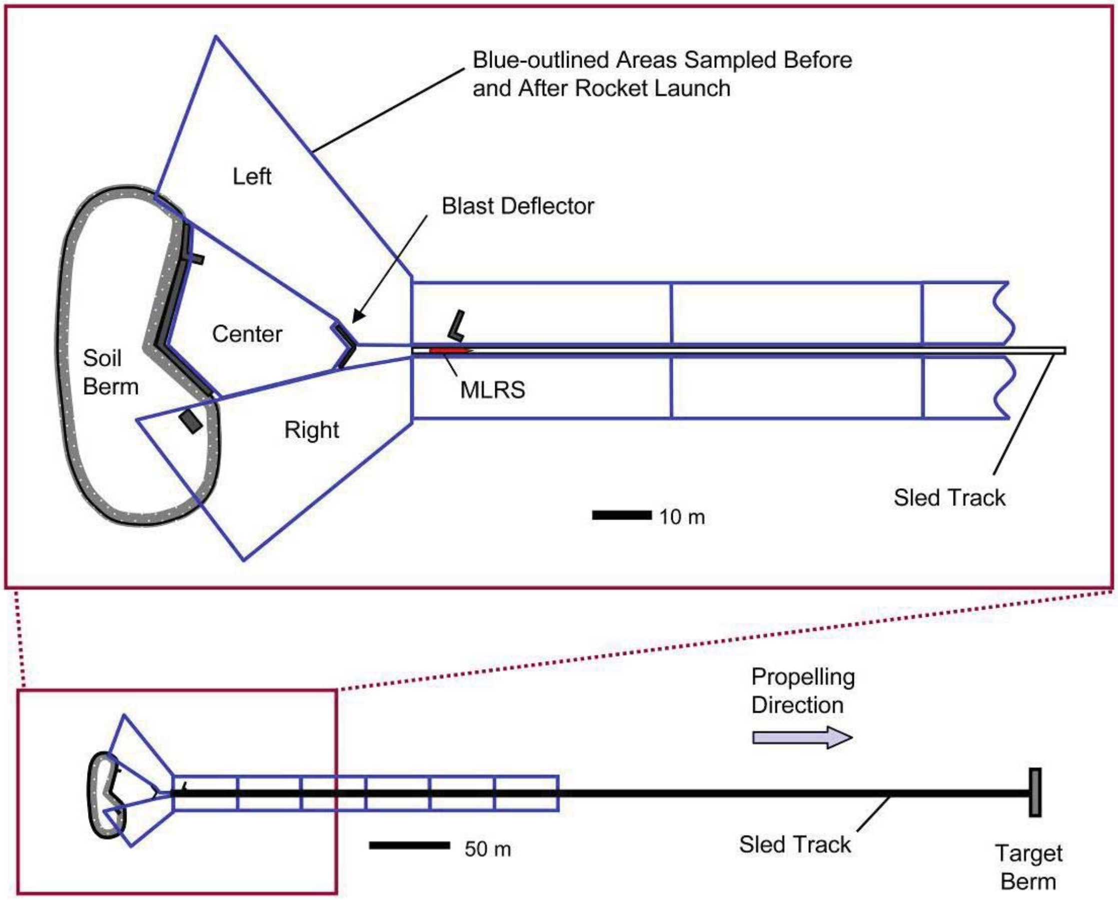

Figure A4-1. Diagram of sled track including sampling areas for multi-increment soil samples.

and the cohesiveness of the soil. In all cases, we collected multi-increment surface soil samples 0 to 2.5 cm below the surface; the number of increments per sample ranged from 38 to 82. In some cases, however, we could not push the sampler a full 2.5 cm into the hard-packed soil; those increments were from shallower depths.

All soil samples were returned to the laboratory by overnight carrier. Soil samples from this test were dry and were processed without further air-drying. Sample weights varied from 1320 to 3801 g. Each sample was passed through a 10-mesh (2-mm) sieve to remove oversized material. The entire fraction of the sample that was less than 2 mm was ground in portions that did not exceed 600 g using a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck-mill grinder. Each portion was ground five times for 60 seconds, reducing the particle size of the material to a flour-like consistency (< 70 µm). After all the portions for a given sample were ground, the portions were combined and mixed thoroughly, and spread out on a tray to form a 1-cm-thick layer. Subsamples were obtained by collecting 30 increments randomly from the entire thickness of the pulverized material.

A 10.0-g portion of each soil was extracted with 100 mL of reagent-grade water from a Milli Q, reagent-grade water system (Millipore Corp.) for 18 hours on a platform shaker. All aqueous extracts were passed through a 0.45-µm Millex-HV filter unit (Millipore Corp.) and perchlorate was determined with ion chromatography using suppressed conductivity detection according to the general procedures outlined in EPA Method 314.0 (US EPA 1999). The analytical detection limit for Method 314.0 was 10 µg/kg. Because none of the samples were determined to have perchlorate concentration above this value, portions of a few soil samples were sent for analysis by Method 314.0 analysis using equipment with a lower detection limit (1.0 µg/kg). An additional subset of samples was sent to a commercial laboratory for LC/ESI/MS (Liquid Chromatography Electrospray Ionization Mass Spectrometry) according to Method 331.0 (US EPA 2005).

Results and Discussion

Results of analysis of soil samples collected before and after the rocket was fired are presented in Table A4-1. We suspected that the largest mass of propellant would be deposited behind the firing position, as had been found for smaller, shoulder-fired rockets (Jenkins et al. 2004). For that reason, we collected triplicate field samples on the left and right side of the deflector structure behind the firing point (Fig. A4-1). The mean concentrations in soil on the left side of the deflector before and after the firing of the MLRS were 6.0 and 5.9 µg/kg, respectively. Similarly, the mean concentrations on the right side of the deflector were < 1.0 and 2.3 µg/kg, respectively. In neither case was the soil concentration after firing significantly different from the concentration before firing at the 95% confidence level. The perchlorate concentrations before and after the rocket firing in the center behind the deflector were < 1.0 and 1.3 µg/kg, respectively.

Soil samples were also collected along the sled track at distances from 0 to 274 m ahead of the firing point both before and after the rocket fired (Table A4-1). Eighteen samples were analyzed from those collected. The mean concentration for the nine samples collected before the firing was <1.0 µg/kg and the mean concentration for the nine samples collected after the firing was also < 1.0 µg/kg. Thus, we were not able to detect a significant increase in the perchlorate concentration either behind the firing line or along the sled track after a single MLRS rocket was fired.

Even though the amount of perchlorate deposited from this rocket was too low to measure, we can estimate the mass of perchlorate that would have had to be deposited for us to measure a significant increase in concentration. We made this estimate by calculating the surface area from which soil samples were collected, multiplying by the 2.5-cm depth sampled to compute the volume of soil in this zone, and multiplying by an estimate of the bulk density of soil (1.7 g/cm^3). The total mass of soil was estimated at 3.31×10^5 kg. Because the total area of deposition is probably greater than the area we sampled, we multiplied this mass by 2. If deposition from the

Table A4-1. Concentration of perchlorate in surface soils (0–2.5 cm) at Eglin AFB sled track before and after MLRS rocket firing. Samples consist of 38 to 60 increments.

Location				Perchlorate Concentration (µg/kg)				
				Before		After		
Position	Side	Distance		CRREL*	EL†/Other	CREL†	EL†/Other	Difference
Behind	Left	0–46 m	Rep 1	< 10	6.3†	< 10	6.8†	
			Rep 2	< 10	5.9	< 10	4.9	
			Rep 3	< 10	5.7	< 10	5.9	
		mean		< 10	6.0	< 10	5.9	–0.1
	Center	0–46 m		< 10	< 1.0†	< 10	1.3†	> 0.3
	Right	0–46 m	Rep 1	< 10	1.0	< 10	1.0	
			Rep 2	< 10	< 1.0	< 10	1.5	
			Rep 3	< 10	< 1.0†	< 10	4.3†	
		mean		< 10	< 1.0	< 10	2.3	> 1.3
Ahead	Right	0–46 m	Rep 1	< 10	< 1.0	< 10	< 1.0	
			Rep 2	< 10	< 1.0	< 10	< 1.0	
		mean		< 10	< 1.0	< 10	< 1.0	ND
	Left	0–46 m	Rep 1	< 10	1.1	< 10	< 1.0	
			Rep 2	< 10	< 1.0	< 10	< 1.0	
		mean		< 10	< 1.0	< 10	< 1.0	ND
	Right	46–92 m		< 10	< 1.0	< 10	< 1.0	ND
	Left	92–137 m		< 10	1.4	< 10	3.5	2.1
	Right	137–183 m		< 10	< 1.0	< 10	< 1.0	ND
	Left	183–229 m		< 10	< 1.0	< 10	1.2	> 0.2
	Right	229–274 m		< 10	< 1.0	< 10	< 0.1	ND

* Ion chromatography method.

† Data from EL-Omaha - Ion chromatography; other results from contractor laboratory - LC/EIS/MS method.

rocket raised the perchlorate concentration in the soil within this zone by 1 µg/kg, the mass deposited would be 662 mg. Pooling the standard deviations of the data sets that had three measured values above the analytical reporting limit before or after the rocket was fired, we can estimate an average total measurement uncertainty of 1.2 µg/kg. Thus, to measure a significant concentration increase at the 95% confidence level, the soil concentration would have to be raised by 2.4 µg/kg. Thus, the amount of perchlorate deposition would have to have been at least 1.6 g to be detected. Because we were unable to detect a significant increase in concentration in this experiment at the 95% confidence level, we can assume the deposition of perchlorate was less than 1.6 g. Because the rocket initially contains 57.4 kg of perchlorate, at least 99.997% of the perchlorate is destroyed during firing. Thiboutot et al. (Chapter 6 in Jenkins et al. 2007) estimated that only 2 mg was deposited when an Mk58 rocket motor that contains 47 kg of ammonium perchlorate was fired. Our findings are consistent with their estimate; however, our values are more uncertain because we were not able to measure any significant perchlorate deposition.

Overall, the firing of one MLRS rocket did not increase the perchlorate concentration in the soil at the sled track above background levels. The efficient burning of the rocket motor appears to destroy at least 99.997% of the perchlorate in the motor. This result is consistent with that found by the Canadians for the AIM-7 missile test (Chapter 6 in Jenkins et al. 2007). Oxley et al. (2009) found that perchlorate residues of about 0.0022 % remained compared to the initial perchlorate present in the rocket formulation. They concluded that "the large quantities of perchlorate in propellants are effectively destroyed during the burning process leaving minimal perchlorate residue."

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Appendix A5. Case Study: Site Inspection at the Former Farragut Naval Training Center/ Idaho Department of Fish and Game Farragut Firing Range Athol, Kootenai County, Idaho

HARRY CRAIG, KATIE ADAMS; US EPA REGION 10
SUSAN BIGL, SUSAN TAYLOR; USA ERDC/CRREL

The following is a summary of a site inspection conducted by EPA Region 10 at the Idaho Department of Fish and Game Farragut Firing Range (Farragut) in Athol, Idaho (Techlaw 2010). Multi-increment samples were collected to determine average concentrations of both metals and energetic compounds at a portion of this small arms training facility.

Site History and Description

Farragut served as a Naval training station from 1942 to 1944 and was decommissioned in June 1946. In 1950, the DoD conveyed the site to Idaho Fish and Game and the site is currently used by the Idaho Department of Parks and Recreation as a public firing range (Helmich et al. 1999, Leptich et al. 2005).

The Farragut site is approximately 1000 ft long by 600 ft deep. The western half remains unchanged since the Navy built it during World War II and is the area studied during this site inspection (Figure A5–1). The southern 520-ft wide shooting bay is directed towards eight targets at the northern portion. The range floor, the area between the firing line shelter and the targets, is overgrown with vegetation. Just to its north is an 8-ft deep concrete pit extending the length of the range, behind which is an impact berm approximately 30 to 40 ft higher than the top of the pit. Beyond the impact berm is forested acreage. Samplers observed shooting debris scattered throughout the bay during their 2008 site reconnaissance and 2009 SI sampling event.

Potential Contaminants of Concern

The purpose of the SI was to measure the concentrations of metals in the soils. Lead is deposited at firing ranges as lead shot and bullets, most of which are in the berm soils. Since lead oxidizes when exposed to air and dissolves when exposed to acidic water or soil; it has the potential to migrate through soils to groundwater. Other chemicals of concern at small arms ranges include arsenic and antimony (from ammunition), nickel (coating on some lead shot), copper, zinc, strontium, and magnesium (from tracer rounds used in machine guns), and polycyclic aromatic hydrocarbons (from clay targets and 'wadding' from shotgun shells) (US EPA 2003). Nitroglycerin and 2,4-Dinitrotoluene are commonly used in propellants and were analyzed for in the firing point and background samples.

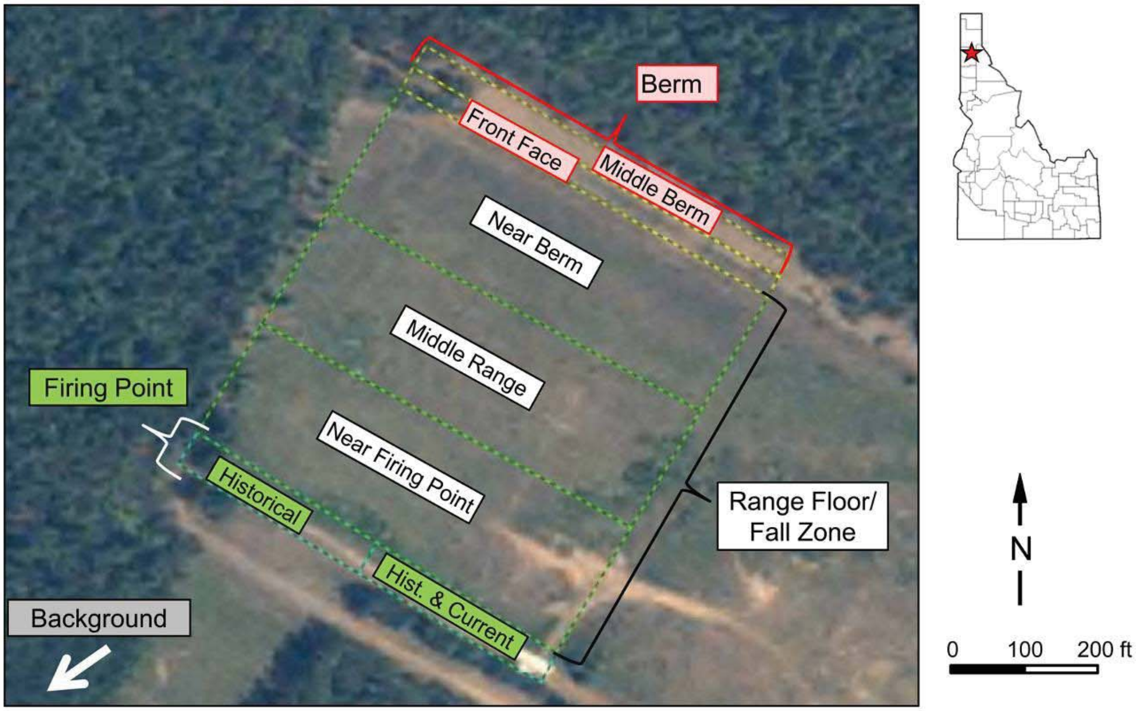

Figure A5–1. Air photograph of the Farragut firing range with overlays showing the boundaries of the sampling units. Inset shows the general location of Farragut. (after Techlaw 2010).

Sampling Methodology

The range was divided into seven sampling units, two at the firing line, three within the range floor, and two on the target berm (Fig. A5–1). A total of nine multi-increment samples were collected: one from each sampling unit, one background sample, and one duplicate from the near range floor (Techlaw 2010). The Range Floor samples were built from 60 increments; all others had 30 increments (Table A5–1). The background sample was collected from an area similar in size to the firing point, with a similar substrate, and approximately 0.3 mi up-gradient of the Farragut site.

A die was rolled to randomly select the starting point in the northwestern corner of each sampling unit and MIS samples were collected on an even spacing from there (Fig. A5–2). The sampling team used a handheld Garmin ETrex GPS unit to record GPS coordinates of all sample locations. Samples were collected first from sampling units thought to be the least contaminated and then from those expected to be most contaminated. Increments from the firing line, range floor, and the background location were collected 0 to 2 inches below the surface. Increments collected in the Berm and Target Areas were collected from 0 to 12 inches from the surface, assuming that bullets would penetrate more deeply into the berm. All of the samples were obtained below the vegetative cover. After collection, the combined soil increments were sieved with a number 14 USA standard testing sieve. The single homogenized MIS sample was then transferred to a 32-oz high-density polyethylene (HDPE) container.

Table A5–1. Sampling units evaluated.

Unit	Sampling Unit Description	Increments
1	Historical Firing Pt.	30
2	Historical and Current Firing Pt.	30
3	Near Firing Pt. Range Floor/Fall Zone	60
4	Middle Range Floor/Fall Zone	60
5	Near Berm Range Floor/Fall Zone	60
6	Front Face Berm	30
7	Middle Berm	30
8	Background Sample	30

Analysis

All samples were analyzed for target analyte list (TAL) metals; the two firing point samples and the background sample were also analyzed for explosives and propellant compounds (Techlaw 2010). Both types of analysis were conducted by the EPA's Manchester Environmental Laboratory. The metals analysis followed EPA Method 200.7/200.8. Explosives and propellant residues were measured by high performance liquid chromatography (HPLC) using a dual wavelength ultra violet (UV) detector using EPA Method 8330B.

Specifics regarding QA/QC performed are described by Techlaw (2010). Concentrations considered significantly above background were defined in the SI plan, via a consensus based approach, as those that were at least three times greater than the background concentration when the background concentration equaled or exceeded the detection limit.

Results

Analyses of the background sample detected all 13 analyte metals but no energetic compounds (Table A5-2). The range samples had elevated concentrations of lead, copper and antimony with the highest concentrations in the berm soils and decreasing concentrations towards the firing point. The berm face was also found to have elevated cadmium; arsenic was found at the active firing point, on the range floor and in the berm face. Of the suite of targeted energetics compounds (17 analytes in Method 8330B) only nitroglycerin and 2,4-DNT were detected in the firing point sampling units. This result is expected as these two compounds are used in propellants whereas other energetic compounds, such as TNT and RDX, are not.

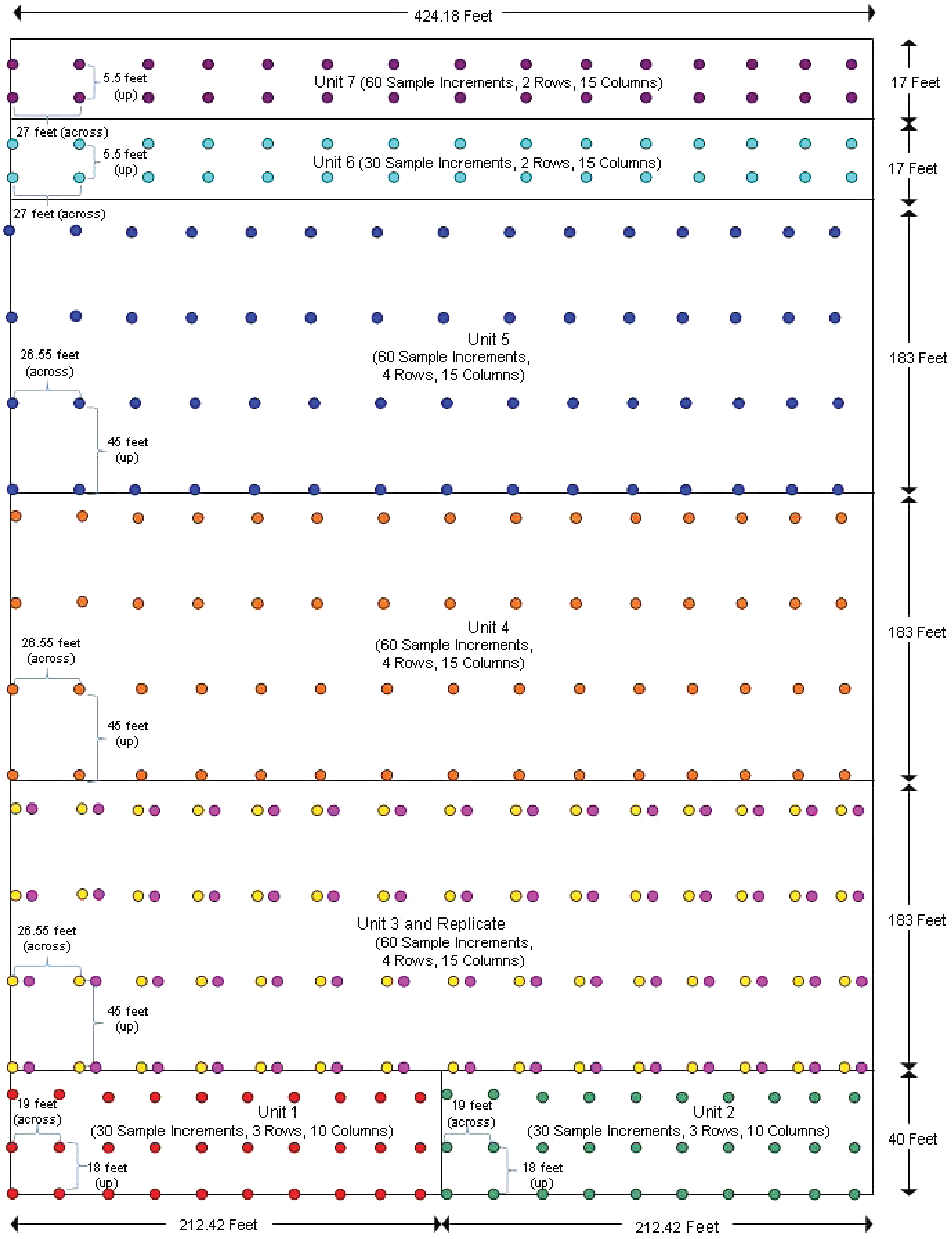

Figure A5–2. Schematic of sample increment locations at Farragut Firing Range.

Table A5–2. Concentrations of metal and energetic compounds in Farragut Range MIS Samples. Values underlined and in bold are over three times higher than the background concentrations.

Location	**Firing Point**		**Range Floor**				**Berm**		**Background**
	Historical	Both	Near Firing Point		Center	Near Berm	Face	Middle	
TAL Metals (mg/kg)			*Rep 1*	*Rep 2*					
Antimony	--	--	**31.0**	**27**	**220**	**24.0**	**400**	**180**	< 4.6
Arsenic	18	**30.9**	17	17	**24.3**	16	**23.8**	23.1	7.8
Barium	201	186	255	245	204	100	97.9	150	291
Beryllium	0.63	0.685	0.67	0.706	0.598	0.502	0.561	0.726	0.678
Cadmium	--	0.64	--	--	--	--	**2.01**	--	0.54
Chromium	10.4	15.1	9.29	9.7	10.5	14.5	13.1	14.1	8.48
Cobalt	8.0	11.8	5.74	5.92	6.09	6.79	6.59	7.67	5.13
Copper	**46**	**69**	**57**	**52**	**330**	**100**	**1200**	**940**	14
Lead	**67.2**	**202**	**1,510**	**1,670**	**7,130**	**2,470**	**24,100**	**21,800**	20.5
Manganese	716	652	715	707	703	507	555	645	1,100
Nickel	12.7	18.2	10.2	10.3	11.0	11.3	12.9	14.7	9.9
Thallium	10	11	14	14	12	11	11	14	14
Vanadium	17.8	21.2	22.5	23.6	21.0	24.1	20.7	26	22.8
Zinc	74.1	79	75.7	76.9	99.8	68.1	193	175	69.4
Nitroaromatics, Nitramines, and Nitrate Esters (mg/kg)									
DNT	**0.83**	**4.2**	--	--	--	--	--	--	--
Nitroglycerin	**29**	**170**	--	--	--	--	--	--	--

TechLaw collected a duplicate multi-increment sample from the Range Floor nearest the firing points to estimate the overall error from collecting, processing, sub-sampling and analyzing these samples. Comparison of the concentrations obtained from these two multi-increment samples show excellent agreement indicating that multi-increment samples worked well for estimating the concentrations of metals in these soils.

Lastly, the Manchester Environmental Laboratory estimated both the carryover from one sample to the next and the metals introduced by the grinding process when metallic grinding equipment was used. Ottawa Sand was processed using the same equipment used to pulverize the range samples. Table A5–3 shows the elemental concentration of Ottawa sand compared to Ottawa sand ground after a highly contaminated sample and after a background sample. Also listed is the metal composition of the metal grinding bowl. The results show increases in the concentrations of chromium, copper, manganese, and lead in the Ottawa sand. For lead, grinding introduced ~ 4.7 mg/kg into the sand, about one quarter the background level of 20.5 mg/kg and a value order of magnitude lower than any of the lead concentrations in the samples. Although these additions could be significant for trace metal work, they are unlikely to be important for contaminated range soils.

Table A5–3. Metals in Ottawa Sand.

Metal Analyte	Concentration (mg/kg)			
	Ottawa Sand			In Steel Bowl
	Unground	Ground		
		After Sample	*After Background*	
Al	20.8	57.2	58.5	
Ca	201	215	227	
Fe	1,550	9,800	7,550	> 95%
K	53	67	76	
Mg	132	55.1	61	
Na	7.6	23	19	
Ba	ND[†] (<0.15)	1.41	1.27	
Co	0.39	0.77	0.68	2.0
Cr	ND (<.76)	3.1	2.1	2.5
Cu	1.7	5.08	4.32	5.0
Mn	1.36	82.5	56.9	20.0
Ni	1.4	3.1	2.7	5.0
Pb	ND (<2.3)	4.7	ND (<3.3)	2.0
Zn	ND (<.38)	0.50	ND (<0.54)	2.0

[†] Not Detected

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Appendix B. Fundamental Error

It is important when considering sampling/subsampling efforts to characterize the concentrations of munition constituents in soil to understand that these residues have been largely heterogeneously deposited in source regions as particles of various sizes. Whether this is from low order detonations at impact areas or propellant residues at firing points, these residues remain as particles until they are dissolved or leached by precipitation. Thus soils in theses source zones contain the normal array of mineral and organic substrates commonly encountered in soil as well as particles of the energetic compounds with a wide variety of particles sizes randomly distributed throughout.

It is difficult to collect representative soil samples to estimate target analyte concentrations when the analytes of interest are present in particulate form and distributed in an extremely heterogeneous fashion. It can be just as difficult to obtain a representative subsample from a bulk sample under these conditions. But it must remembered that only a small portion of the total soil from a site is actually extracted to estimate analyte concentrations. Thus, it is critical the portion actually chosen for extraction and determination is representative of the soil sample collected and of the sampling unit.

Heterogeneity exists at two scales with the first due to unequal deposition of residues within the area sampled, which is referred to as “distributional heterogeneity.” On a smaller scale, the particles of residue vary in size (and thus mass and concentration), as do those of the soil matrix itself. Collecting a soil sample that adequately represents all the particles sizes of both residue and soil matrix is very difficult, and the difficulty increases as the sample size decreases. This form of heterogeneity is called “compositional heterogeneity.”

It is very important to consider compositional heterogeneity when selecting an adequate subsampling protocol for soil samples containing energetic residues. Because only a portion of the total sample will be used for extraction and analysis, a subsampling error is introduced, which is a function of the ratio of the subsample mass to that of the bulk sample. Clearly it is more difficult to adequately represent all the particles sizes present as the total mass of the subsample is reduced. Also, the magnitude of the subsampling error increases as the particle sizes of the energetic residue increases. This leads to the concept of “fundamental error (FE).” FE, in this case, is the error in representing the bulk sample due to the inability to adequately represent the bulk sample’s particles size distribution within a subsample of a given mass. It can be thought of as the unavoidable error when subsampling a particulate population and it can be estimated using sampling theory as devised by Pierre Guy (Pitard 1993). The FE error is the minimum subsampling error that remains when all other subsampling operations are perfect. It can only be decreased, by increasing the mass of the subsample, or by reducing the particles sizes of the residue and matrix.

This Appendix addresses FE, the most important statistical parameter to understand when sampling soil containing particulates. This error is fundamental to the composition of the particles (or other items or fractions) of the lot being chemically or physically different: that is, it is a result of the compositional heterogeneity (CH) of the lot. In this definition of FE, the lot is also known as the population, sampling unit, sampling area, or area of concern. Thus, this is the only sampling error that can never be eliminated. To obtain an accurate representation of CH, one must be sure the samples are always representative of all the particle size fractions present. The relative variance of the FE (s^2_{FE}) can be estimated before sample selection and may be reduced by decreasing the diameter of the largest particles to be represented or by increasing the mass of the sample (U.S. EPA 2003).

Fundamental error and the incremental sampling theory were developed by Pierre Gy to obtain representative soil samples containing minerals from heterogeneous media (Pitard 1993). The study of sampling of particulate materials starting in the 1950’s and culminated in Gy’s final theory in the 1980’s and 1990’s. Initially this theory was developed for the mining industry to estimate the value of mineral deposits. The sampling strategy described in this document was refined to address MC, by adapting Gy’s principles to address the major confounding factors for obtaining project suitable environmental data. To representatively estimate the concentration of a given constituent in an area where there has been a release into the environment, the sampling strategy and sample processing protocol must address the compositional and distributional heterogeneity, to the degree necessary to meet the DQOs (Ramsey and Hewitt 2005).

Compositional heterogeneity results from the fact that individual particles within a population often have different concentrations of target analytes. This heterogeneity is at a maximum when some of the target analytes are present as discrete particles. Error due to compositional heterogeneity is called the FE and is inversely related to the sample mass. Distributional heterogeneity is due to uneven scattering or release of COPC across the site, sometimes with a systematic component as well as a short-range random component. Error resulting from distributional heterogeneity is inversely related to the number of increments used to build the sample. This error is at a maximum when a single discrete sample is used to estimate the mean for a large sampling area.

The recognition of this approach for the collection and processing of environmental samples was enhanced by its documentation in Method 8330B (US EPA 2006). To reduce the influence of these error sources when estimating the mean concentration of an analyte within a sampling area, Method 8330B recommended the collection of 30 or more evenly spaced increments to build a sample with a total sample mass >1 kg (Jenkins et al. 2004a, 2004b, 2005, 2006, 2008;

M.E. Walsh et al. 2005; Hewitt et al. 2007). The objective of this sampling technique is to obtain a representative amount of every particle size and composition within the lot. In the case of residues of energetic compounds this would include small (< 2mm) pieces of high explosive materials (e.g., TNT, Composition B, Tritonal, etc.), propellants, and rocket fuels, of a variety of configurations (e.g., crystalline spheres, elongated fibers, etc.). Of equal importance, the sampling design should not over-sample or miss any portion of the sampling area.

The field or laboratory, or both, processing protocols must also address the compositional and distributional heterogeneity to ensure that subsamples are representative of the field sample to the degree specified in the DQOs. That is, the entire field sample must be handled and processed in a manner that allows a sample split or any given subsample aliquot, to accurately represent the original bulk sample. Table B-1, found at the end of this Appendix, is an example of how accuracy can be demonstrated for energetic residues in a field sample. In the case of residues of energetic compounds, Method 8330B recommends the entire field sample be air dried and then passed through a #10 (2-mm) sieve. This step also provides a safety feature, since energetic materials >2 mm are excluded from grinding. Thus, splitting the sample in the field is not recommended, even if the sample can be air-dried and sieved. Once sieved, the <2 mm fraction of the sample is then mechanically pulverized to reduce the particle size of both the matrix and constituents of concern to <0.075 mm. Pulverization was deemed necessary since energetic residue particles <2 mm exist as a variety of sizes, shapes and compositions. That is, even after air-drying and sieving, the compositional heterogeneity is too great within the <2 mm fraction to ensure that subsamples or sample splits would retain representative portions of energetic residues (M.E. Walsh et al. 2002; Hewitt et al. 2007, 2009). To further reduce the uncertainty among subsamples, Method 8330B recommends a 10-g subsample size be obtained by combining many (≥ 30) smaller increments.

According to Pierre Gy's theory to assess the overall sampling error (OE) one must sum the total sampling error (TE) and the analytical error (AE). Equation 1 allows an estimation of the overall measurement quality by evaluating error at all stages; including the representativeness of the sample and whether the same types of particles are in the same proportions as the population.

$$1\} \qquad OE = TE + AE$$

where:
OE = overall sampling error,
TE = total sampling error, and
AE = analytical error.

Total sampling error can be further refined into the total sampling error occurring in the field (TE_F) and the total sampling error occurring in the laboratory (TE_L). Thus,

$$2\} \qquad OE = TE_F + TE_L + AE$$

where:
OE = overall sampling error,
TE_F = total sampling error occurring in the field, and
TE_L = total sampling error occurring in the laboratory.

Pierre Gy's theory also recognizes seven basic sampling (TE) errors:

1. Fundamental Error (FE)
2. Grouping and segregation Error (GE)
3. Long-range Heterogeneity Fluctuation Error (CE_2)
4. Periodic Heterogeneity Fluctuation Error (CE_3)
5. Increment Delimitation Error (DE)
6. Increment Extraction Error (EE)
7. Preparation Error (PE)

Moreover, Pierre Gy established the relative variance of the fundamental error, s^2_{FE}, can be estimated from the following equation (Eq. 3):

$$3\}\ s^2_{FE} = c\beta fgd^3\ (1/M_s) - (1/M_L) \qquad s^2_{FE} = \left(\frac{1}{M_s} - \frac{1}{M_L}\right) c\beta fgd^3$$

where:
s^2_{FE} = relative variance of the fundamental error,
M_s = mass of the sample, g
M_L = mass of the lot (population, sampling unit, area of concern), g
c = constitution parameter,
β = dimensionless liberation parameter,
f = dimensionless shape parameter,
g = dimensionless size range parameter, and
d = diameter of the largest particle, cm

However, since the mass of the sample is generally much smaller than the mass of the lot the formula can be reduced to:

$$4\} \qquad s^2_{FE} = c\beta fgd^3/M_s$$

This equation is often referred to as the FE equation for nuggets. The constitution parameter, c, depends upon the amount of the analyte of interest in the lot and the mean density of the lot (Gy

1998). If the amount of analyte of interest in the lot is small, analyte of interest <<1, then an approximation for the constitution parameter is given by:

$$5\} \qquad c = \delta_M/a_L$$

where:
c = constitution parameter,
δ_M = mean density of the lot, and
a_L = decimal fraction of analyte of interest in the lot.

The dimensionless liberation parameter, β, can have values from zero to one. The parameter is zero when the components are completely homogenized (an impossible situation) and is one when the components are completely liberated. It is best to set $\beta = 1$ if one is not certain of the state of liberation, which is typically the case with residues of MC. The dimensionless shape parameter, f, also can have values from zero to one. For a sphere $f = 0.52$. For most compact particles f has values near 0.5. The dimensionless size range parameter, g, also can have values from zero to one. Some values used in practice are:

Undifferentiated, un-sized materials mean value	$g = 0.25$
Undersized material passing through a screen	$g = 0.40$
Oversize material retained by a screen	$g = 0.50$
Material sized between two screens	$g = 0.6/0.75$
Naturally sized materials, e.g. cereal grains	$g = 0.75$
Uniformly sized objects, e.g. bearing balls	$g = 1.0$

Examples: Fundamental Error for Field Sampling

Based on assuming the following values for the parameters in Equation 4 for the relative variance of the FE: $\delta_M = 1.6$ g/cm^3 (a typically density for soil), $\beta = 1$ (as suggest above), $f = 0.5$ (also as suggest above), $g = 0.25$ (for un-sieved soils), and $d = 0.2$ cm (from the common definition of what constitutes soil, but is also potentially, the size of the contaminant of concern), one can solve for either the relative standard deviation of the FE or the mass of the sample, both to within a single significant figure, for anticipated situations. Some example calculations follow:

Example A: MIS Application:

If the concentration of the analyte of interest is 1 mg/kg (a_L = 1 e-06), then to theoretically achieve a relative standard deviation for FE of 15% (S^2_{FE} =0.225), the mass of the sample needs to be at least 71 kg. Likewise, for a 10 or 100 mg/kg concentration, 7.1 or 0.71 kg, respectively, of sample mass is needed to approach this level of total measurement uncertainty.

Conversely, if M_s = 2 kg (2000 g) and a_L = 1 e-04, 1 e-05 or 1 e-06, then the relative standard deviation for FE one could anticipate would be, respectively, 8.9%, 28%, and 89%.

Example B: Discrete Sampling Application:

If M_s = 180 g (mass of soil in a 4 oz jar) and a_L = 1 e-04, 1 e-05, or 1 e-06, then the relative standard deviation for FE is, respectively, 30%, 94%, and 298%. However, if only a 20 g aliquot is removed from the top of the sample container, uncertainty increases to 89%, 283%, and 894%, respectively, at these three concentrations. It should be noted that there are two fundamental errors associated with the overall error, the FE for field sampling, (which results in the mass of sample sent to the laboratory), and the FE associated with laboratory subsampling.

In the majority of cases it is impractical to estimate the FE based on a prior knowledge of the physical dimensions and shape factors associated with the MC of interest. These parameters must also include the sizes and shapes of non-MC particles in the sample as well. Indeed, the size distribution of particles is seldom known and their shape is often highly irregular and often unique. Perhaps in the case of lead shot, one could anticipate that MC would be round and of uniform density. One alternative is to estimate FE empirically, after dismissing the physical parameters in Equation 2. This can be accomplished for a sample lot based on the assumption that IH_L is the constant factor of constitutional heterogeneity (i.e., invariant or constant heterogeneity):

$$6\} \qquad S^2_{FE} = (1/M_S - 1/M_L)\ IH_L$$

where:
S^2_{FE} = relative variance of the fundament error,
M_s = mass of the sample,
M_L = mass of the lot (population, sampling unit, area of concern),
c = constitution parameter,
β = dimensionless liberation parameter,
f = dimensionless shape parameter,
g = dimensionless size range parameter,
d = diameter of the largest particle, and
$IH_L = c\beta fgd^3$.

Equation 6 then can be solved for IH_L

$$7\} \qquad IH_L = S^2_{FE}\ (M_S)$$

Under these conditions IH_L is the product of S^2_{FE} times the mass of the sample, moreover, if distributional error is minimized, S^2_{FE} can be estimated from the variance of several measurements of the sample lot (in this case a large field sample) as follows:

$$8\} \qquad S^2_{FE} \approx s^2 / \times^2$$

where:
S^2_{FE} = relative variance of the fundament error,
s = variance of several measurements of the sample lot, and

x = average soil concentration.

To minimize the distributional error variable within a sample without affecting the particle size of the matrix or of the constituents of interest, the sample is split into equivalent mass fractions, with a rotary splitter. With this apparatus, a sample of 1 or more kg, is incrementally split more than a couple thousand times, thus, more than 500 increments are combined in a single split. Table B-2 (found at the end of the appendix) shows estimated samples masses needed to achieve different levels of sampling uncertainty (15 and 30%) using this empirical approach. The range of sample masses estimated by this approach is in good agreement with those estimated above.

The theoretical and empirical estimations of uncertainty only assess the FE in the field during sampling. There is also FE associated with the laboratory processing and analysis phases of the analytical process. Therefore, to achieve even these levels (15 and 30%) of uncertainty, the entire sample (3 g to 70 kg) must be analyzed, i.e., no error can be attributed to these additional steps, which clearly is unreasonable. To allow for uncertainty to be introduced as a consequence of sample preparation and analysis, a target value of 15% uncertainty, for field sampling is recommended, and because the concentration often is not know a priori to sampling, a kg or larger sample size, is recommended. Moreover, it should be recognized in some cases even a 2 kg sample mass may insufficient to meet project DQOs.

This same equation can be used to look at the FE associated with taking a subsample using Methods 8330B and 3050B. As the subsample becomes smaller, uncertainty increases, particularly when the density of the COC is much greater than the matrix (e.g., Pb ρ = 11.4 g/cc) due to segregation error. Assessment of segregation error is beyond the scope of this document. However, segregation error is a possible explanation for the much greater uncertainty associated with Pb as compared to energetic residues, for a given concentration (Table B-2). Even for energetic residues, e.g., TNT and Comp B, with densities of around 1.8 g/cc, depending on the formulation and manufacturing, a density that is similar to soil, 2 to 10-g subsamples of unprocessed materials, results in an unacceptable level of uncertainty, except when concentrations are exceed 1000’s to 10,000’s of parts per million (e.g., 0.1 to 1% w/w, see Table B-2).

Example C: Fundamental Error for Laboratory Sub-Sampling

A. For samples, that are sub-sampled in the laboratory, but not ground, but are <2 mm:

If M_s = 1 g (mass of soil for a typical metals digestion) and a_L = 1 e-04, 1 e-05, or 1 e-06 then the fundamental error is, respectively, 400, 1265, 4000%.

If M_s = 10 g (mass of soil for Method 8330B) and a_L = 1 e-04, 1 e-05, or 1 e-06, then the fundamental error is, respectively, 126, 400, 1265%.

B. For samples comminuted (ground) to <0.075 mm (<0.0075cm), and then sub-sampled (i.e. for EPA 8330B):

If M_s = 1 g (mass of soil for a typical metals digestion) and a_L = 1 e-04, 1 e-05, or 1 e-06, then the relative standard deviation for fundamental error is, respectively, 3, 9, 30%.

If M_s = 10 g (mass of soil for EPA 8330B) and a_L = 1 e-04, 1 e-05, or 1 e-06, then the relative standard deviation for fundamental error is 0.9, 3, 9%.

Clearly, if samples are not ground to a fine powder, and concentrations below 100 mg/kg are important, either numerous aliquots ($n \geq 12$) are needed to to obtain a reasonable estimate of the average concentration, or no reasonable degree of confidence can be associated with the data. Even at concentrations in the 1000 mg/kg (0.1% w/w), the uncertainty is on the order of 100%, when the analytical method recommends a 1-g subsample. Contrarily, if the entire sample is ground, reasonable levels of precision can be obtained. Furthermore, accuracy can be demonstrated for energetic residues, based on whole sample extraction (Table B-1), or can be strongly inferred by the extraction and analysis of 15 replicate subsamples, in the case of metals.

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Table B-1. Comparison between bulk sample concentration and average subsample concentration after Method 8330B processing.

Location / Sample	Portion	Mass (g)	Acetone (mL)	Concentration (mg/kg)					
				Statistic	HMX	RDX	TNT	2,4-DNT	NG
Demolition Range (MI-9)	Bulk	1766	3540		**2.02**	**11.9**		**4.81**	
	R1	10.0	20.0		1.98	11.7		4.58	
	R2	10.0	20.0		2.00	11.6		4.92	
	R3	10.0	20.0		1.98	11.8		5.22	
				Ave	**1.99**	**11.7**		**4.91**	
				Std Dev	0.009	0.090		0.320	
				%RSD	0.48%	0.77%		6.53%	
				RPD *	**1.4%**	**1.7%**		**2.1%**	
Firing Point Fox (MI-10)	Bulk	1196	2400						**4.21**
	R1	10.0	20.0						4.00
	R2	10.0	20.0						5.04
	R3	10.0	20.0						4.06
				Ave					**4.37**
				Std Dev					0.584
				%RSD					13.4%
				RPD					**3.7%**
Low Order #3 (MI-5)	Bulk	1278	2560		**2.76**	**14.3**	**1.56**		
	R1	10.0	20.0		2.72	14.1	1.60		
	R2	10.0	20.0		2.72	14.1	1.60		
	R3	10.0	20.0		2.60	13.9	1.63		
				Ave	**2.68**	**14.0**	**1.61**		
				Std Dev	0.035	0.125	0.016		
				%RSD	1.26%	0.89%	1.00%		
				RPD	**2.9%**	**2.1%**	**3.2%**		
Hand Grenade Range (MI5)	Bulk	2526	5060			**0.645**			
	R1	10.0	20.0			0.592			
	R2	10.0	20.0			0.598			
	R3	10.0	20.0			0.576			
				Ave		**0.589**			
				Std Dev		0.011			
				%RSD		1.93%			
				RPD		**9.1%**			
Firing Point Juliet Tower (MI-5)	Bulk	1935	3880					**0.964**	**2.97**
	R1	10.0	20.0					0.88	2.38
	R2	10.0	20.0					1.09	2.84
	R3	10.0	20.0					1.17	3.36
				Ave				**1.05**	**2.86**
				Std Dev				0.152	0.490
				%RSD				14.5%	17.1%
				RPD				**8.5%**	**3.8%**

* RPD - Relative percent difference between average and bulk concentration.

Table B-2. Estimates of field sample mass required to achieve either a 15 or 30% uncertainty, based on P. Gy sampling theory, i.e., constant factor of compositional heterogeneity (IHL). Energetic residues were from MIS samples collected on impact ranges and at a firing point. Those with metals were collected on the face of an earthen back stop for a small arms range.

Mass of Sample Splits (n=12) Aver ± Std Dev*	Analyte	Average Conc. (mg/kg) ± Std Dev	Sampling Uncertainty 15% RSD**	Sampling Uncertainty 30% RSD
203±4.5	RDX	1.7±1.8	10 kg	3 kg
200±6.5	RDX	2.1±0.96	2 kg	0.5 kg
203±6.1	2,4-DNT	1.0±0.73	5 kg	1 kg
†200±6.5	2,4-DNT	4.5±1.6	1 kg	0.3 kg
200±6.5	NG	1370±46.8	0.01 kg	0.003 kg
203±4.5	NG	1650±82.4	0.02 kg	0.006 kg
203±7.9	Pb	200±94	2 kg	0.5 kg
200±5.8	Pb	1380±189	0.2 kg	0.05 kg
* Standard deviation ** Relative standard deviation † Walsh et al., Soils and Sediments				

Appendix C. A Practical Guide to Sampling

(This Appendix was originally published in **MMRP GUIDANCE DOCUMENT FOR SOIL SAMPLING OF ENERGETICS AND METALS)**

Safety Considerations

In areas where UXO, discarded military munitions, or materials potentially presenting an explosive hazard are present or may exist, field activities are supervised by military EOD personnel or qualified UXO technicians. The on-site UXO technician will conduct a surface access survey and a subsurface survey for anomalies before any type of activities commence, including foot and vehicular traffic. Procedures for these measures should be described in the Contractor's Site-Specific Work Plan and modified in their site-specific plans as required.

Although uncommon, soils containing energetic compounds at concentrations that present risk of detonation or deflagration, exceeding 100,000 mg/kg (10%), may be encountered in the vicinity of ruptured munitions or partial detonations (low-order) on ranges, at manufacturing facilities, or in disposal areas such as OB/OD sites, and near burial pits. In these areas pieces of explosives are often seen on the ground. TNT is yellow but turns reddish brown when exposed to sunlight and often has a reddish halo on the soil surrounding the solids. RDX is white to light yellow but does not photo-degrade to form red compounds. Consequently, Comp B is less highly colored than TNT as it only has ~40% TNT in this formulation. Pieces of C4 explosive are often encountered where blow-in-place has been used to destroy UXO or where demolition training has occurred. Pieces of C4 are white in color. Visible or otherwise identifiable pieces of explosive compounds should not be incorporated into the soil samples. The EXPRAY Kit (Plexus Scientific, Silver Springs, MD) or EPA Methods 8515 and 8510 (US EPA 1996, 2000) may be useful for screening suspected explosive material or potentially very high concentrations in soil before sampling and shipping soil samples off site.

Sampling Tools

An unbiased sampling scheme must be developed and carefully followed to uniformly sample the volume of soil within the boundaries of the sampling unit. The fundamental requirements for increment collection are:

- an unbiased pattern throughout the entire sampling unit
- complete and uniform sampling across the specified depth interval
- uniform size/mass of increments

A sampling methodology is considered unbiased if all of the particles in the sampling unit have the same probability of being included in the sample (Gy 1998). To obtain a sample that is representative of the population in terms of particle type, size, and proportion, the volume of soil in each increment must be constant.

Coring devices that assure a uniform diameter core through the entire sampled interval are preferred for increment collection. Most devices such as a garden trowel or hand auger do not control the amount of material per increment or ensure representative proportions of material from throughout a specific depth interval. They are likely to introduce bias into the sampling, particularly when more than one sampler is involved in sample collection. Although their use may be unavoidable for coarse gravelly soils, such tools are not recommended (Pitard 1993).

A variety of hand operated coring devices designed for surface sampling (e.g. < 6 inch depth) are widely available from a various vendors. “Pogo-stick”-type coring devices patterned after prototypes designed by CRREL (Fig. C-1). Where suitable cohesive soils are present, a coring device makes it easier and faster to collect uniform, representative increments from a consistent depth interval. For highly compacted or cemented soils, split barrel samplers with a drive shoe

Figure C-1. CRREL Coring Device (CRREL 2004a; CRREL 2009). Note various size coring shoes. Increment cores from a single Sampling unit should be of the same size can be driven manually using a slide hammer or used with a direct push drill rig. They may work well for deeper samples. Graduated plunger devices or coring devices such as an Encore sampler will provide a consistent volume for obtaining increments from conventional deeper cores (e.g. split barrel, Shelby tube, etc.). The diameter of the cores should be adjusted to obtain a total dry weight sample mass of 1 kg to 2 kg for the prescribed number of increments. Keep the tip of your sampling tool sharp. In the case of the CRREL corer the tip is made of stainless steel. Although stainless steel does not react with most analytes, it is not hard and will deform when sampling coarse soils or encountering rocks.

Project planning should provide discussion of sample collection and identify contingency actions in case sample collection difficulties are encountered. Taking a wide variety of implements into the field may help ensure the greatest likelihood of successful sample collection.

Determining Sample Size and Number of Increments Required

To ensure that the multi-increment sample will not “miss” contamination of concern within the sampling unit, a sufficient number of increments need to be collected. The number of increments required to obtain a representative multi-increment sample and to meet the required level of reproducibility specified in the DQOs, depends on the distributional heterogeneity of analytes within the sampling unit. The number of increments required to represent a sampling unit is not directly related to the size of the sampling unit but depends only on the degree of the variability within the sampling unit. (In statistics, the number of measurements required to characterize a population does not depend on the size of the population, but on the variability of the population.) There is, however, a general correlation between size and variability because a larger sampling unit potentially encompasses greater variability. For example, large sampling units on an impact range may be more likely to contain multiple low-order detonations. In choosing the size of the sampling unit, consider the mode of contamination.

Field studies show that 50 to 100 increments are required to achieve good reproducibility (e.g. %RSD <30) among replicates at active firing ranges where energetic compounds are heterogeneously distributed. Statistical investigations also support this number of increments for acceptable reproducibility (US EPA 2003). Just as increasing the number of discrete samples analyzed from a given area reduces the variability of the estimated mean concentrations of the area, increasing the number of increments for a multi-increment sample reduces the variability of the estimated mean concentrations among replicate multi-increment samples. However, increasing the number of increments above 100 provides only marginal improvement in precision in most cases.

The number of increments must be balanced with the mass of each individual increment to yield a total sample mass that is sufficient to overcome the compositional heterogeneity of the soil (Table C-1). Adequate total sample mass for typical soil-size particles (< 2 mm) has been empirically demonstrated to be 1 to 2 kg (based on analyses of explosives).

The number of increments per unit area should be the same for sampling units that will be compared directly to each other, or to the same decision criteria. This will help assure that the results being compared have the same precision from the different sampling units. It also will support application of the precision determined by replicate sampling of one sampling unit to similar units that were sampled at the same increment spacing.

Table C-1. Number of increments collected using different coring device diameters to obtain a given sample mass. Highlighted in yellow is the optimum range (Walsh 2009).

Corer Diameter (cm)	Sample Mass* (g)		
	1,000	1,500	2,000
	Number of increments to reach sample mass (g)		
1.00	340	509	679
1.25	217	326	435
1.50	151	226	302
1.75	111	166	222
2.00	85	127	170
2.25	67	101	134
2.50	54	81	109
2.75	45	67	90
3.00	38	57	**75**
3.25	32	48	64
3.50	28	42	55
3.75	24	36	48
4.00	21	32	42
4.25	19	28	38
4.50	17	25	34
4.75	15	23	30
5.00	14	20	27
* Assumed: Dry bulk soil density = 1.50 g/cc, increment core length = 2.5 cm			

Multi-increment Collection Design

The systematic random sampling design is best suited for multi-increment sampling. Using this technique, uncertainty in the data can be quantified by collecting replicate samples. Other sampling designs and probabilistic sampling schemes are described in the EPA guidance document QA/G-5S (US EPA 2002).

The systematic random approach is the most commonly used and most reproducible sampling pattern (Fig. C-2). The key steps for collecting this type of sample are:

- Sub-divide the sampling unit into uniform grid cells, 100 cells if you want to take 100 increments.
- Randomly select a single increment collection point in an initial grid cell.
- Collect increments from the same relative location within each of the other grid cells.

When collecting replicate samples, randomly select a different starting point in the first cell and build a sample with increments from that relative position in each grid cell.

This process is quite straightforward in a square- or rectangular-shaped sampling unit. When the shape of the area to be sampled is irregular, a systematic random sample can still be collected as shown in Figure C-3. The sampler walks along lanes with defined spacing and collects increments at a specified interval. An explanation of how to determine sample spacing in this case is discussed below.

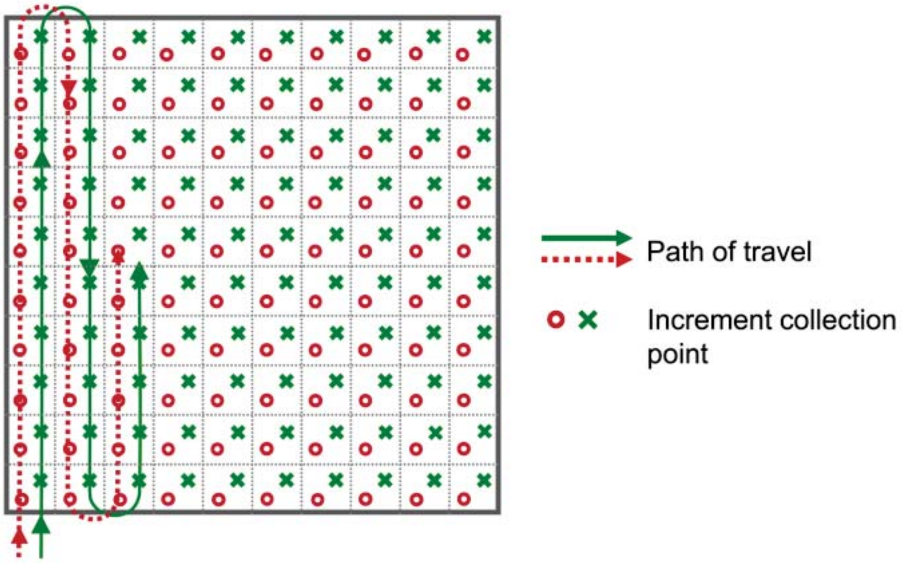


Figure C-2. Systematic random sampling pattern for collecting two (replicate) 100-increment samples in a square sampling unit.

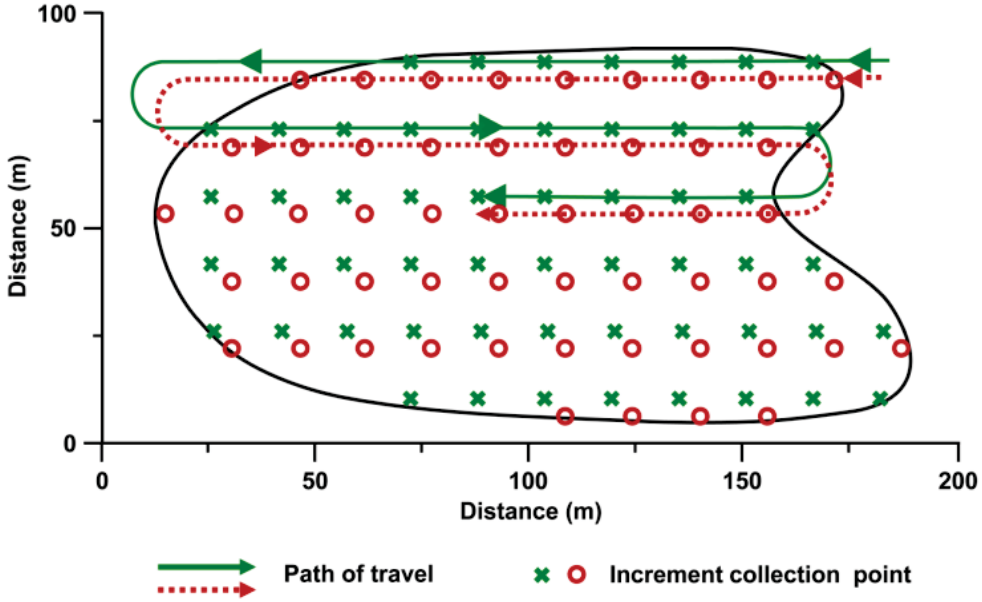
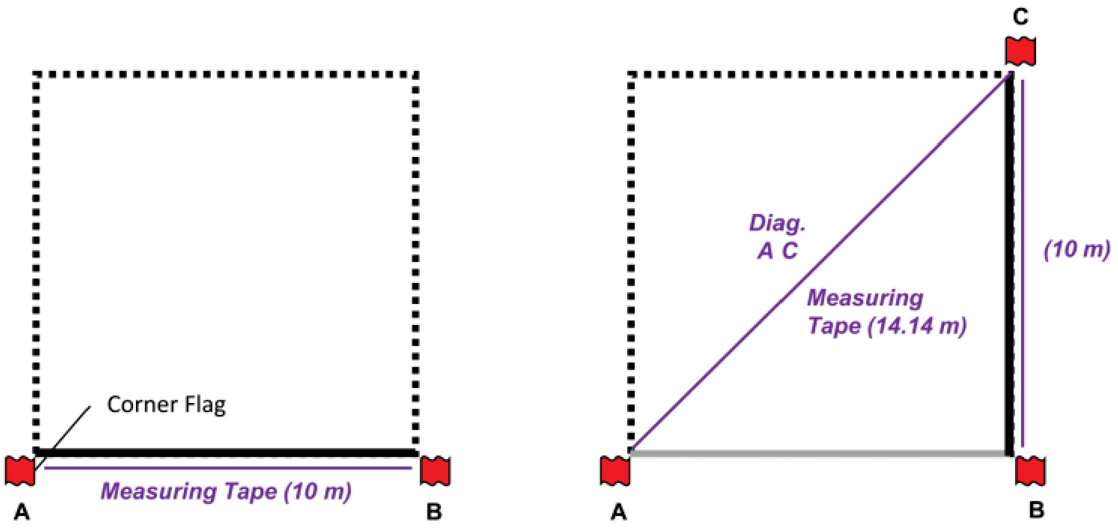


Figure C-3. Pattern of systematic random sampling for collecting two (replicate) 50-increment samples in an uneven-shaped Sampling unit, located within the solid black line.

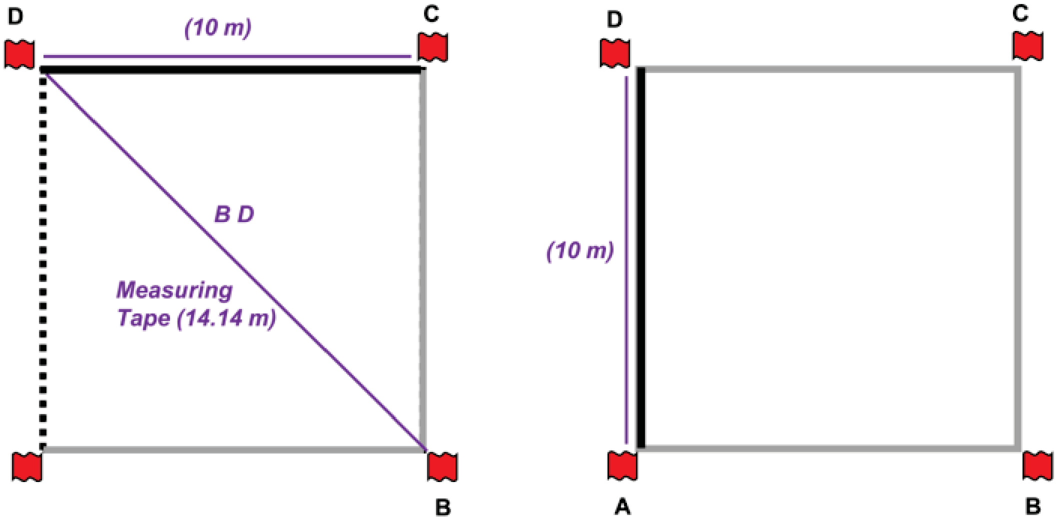
Setting up the Sampling unit

Establish Sampling unit Corners.

We describe here how to establish the corners of a square sampling unit, using a 10 × 10-m sampling unit as the example (Fig. C-4); this is easily modified for any rectangular shape. Step 1: Place a flag (or painted lath) at Corner A and use either a measuring tape or a rangefinder (for larger Sampling units) to establish a baseline 10 m in length to the second flag at Corner B. Step 2: Swing the tape 90° to get an orthogonal side 10 m from Corner B to the approximate location of Corner C. To verify perpendicularity and the correct position of Corner C, use a second tape (or rangefinder) on the diagonal from Corner A to Corner C, calculating the appropriate diagonal length using $AB^2 + BC^2 = Diag^2$ (in this case, the diagonal equals 14.14 m). Mark the position of Corner C where the two tape end points from Corners A and B coincide. Step 3: Move the tape used to measure the diagonal to Corner B and use the same principle and two tapes, diagonal from Corner B and 10 m from Corner C to establish Corner D, maintaining the length of BD equal to 14.14 m. Step 4: Check (and adjust) the location of Corner D by verifying the length from Corner A to Corner D is 10 m (in this case).



Step 1. Establish baseline. **Step 2. Establish first orthogonal line.**



Step 3. Establish Corner D. **Step 4. Verify length of second orthogonal line.**

Figure C-4. Steps to layout a rectangular sampling unit. The side being defined is shown as a thick black line. Positions of the measuring tape used to define corner locations are shown as thin purple lines.

Determine Lane Spacing and Markers

The next step is to determine the number of lanes within the sampling unit and the increment spacing per lane to collect the proper number of sample increments. Our goal is to develop a pattern with evenly spaced sampling points. The following describes an approach to design this pattern.

This example determines sample spacing based on the assumptions:

- the sampling unit is a 10 × 10-m square,
- a systematic-random sampling pattern, and
- at least a 50-increment sample.

First determine the square root of the number of increments: $\sqrt{50} \cong 7.07$, then divide the length of a side in the Sampling unit by the square root you just calculated: 10 m / 7.07 = 1.41 m. This calculation indicates that the distance between sampling lanes should be 1.41 m. However, marking lanes every 1.41 m would result in (10/1.41) or 7.1 lanes. Although a 7.1 × 7.1 division does provide 50 sampling cells (one for each increment), the number of lanes must be a whole number. In this case, a good choice would be to have seven lanes (1.42 m wide) along one axis, and collect eight soil increments along each lane at 1.25-m spacings (10 m/8 = 1.25 m). This design provides 56 cells a few more than our target of 50-increments (Fig. C-5). The size of other sampling units and the number and placement of increments can be estimated in a similar way.

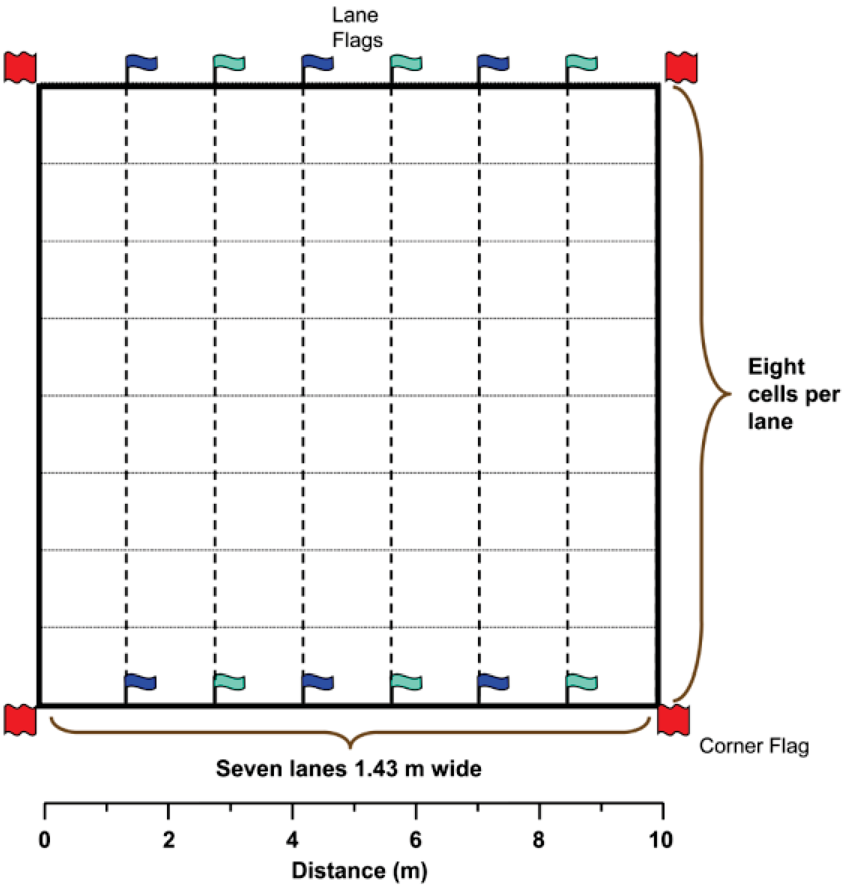


Figure C-5. Sampling unit divided into seven lanes with eight cells in each lane. Placing alternating colored flags at the intersections of lanes helps with visualizing the walking path.

Once the number of lanes is established, mark the division between lanes with a pin flag or some other indicator. Plastic-stemmed flags are better than metal-stemmed pin flags as they do not interfere with magnetometer readings. It is helpful to use flags with two colors and alternate them to help samplers walk the correct path (Fig. C-5).

Collecting the Sample

Once the sampling unit and lane positions are marked, the first step in collecting the sample is to determine your first increment collection point within the starting cell. This must be done randomly, using a random number generator, a calculator or a die. Two numbers are needed to define the sample location within the cell (an X and a Y coordinate starting from a corner of the sampling unit). It is best to choose a manageable number of divisions for the cell. In our example, the cell dimensions are 1.42 m in the X direction and 1.25 m in the Y direction. You could choose to use six divisions in each cell, which in this case for the X direction would be 0, 0.28, 0.56, 0.85, 1.14, 1.42 m, and in the Y direction would be 0, 0.25, 0.5, 0.75, 1.0 and 1.25 m. (A number on the die can be used to represent one of the choices, e.g. 1 = 0, 2 = 0.5, and so on.) Figure C-6 shows an example in which the lower left-hand corner is the starting cell, the origin position within that cell (x=0, y=0) is its lower left-hand corner, and the collection position for the first increment is x= 0.85 and y= 0.25 as shown by the green “×” symbol.

After collecting the first increment at that position, all subsequent increments should be positioned as close as possible to the same location within each cell as illustrated by the other green “×” symbols in Figure C-6. Using the flags as aids, start in one corner of the sampling unit and collect increments up and back along the marked lanes as shown schematically in Figure C-6. Offset the location of an increment, by as little as possible, if you encounter a rock outcrop or tree roots. Figures C-2 and C-3 show how to take two MI samples from the same sampling unit. Here again, randomly choose your starting sampling point and then collect increments from the same location within each cell.

Another useful aid to help samplers stay in the proper lane is a wooden lath with colorful flagging attached. One “end of lane marker” is used on each end of the sampling unit (Fig. C-7). Position the lath at the far end of the upcoming sampling lane. When you reach the end of that lane, move the lath two lanes over before collecting down the adjacent lane, as shown in Figure C-7. End of lane markers are especially helpful for sampling sampling units with uneven terrain or tall vegetation but we use them routinely as they save time and help the samplers follow their lane.

Sampling in teams of two allows one person to collect the soil increments while the other holds the sample bag and keeps count of the number of increments (Fig. C-8). A small mechanical counter is handy for keeping track of the number of increments, as it is easy to lose count.

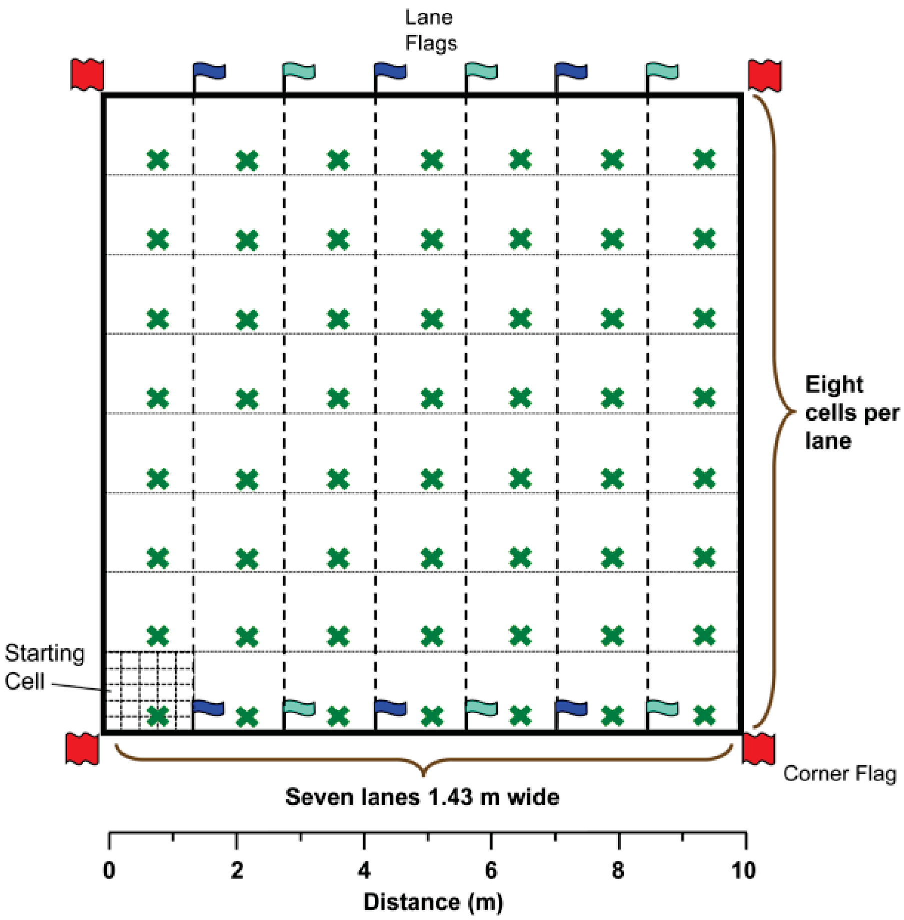


Figure C-6 Systematic random collection pattern for a 56-increment sample in a 10 x 10-m square sampling unit. Increment locations designated by the green x symbols. Increments should be collected at the same relative position within each collection cell.

Results will be more consistent if each person does the same job for all replicates. You do not need to clean the sampling tool between increments within a sampling unit or between replicate samples within a sampling unit. The tool must be decontaminated before sampling a new sampling unit. Rinseate blanks can be taken between sampling areas but the concentration in these blanks is typically negligible.

We use clean polyethylene sampling bags rather than sample bottles for MI samples (Fig. C-8). Label the outside of the sample bag and the tag that will go on the outside of the sample bag, and record in a logbook sample information such as date, site, sampling unit, # of increments, increment diameter and depth, replicate #, and name of sampler. Decide upon and document a labeling and numbering scheme before going to the field. Double bag the sample after collecting to reduce cross-contamination during sample storage and shipment. A good procedure is to use a cable tie to close the bag and attach the identification tag. Photos are extremely helpful and provide visual documentation. A list of sampling supplies is in Table C-2, which is positioned at the end of this Appendix.

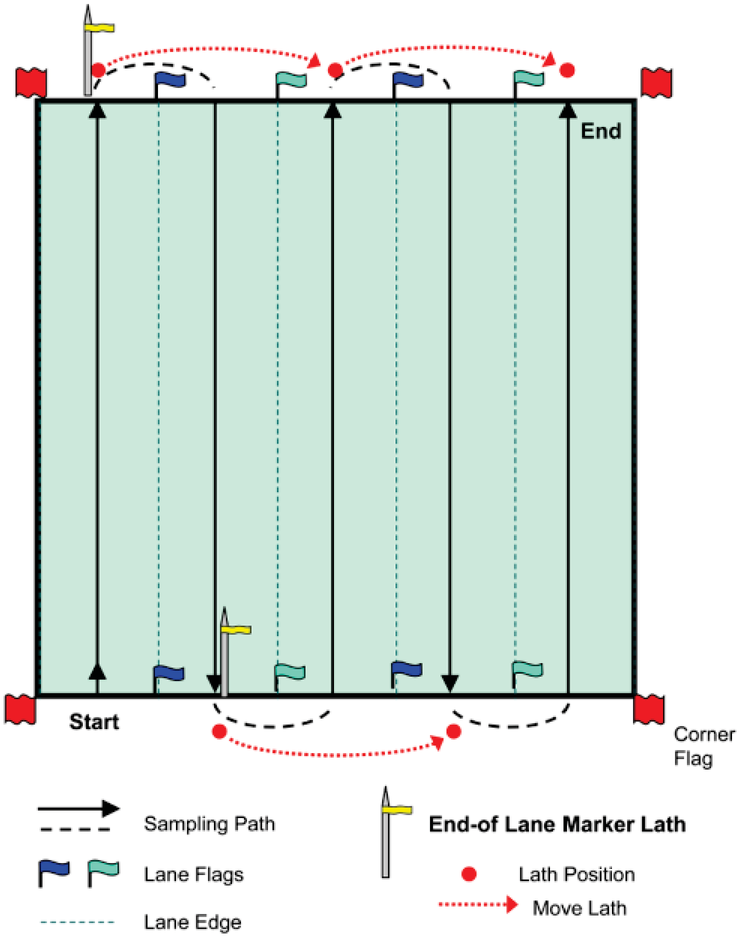


Figure C-7 Schematic of a typical walking path traversed while collecting a multi-increment sample in a square sampling unit. Increments are collected along the solid black line, traveling to the next lane is shown as a dashed black line. A marker lath is used on each end to help accurately position increment locations. The lath is moved to every other lane on each side.

Figure C-8. Photo of a two-person team collecting a multi-increment sample.

Note: Once collected in the field, it is tempting to split the samples and only send a small portion of each sample to the laboratory. Do NOT split the sample. Hewitt et al. (2009) studied the magnitude of field splitting error and found it to range from 4.7 to 120% with a median value of 43.1%. Such a high error necessitates shipping the entire 1 to 2 kg sample to the laboratory for processing and analysis.

Additional Considerations for Irregular Shaped Areas

To determine an appropriate sample spacing for collecting an IS from an unevenly shaped sampling unit using a systematic random pattern (e.g. Fig. C-3), you must first estimate the area to be sampled. If known in advance, you can do this prior to arriving at the sampling site with a GIS or air photo. If this is done on site, use a measuring tape or rangefinder to temporarily divide the area into multiple small rectangles and triangular shaped units and determine their individual areas, then sum them to determine the total area, *A*. Next, determine the theoretical length, *L,* that a side would have if the equivalent area were a square by taking the square root of area *A*.

$$L = \sqrt{A}$$

Then, find the increment spacing, *S,* using the same logic as presented earlier for a square sampling unit. This is done by dividing your theoretical "side" length by the square root of the number of increments, *N*:

$$S = L / \sqrt{N}$$

The next step would be to establish an appropriate number of lanes traversing the long dimension of the sampling unit and collecting increments at the spacing just determined. It is important to keep the increment spacing as even as possible throughout the space sampled. The exact number of increments is not as critical as obtaining the minimum number determined by the DQOs. The method described above can also be used to determine sample spacing in rectangular shaped sampling units.

Collecting samples around ruptured rounds

Because a partially detonated bomb, a dumpsite, a ruptured munition, or other ordnance item will have contaminant concentrations significantly higher than the other areas in a site, they should be sampled as separate sampling units. The sampling unit should encompass the area of any visible residue chunks and any surface discolorations. EOD personnel or UXO technicians should remove any chunk explosives (these should be weighed separately) so they are not inadvertently incorporated into the sample. To prevent cross contamination, samples collected where chunk residues were present should be double bagged and segregated from other samples during transportation, storage, and laboratory processing (US EPA 2006, page A-13).

When ordnance disposal (blow-in-place) coincides with site characterization activities, pre- and post-detonation multi-increment samples can help establish if residual MC is pre-existing or due to the blow-in-place operation, or both (Pennington et al. 2008; USACE 2007). This is more likely at the RI stage during intrusive operations, and during removal and remedial actions.

How to deal with vegetation in a sample.

Appendix A of EPA Method 8330B recommends including surface vegetation and plant matter in the sample increments from active ranges. However, vegetation should be included only if necessary to satisfy DQOs, for example if the study is trying to determine the total amount of a contaminant deposited by airfall onto a recently used range. If vegetation is included, it remains with the sample until it is sieved. During this step the vegetation should be broken in smaller pieces to release trapped particles. The majority of vegetation does not pass through the sieve and therefore is not part of the sub-sample extracted for analysis.

At MMRP sites or other sites where surface vegetation clearly post-dates any contaminant release, vegetation in the sample should be removed during laboratory processing. Note that some types of vegetation, i.e. mosses, can be long-lived. Do not bias your samples trying to avoid vegetation. At MMRP sites, dissolved contaminants may have migrated deeper into the soil, or contaminant particles buried or transported by post-release processes. These factors should be considered and described when delineating Sampling units at MMRP ranges.

Sub-surface sampling

Range characterization studies show that the highest concentrations of energetic compounds are at firing positions, near targets, and where demolition activities are performed (Hewitt et al. 2007, Jenkins et al. 2006) and that most of the energetic residues remain on the surface (Figure C-9). Sub-surface sampling may be needed for ranges where the surface has been physically altered, where energetic residues are found on the surface at high concentrations, and to address human risk concerns when soils are excavated during construction activities. At demolition and disposal and hand grenade ranges, where a common management practice is to periodically fill craters, energetic residues are found at depth. Energetic residues can also be buried when surface soils are removed, redistributed or covered with clean soils. Generally contaminants dissolved by precipitation are not detectable in subsurface soils because they are only present within the small amounts of soil moisture.

The best way to sample the distribution and concentration of energetic compounds in three dimensions has yet to be determined. We recommend taking multi-increment samples, although we recognize that these samples can be difficult and time consuming to collect. Depending on the DQOs depth profiles can be collected in 10-cm intervals down to a depth of at least 30 cm. Sample increments from the same 10-cm depth interval (0–10 cm, 10–20 cm, and 20–30 cm)

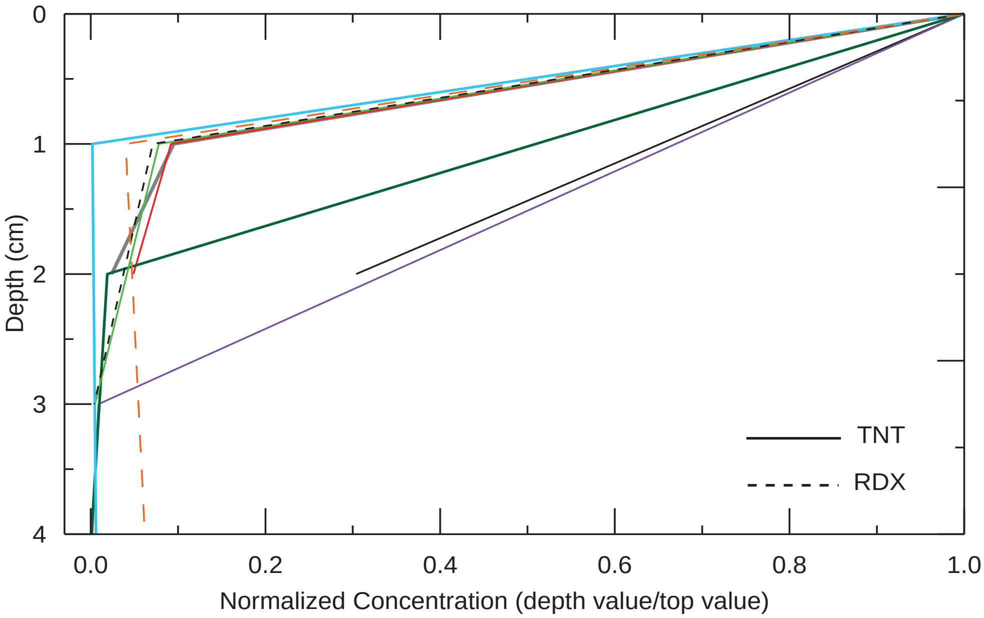


Figure C-9. Normalized profile showing decreasing concentration in energetic compounds with depth directly beneath seven TNT chunks (> 2 cm) found on the surface at Fort Bliss and two chunks of Composition H-6 at 29 Palms. Equivalent samples are shown in the same color.

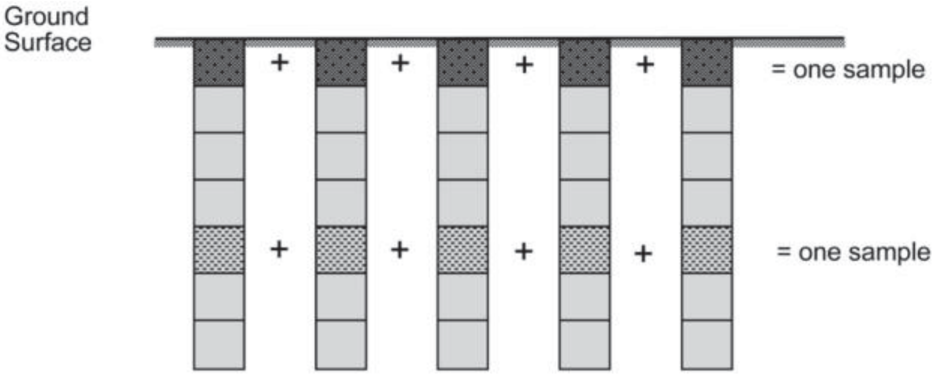


Figure C-10. A schematic showing how increments from equivalent depth intervals are combined into a multi-increment sub-surface sample.

should be combined to produce a multi-increment sample (Fig. C-10). The depth intervals sampled (lifts) need not be 10 cm as in the example given above but can be 2 cm or 30 cm depending on the information required. If only a few depth profiles are combined, the data might be suited for determining the depth to which residues have been mixed into the soil profile but not to estimate the average concentration for a subsurface layer over a large horizontal cross-sectional area. To achieve this second objective, 50 to 100 increments should be collected. For depths below 30 cm, a surface geophysical survey may not be sensitive enough to detect UXO; therefore, down-hole clearance must be performed.

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Table C-1: Soil Sampling Field Kit supplies

Items in **bold** font are essential.

Item Description	Qty*	Purpose	Source / Part Number**
Sampling Tools			
Coring tools		*Obtain soil sample increments*	
Coring tool	(1)		CRREL or Centauri Labs
2-cm-diameter coring bit	1		
3-cm-diameter coring bit	2		
4-cm-diameter coring bit	1		
Support Tools and equipment		*Adjust and repair coring tool*	
Wrench, 9/16"	2	Adjusting lock-nuts	M-C # 5400A18
File, metal, half-round	1	Sharpening ID of coring bit	M-C # 6073A11
Hammer, Dead-blow, 1#	1	Ejecting stuck core	M-C # 6051A31
Pliers, slip joint, 2.25"	1	Installing coring bits	M-C # 5368A14
Pin, 5/16 x 1.25"	1	Spare connecting pin	M-C # 93750A402
Tool, multi-purpose	1	Handy for many tasks	(e.g. Leatherman)
Nuts, Hex, SS, 3/8-24	4	Replacements	
Nuts, Flange, Serrated, SS, 3/8-24	2	Replacements	
Tape Measure, Metric, 3-m	2		M-C # 68025A55
Splitting tools		*Used to subsample cores*	
Putty Knife (Modified)	1	Sharpen one edge, tooth the other	M-C # 3658A13
Putty Knife	1		M-C # 3658A31
Scoops		*Used where corers do not work*	
Stainless #2	2		AMS #428.02 or 427.82
Cleaning Equipment and Supplies			
Equipment		*Durables*	
Stainless steel pads	6		M-C # 7364T75
Brush, parts-cleaning	1		M-C # 7448T67
Bottle, spray, 16 oz	1	For Acetone	M-C # 9864T52
Bottle, spray, 4-L	2	For Water	M-C # 9864T15
or **Sprayer, compression**	1	For Water	M-C # 9864T15
Bottle, HDPE, 4-L	2	Extra water storage	M-C # 7528T36
Pail, 20-L, w/ cover	1	Field waste storage	M-C # 4344T71
Supplies		*Disposables*	
Kimwipes or Techwipes	2		M-C # 7036T12
Acetone		0.5 to 1L should work.	
Sample Collection Materials			
Decision Unit demarcation		*Marking area to be sampled*	
Flagging, PVC stake	24	Color, qty, and size discretionary	FSI # 33702
Wrench, Allen, T-handle,	2	For setting pin flags in hard soil	M-C # 5374A55
Stake, survey, 4-ft	6	Marks corners and active lanes	
Tape measure, 30-m	2	Lay out DU	FSI # 39941
Tape measure, 8-m	2		FSI # 39415
Rangefinder, Nikon 1200 7 x 35	1	11 - 1200 yd	Eagle Optic # RAN-NK-8358
Flagging, roll, pink, orange	2	For marking avoidance items	FSI # 57905

Soil Sampling Field Kit components and supplies (cont.).

Item Description	Qty*	Purpose	Source / Part Number**
Sample Collection Materials, cont.			
Collection		*For field samples*	
Bags, clean, PE, 15"x 15", 6 mil	100	(EPA Level 100 clean)	KNF # 300010-02 (LB 106:1515)
or **Bags, clean, PE, 17"x 12", 6 mil**	100		KNF # 300010-02 (LB 106:1217)
Ty-wraps, black, ss tongue	200	For bags and tags	M-C # 6614K54
Tags, 2.5"x 5" self-laminating	120		Brimar (Ref. Invoice #96886)
Counter, handheld, pushbutton	2	For keeping track of increments	M-C # 1707T5
Personnel Protective Equipment		*Visibility and worker protection*	
Gloves, latex, diamond-grip	20	Hand protection (sized M, L, or XL)	C-P # EW-86231-31, 32, or 33
Vest, surveyors		(High-visibility orange)	
Site-specific (masks, etc.)		Dependent on area of operation	
Documentation			
Book, recording, level	2	Field sample logging and notes	FSI # 49496 (Rite-in-the-Rain ®)
Marker, black, fine-point, permanent	6	Marking bags and tags	(Sharpie)
Marker, black, X-fine point	6	Field book and tags	
Other			
Container, storage, lockable	2	To carry kit	(Rubbermaid Action-Packer, 24-gal)
Locks, keyed-alike	4	To lock the storage boxes	M-C # 1834A36
Water bottles		For personal use	

* Quantities shown recommended for each tool;

** Sources: M-C: McMaster-Carr; AMS: Art's Mfg. & Supply Inc. (http://www.ams-samplers.com/); FSI: Forestry Suppliers, Inc. (http://www.forestry-suppliers.com/); KNF: KNF Clean Room Products, Corp. (http://www.knfcorporation.com/); Brimar: Brimar Industries Inc. (http://www.brimar.com/); C-P: Cole-Parmer, Inc. (http://www.coleparmer.com/); GPL: GPL Laboratories, LLLP; Undesignated items are locally available.