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Guide for Characterization of Sites Contaminated with Energetic Materials

Sonia Thiboutot, Guy Ampleman, and Alan D. Hewitt

February 2002

Abstract: One consequence of the development, testing, and firing of ammunition is the potential contamination of test sites by high explosives, propellants, and pyrotechnics. These energetic compounds pose particular environmental concerns because of their unusual chemical, physical, and toxicological properties. For this reason there is a need to scrutinize past and current defense activities to ensure that they have had no adverse effect upon the surrounding environment. The need for environmentally sound policies, especially within the context of base closures and demilitarization, makes studies of the environmental impact of munitions an increasingly important issue. Moreover, in the future the implementation of environmentally benign defense activities should be encouraged.

All aspects of the life cycle of munitions can affect the environment or human health. Produc-

tion and firing of munitions, demolition procedures, and destruction of outdated ammunition can all cause dispersion of energetic compounds into the environment. These various scenarios lead to different patterns of contamination, thereby creating a need for a general protocol that is applicable in all circumstances. The goal of this guidance document is to collate information relevant to the characterization of sites contaminated by energetic materials. This guide will serve as a reference for future sampling campaigns on sites potentially contaminated with explosives. The characterization of training and firing ranges, demolition, and open burning/open detonation ranges will allow assessment of the environmental impacts of these various operational activities. In addition, it will provide information critical to the establishment of future operational requirements and procedures that minimize environmental damage.

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PREFACE

This report was prepared by Dr. Sonia Thiboutot and Dr. Guy Ampleman, Canadian National Defence Scientist, Defence Research Establishment-Valcartier (DREV), Val-Belair, Quebec, and Alan D. Hewitt, Research Physical Scientist, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire. The authors gratefully acknowledge Dr. Clarence L. Grant and Dr. Thomas F. Jenkins for their review of this manuscript.

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ABBREVIATIONS

ACN	acetonitrile
2-ADNT	2-amino-4,6-dinitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
AP	ammonium perchlorate
2,4-DANT	2,4-diamino-6-nitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
DNB	dinitrobenzene
DND	Department of National Defence, Canada
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
3,5-DNA	3,5-dinitroaniline
ECD	electron capture detector
EIA	enzyme immunoassay
EM	energetic materials
FAC	field analytical chemistry
GC	gas chromatography
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	high performance liquid chromatography
KTA	key technical area
MHT	maximum holding time
MS	mass spectrometry
NB	nitrobenzene
NC	nitrocellulose
NG	nitroglycerine
NQ	nitroguanidine
2-NT	2-nitrotoluene
3-NT	3-nitrotoluene
4-NT	4-nitrotoluene
OB/OD	open burning/open detonation
PETN	pentaerythritol tetranitrate
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
SPE	solid-phase extraction
SPME	solid-phase microextraction
2,4,6-TAT	2,4,6-triaminotoluene
tetryl	2,4,6-trinitro-phenylmethylnitramine
TNB	trinitrobenzene
TNT	trinitrotoluene

Guide for Characterization of Sites Contaminated with Energetic Materials

SONIA THIBOUTOT, GUY AMPLEMAN, AND ALAN D. HEWITT

1 BACKGROUND

One possible consequence of munitions development and testing is the potential contamination of the environment by the ingredients of high explosives and propellants. Despite the potential for widespread contamination, there continues to be an operational need for deployment of these materials. Testing and training with conventional weapons on ranges is a necessary function for maintaining armed services combat readiness. To ensure that such activities can be conducted on a sustainable basis, without long-term ecological damage or risk to human health, range-management practices need to be developed that help minimize the impact of explosives and their by-products in soils, water, air, and biota. No comprehensive study has yet been undertaken to characterize the quantities, transport properties, or outcomes of energetic materials and their by-products in the environment. The task of identifying the extent of contamination becomes complicated when the contaminants are energetic materials. Energetic materials do not behave like other known soil or water contaminants and pose a significant hazard when unexploded ordnance is also present.

The end of the Cold War has resulted in the closure of many military bases and munitions production sites. At the same time, a growing awareness has arisen in environmental issues that has led to the adoption of R&D programs related to the environmental impact of energetic materials. It is within this context that an effort was proposed to develop a protocol for the characterization of sites potentially contaminated by energetic materials. Many sites, such as impact areas, training ranges, demolition, and open burning/open detonation (OB/OD) ranges, used to destroy out-of-specification materials are likely to be contaminated with energetic substances (Jenkins and Walsh 1987, Major et al. 1991, Cragin et al. 1985, Selim and Iskandar 1994, Fellows et al. 1992, EPA Handbook 1993). Former explosive manufacturing sites are also likely to be contaminated with energetic compounds. The handling of wastewater during the manufacturing

process is one major source of contamination. For example, a single TNT manufacturing plant can generate over 1.8 megaliters (480,000 gal) of wastewater per day (Yinon 1999). Only a limited number of studies have been published up to now on the characterization of military testing and training ranges (Ampleman et al. 1998, 2000; Thiboutot et al. 2000; Jenkins et al. 2001).

To assess the extent of explosive contamination, it is necessary to detect and identify explosives and their degradation products in groundwater and soil. The development of a sampling guide for explosives-contaminated sites must therefore include all of the currently accepted practices for sampling, analysis, and management of environmental data. In addition, this sampling guide needs to specifically address relevant aspects of explosives contamination. To accomplish this task, the guide briefly discusses the major issues involved with the characterization of explosives materials in the main body of the text and uses appendixes to provide more detailed descriptions of the procedures and methodologies currently recommended for these tasks.

Definition of Energetic Materials

Conventional weapons use energetic materials (EM) in the form of propellants, explosives, and pyrotechnics. A brief description of each type of EM is given below.

Explosives are classified as 'primary' or 'secondary' based on their susceptibility to initiation. Primary explosives, which include lead azide, lead styphnate, and mercury fulminate, are highly susceptible to ignition and are often referred to as initiating explosives, since they can be used to ignite secondary explosives. Secondary explosives are much more prevalent on military sites than primary explosives. They include trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine or research development explosive (RDX), octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or high melting explosive (HMX), and 2,4,6-trinitro-phenylmethylnitramine or tetryl. Since they are formulated to detonate under specific circumstances, secondary explosives are often used as main charges or boosting explosives. Secondary explosives fall into two main categories: (1) melt-cast explosives, based primarily on TNT, and (2) plastic-bonded explosives (PBX), which consist of a polymer matrix filled with a crystalline explosive such as RDX. Secondary explosives can also be classified according to their chemical structure. For example, TNT and trinitrobenzene are classified as nitroaromatics, whereas RDX and HMX are nitramines. The physical and chemical properties of nitroaromatics and nitramines are presented in Table 1 (Walsh et al. 1995).

Table 1. Physical and chemical properties of nitroaromatics and nitramines.

Analyte	Molecular weight	Melting point (°C)	Boiling point (°C)	Water solubility (mg/L)	Vapor pressure at 20°C/torr
TNT	227.13	80.1–81.6	240 (explodes)	130 (20°C)	1.1×10^{-6}
RDX	222.26	204.1	(decomposes)	42 (20°C)	4.2×10^{-9}
HMX	296.16	276–280	(decomposes)	5.0 (25°C)	3.3×10^{-14}
TNB	213.11	122.5	315	34 (20°C)	2.2×10^{-14}
DNB	168.11	89.6	300–303	460 (15°C)	3.9×10^{-3}
Tetryl	287.14	129.5	(decomposes)	80	5.7×10^{-9} (25°C)
2,4-DNT	182.15	70	300 (decomposes)	270 (22°C)	2.2×10^{-4} (25°C)
2,6-DNT	182.15	64–66		206 (25°C)	5.6×10^{-9}
2-ADNT	197.17	176		2,800	4×10^{-5}
4-ADNT	197.17	171		2,800	2×10^{-5}

Propellants include both rocket and gun propellants. Most rocket propellants consist of a rubbery binder filled with ammonium perchlorate (AP) oxidizer and possibly powdered aluminum as fuel. Propellants may also be based on a nitrate ester, usually nitroglycerine (NG), nitrocellulose (NC), or a nitramine such as RDX or HMX. Gun propellants usually are single based (e.g., NC), double based (e.g., NC and NG), or triple based (e.g., NC, NG, and nitroguanidine [NQ]). Single-based propellants may also contain 2,4-dinitrotoluene (2,4-DNT).

Pyrotechnics include illuminating flares, signaling flares, colored and white smoke generators, tracers, incendiary delays, fuses, and photoflash compounds. Pyrotechnic flares are typically composed of an inorganic oxidizer and metal powder in a binder. Illuminating flares contain sodium nitrate, magnesium, and a binder. Signaling flares contain barium, strontium, or other metal nitrates. Smoke generators are mainly composed of red and white phosphorous, and colored smoke contains organic colorants.

Improper disposal practices and incomplete detonation of munitions can lead to the eventual contamination of soil and groundwater with EM, because they can be leached by rainfall. Propellants are composed primarily of polymeric substances such as NC or nitrate esters such as NG, which require special sampling and analysis techniques. Pyrotechnics, on the other hand, are based mainly on chemicals for which sampling and analytical methods already exist. One important aspect of contamination by pyrotechnics is that the phosphorus can be extinguished if submersed in water. This pyrotechnic can become a significant prob-

lem when dispersed over a wetland environment, since it has a long residence time in water and is very toxic to waterfowl (Racine et al. 1992). The characterization of primary explosives, propellants, and pyrotechnics will not be covered in this guide. Guidance for characterization of propellant contamination will be addressed when future R&D work has identified appropriate sampling and analysis methods for these particular compounds.

This guidance document is targeted at the characterization of secondary explosive compounds in soil and groundwater, because they represent the major environmental threat. Pertinent information related to safe and effective sampling specific to explosive compounds such as TNT, RDX, and HMX have been assembled in this document. TNT and RDX constitute the largest quantity of secondary explosives used in military applications, because they are major ingredients in nearly every munition formulation (Walsh et al. 1995). Several other organic chemical explosives have also been used in specific munition formulations, including 2,4-DNT, HMX, tetryl, and trinitrobenzene (TNB). While some of these chemicals, such as tetryl, are no longer used in current munitions, residues from their manufacture and use remain at contaminated sites. In addition to the chemicals added to explosive formulations, residues from munitions often contain other compounds such as production impurities or decomposition by-products. For example, military-grade TNT often contains a number of impurities, including 2,4-DNT and other isomers of dinitrotoluene and trinitrotoluene (Leggett et al. 1977). In addition, TNT is highly subject to photo and microbial degradation from which a variety of transformation products have been identified (Walsh et al. 1995). The major impurity in production-grade RDX is HMX, which can be present at concentrations as high as 12% (U.S. Department of the Army 1994). The characterization procedure must address all these co-contaminants and take into account the sensitive nature of these compounds toward biotic and abiotic transformations.

This document represents a guide for any environmental officer or site owner who plans to test sites that are potentially contaminated by explosives. It can also serve as a reference for contractors who plan to carry out the site characterization. It will attempt to describe all aspects related to sampling, extraction, analysis, environmental outcomes, and occupational health and safety when characterizing these particular sites. Lastly, this document can be viewed as a literature survey because it contains numerous citations.

Range Types Classification

Activities such as production, firing exercises, demolition procedures, and the destruction of out-of-date or faulty ammunition lead to the possible disper-

sion of energetic compounds in the environment. These various scenarios lead to different patterns of contamination and therefore define a need for a general guide that is applicable in all cases. We have identified the following general types of ranges that could potentially be contaminated by EM:

- Firing ranges
 - Small-arms ranges
 - Artillery ranges
 - Anti-tank ranges
 - Tank/armored personnel carrier (APC) ranges (battleruns)
 - Grenade ranges
- Explosives demolition ranges
 - Steel cutting ranges
 - Woodcutting ranges
 - Concrete cutting ranges
 - Cratering ranges
- Open burning ranges
- Open detonation ranges
- Open burning–open detonation ranges
- Production sites

2 SAMPLING

The accurate chemical characterization of any contaminated site requires the development and implementation of a comprehensive plan outlining several possible sampling strategies. First, the area of interest must be delineated; this may be an entire site or several defined areas within a site. Then appropriate sampling strategies must be selected for that area. The distribution of contaminants is generally site-specific and will depend upon several factors, including the manner in which the contamination occurred, the physical and chemical properties of the contaminant involved, soil type, the geology, and the hydrogeology of the site.

Safety Procedures

Sampling of potentially EM-contaminated soil should only occur after appropriate safety level clearance of the sampling site. High explosives such as RDX, HMX, and TNT have chemical, physical, and toxicological properties different from common environmental contaminants. The potential for an explosion in particular mandates that a very high level of diligence and care be taken with the design and implementation of the health and safety protocols. Exposure of high explosives to heat, shock, impact, friction, and electrostatic charge can lead to violent reactions including detonation, deflagration, and burning or high-rate decomposition. Moreover, care must also be taken to avoid ingestion or inhalation of explosive particles or vapors, because they are toxic to humans. Special safety procedures have therefore been developed for explosives sampling at contaminated sites. As a final consideration, many military ranges may also contain a significant amount of unexploded ordnance on the surface or buried in the soil. This unique and important risk and its proper management are discussed in Appendix A.

Most firing ranges cover large areas, making a comprehensive soil survey of the site an extremely costly and time-consuming exercise. An alternative approach is to start with a hydrogeological study. Screening of the groundwater provides an initial estimate of the extent of site contamination, since it indicates whether explosives and explosive metabolites have leached into the water table. Groundwater samples are obtained using wells, which should be installed under the supervision of a hydrogeologist. However, no wells should be drilled without proper clearance and specific precautions (level 3 clearance is recommended, see Appendix A). Groundwater screening should be accompanied by a preliminary random survey of composite soil samples. If traces of explosives are detected in

the groundwater samples, a more detailed soil-sampling plan should be implemented.

Sample Collection

The unusual nature of explosives as contaminants must also be taken into consideration for all aspects of the sampling, preparation, and analysis of soil or water matrices. For instance, explosives are solid at ambient temperature, and contamination often occurs as various size particles; they dissolve slowly and sparingly in aqueous solution and possess low vapor pressure (Table 1). Therefore, explosives compounds are only transported through soil once they are dissolved in water. Hence, the highest levels of explosive contamination are most likely to occur directly on or near the soil surface, even at sites that have remained dormant for many years. Nevertheless, the spread of contamination will vary, depending upon the specific explosive and the nature of the soil matrix. In many cases, subsurface soil sampling is needed to delineate the transport pathway or the contamination plume. Moreover, the crystalline nature of explosives and their potential association with munition casing fragments often result in a heterogeneous distribution of contaminant particles in the source region. Several studies have reported on the extreme short-range spatial variability that often exists for explosives in surface soils (Walsh et al. 1993; Jenkins et al. 1996a, 1997a, 1997b, 1997c; Thiboutot et al. 1997). For example, groups of seven discrete surface samples (>500 g/sample) collected within 120 cm of each other were found to range in ratios of the highest to the lowest EM concentration, from 3× to greater than 600×, with a median value of 50× (Jenkins et al. 1996a).

To address larger spatial scales and to highlight the use of composite sampling, another study assessed an area between two suspected hot spots (Thiboutot et al. 1997a, b). For this effort a systematic grid was used to divide the region of concern into fourteen 6-m × 6-m grids, then each grid was further subdivided into four 3-m × 3-m subgrids. Large discrete soil samples (top 5 cm of soil from a circle with a radius of 77 cm) were collected in the middle of the 3-m × 3-m grids. Along with the analysis of the discrete samples, a composite sample was prepared from all four of the subgrid samples. Statistical analysis revealed that the concentration estimates for the grid composites (6 m × 6 m) were generally within 25% of the mean of the four subgrid samples. In summary, these studies have repeatedly shown that if discrete samples were used to estimate an average concentration, the sampling error typically exceeded the analytical error by an order of magnitude. The results have also demonstrated that the homogenization of discrete samples and subsequent combination to form a composite sample lead to the minimization of the characterization problems caused by spatial heterogeneity. This ability to prepare composite samples that accurately represent the

mean of the discrete samples also lowers analytical cost. More detailed information regarding the procedures that should be used for surface and subsurface soil sampling can be found in Appendix B.

As discussed above, explosives will slowly solubilize and then migrate toward the groundwater, leading to the formation of a subsurface plume. Therefore, subsurface sampling on the range should be conducted following the detection of a potential surface source region (hot spot, e.g., >10% to 0.1% EM) and after obtaining clearance for unexploded ordnance. One exception to this protocol is when historical records indicate that EM was buried. In this circumstance, surface source regions may not exist, and subsurface sampling will have to be based on existing information. Once EM has been detected in the groundwater, it will be necessary to determine the size and the direction of the contaminant plume to evaluate the potential for impact on domestic water supplies. When groundwater sampling is being performed to monitor spatial and temporal trends within a contaminant plume, the sampling requirements need to be more stringent than those that could be used initially to screen for the presence of EM. That is, samples taken throughout a groundwater-monitoring program should be collected using a protocol that is designed to obtain groundwater that is representative of the formation. Currently, low-flow (or low stress) groundwater sampling is recommended to meet this more stringent objective (U.S. EPA Region 1 1996, Pennington 1996). Appendix C provides additional information related to groundwater sampling procedures, and Appendix D addresses subsurface drilling operations.

Other Co-contaminants

Sites contaminated with explosives often contain other pollutants. Munitions testing and firing may cause the dispersion of other contaminants in the environment, particularly metals, which form part of the ammunition casing, the ignition system, or the target. Ideally, the characterization of metals (e.g., lead, chromium, cadmium, and zinc) should be conducted in parallel with explosives at ranges where metallic shrapnel is generated and dispersed. In addition, certain munitions also contain mercury, and activities such as open burning of obsolete ammunition may lead to the accumulation of polyaromatic compounds. Consequently, based on a historical review of the range records, it may be necessary to monitor for additional analytes.

Atmospheric Impact

The atmospheric impact caused by firing munitions in training exercises or destroying EM by open burning/open demolition (OB/OD) will not be covered in

this report. However, a reader interested in this information is referred to the following documents: Headquarters U.S. Army Armament test series (1992a, 1992b) and a U.S. Air Force study (1994) that report the analysis of gaseous emissions produced by the detonation of large stockpiles of ammunition. Closed-vessel experiments demonstrate that gaseous emissions were almost completely composed of nontoxic gases. However, further research is needed to establish if the detonation of ammunition in OD operations can result in toxic emissions or lead to the dispersion of toxic levels of heavy metal particulates into the environment.

3 SAMPLE PRESERVATION, EXTRACTION, AND ANALYSIS

To obtain reliable analytical results for soil and water samples contaminated with explosives, the pre-extraction maximum holding time (MHT) for a specific set of conditions, listed in Appendix E, should be observed. Because EM-contaminated sites may contain many types of energetic compounds, the methods and techniques used in the extraction and analysis of samples must be robust. Numerous studies have addressed the optimization of the extraction of explosives from soil and water matrices (Jenkins et al. 1986, Bauer et al. 1986, Liquid Chromatographic Method 1986, Jenkins and Grant 1987, Army Environmental Sciences 1989). The accepted soil extraction procedure is the EPA 8330 sonication method that is covered in Appendix F. Aqueous samples require an initial preconcentration step before analysis to transfer the explosives into the appropriate solvent and to enable measurement in the low parts-per-billions ($\mu\text{g/L}$) range. Two methods are available for groundwater extraction: the salting-out method that can be found in Appendix F and the solid-phase cartridge extraction (SPE) method that is described in Appendix G. In the past, the preconcentration method of choice was the salting-out technique; more recently, the SPE technique (Appendix G) is preferred because of its speed, reproducibility, and ease of use.

For precise determination of the analytes in a wide range of matrices, U.S. EPA Method 8330 is preferred (Grant et al. 1993a, b; Appendix F). When analyzing samples suspected of being contaminated with trace levels of EM in both soil and water matrices, gas chromatography coupled with an electron capture detector (GC-ECD, U.S. EPA Method 8095, Appendix F) provides greater sensitivity than Method 8330 (Walsh and Ranney 1998, 1999). Detection limits for Method 8095 are typically two to three orders of magnitude lower than Method 8330 for comparable sample extracts (Table 2). Furthermore, Method 8095 is applicable to all of the analytes covered by Method 8330 along with NG, PETN, and 3,5-dinitroaniline (3,5-DNA).

Field Screening Methods

Field analytical chemistry (FAC) is a rapidly growing application that allows sample analysis to be performed on site. Traditionally, sample analysis has been undertaken at a remote site, therefore requiring sample transportation and storage prior to analysis. These additional steps represent important delays because days and often weeks elapse before information on the identity and quantities of chemicals in the sample become available, deferring the ability to make vital

decisions with respect to human safety and liability. This is particularly true when explosives are the targeted contaminants. Reliable field methods can reduce the unique hazards involved with manipulating, transporting, and storing samples that contain explosives. Furthermore, distribution of analyte concentrations can be assessed on site in real time, thereby decreasing the total number of samples needed to characterize a site. Nevertheless, laboratory-based instrumentation generally provides more precise and accurate analytical data than most field methods. Thus, samples that demonstrate a positive response in a field test should then be tested with an approved laboratory method for increased precision.

Compound	HPLC	GC-ECD	GC-TID
HMX	1	0.025	0.027
RDX	1	0.0034	0.0094
Trinitrobenzene (TNB)	0.3	0.0016	0.0024
Dinitrobenzene (DNB)	0.3	0.00073	0.012
Tetryl	0.7	0.020	0.0017
Nitrobenzene (NB)	0.3	0.017	NA*
1,4,6-trinitrotoluene (TNT)	0.3	0.0013	0.0016
2-amino-4,6-dinitrotoluene (2-ADNT)	0.3	0.002	0.0068
4-amino-2,6-dinitrotoluene (4-ADNT)	0.3	0.0015	0.0010
2,6-diamino-4-nitrotoluene (2,6-DANT)	0.3	0.00069	0.0054
2,4-diamino-6-nitrotoluene (2,4-DANT)	0.3	0.00068	0.0016
2-nitrotoluene (2-NT)	0.3	0.012	NA
3-nitrotoluene (3-NT)	0.3	0.011	NA
4-nitrotoluene (4-NT)	0.3	0.010	NA

*NA Not available

In summary, field screening methods are generally used to

- Establish safety levels for the manipulation of potentially contaminated samples in relation to the 10% threshold safety limit—colorimetric test or GC method recommended (Appendixes H and I).
- Screen soil or water samples for the absence/presence of explosive compounds before they are sent to the laboratory for quantitative analysis.
- Optimize the efficiency of sampling required to delineate the area and depth of contamination of both the soil and groundwater.

Three types of field analytical methods designed for the detection of explosive compounds—colorimetric, immunoassay, and gas chromatography—are covered in this report. The relative merits and disadvantages of these methods are discussed along with guidelines to enhance effective testing, ensure occupational health and safety, provide accurate and reliable results, and reduce total analytical costs of future sampling campaigns. These field analytical methods are described in detail in Appendixes H through J.

4 ENVIRONMENTAL FATE OF EXPLOSIVES

The behavior of explosives exposed to environmental conditions should be considered when characterizing a contaminated site. The environmental fate of TNT, RDX, and HMX can be attributed to three chemical properties:

1. Molecular structure
2. Water solubility
3. Adsorption to soil particles.

For instance, TNT is a nitroaromatic and tends to degrade by photolysis, while nitramines like RDX and HMX do not. TNT is also more soluble and dissolves more rapidly in water than RDX or HMX (HMX being the least soluble). TNT can degrade into 21 metabolites with various solubilities and toxicities. For example, the aminodinitrotoluenes that result from the photolysis or biodegradation of TNT are much more soluble than the parent compound, but they can covalently bind to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with the organic contents of the soil. Moreover, in soils that contain clays, sorption mechanisms are stronger with TNT and its metabolites than for RDX and HMX, which adsorb very poorly to clay minerals (Pennington and Patrick 1990, Haderlein 1996, Townsend and Myers 1996, Li et al. 1997).

Therefore the relative rates of soil leaching of these three explosives can be explained in terms of the relative water solubilities and adsorption strengths. RDX leaches out faster than TNT, which in turn leaches out faster than HMX. TNT and its metabolites are more soluble than RDX, but their migration is inhibited by strong bonding interactions with soil constituents. On the other hand, HMX has a tendency to remain at the surface of the soils, because it is almost insoluble in water.

Interactions with the soil are an important factor when characterizing explosives in terms of bioavailability and extractability. TNT is particularly difficult to characterize because it is easily reduced to amino degradation products, namely 2- and 4-amino-dinitrotoluene (ADNT), 2,4- and 2,6-diamino-nitrotoluene (DANT), and, under anaerobic conditions, 2,4,6-triaminotoluene (2,4,6-TAT). The characterization of TNT derivatives is important in establishing the overall toxicity, remediation, transport, and extractability of TNT. The adsorption and desorption characteristics of TNT and its metabolites are important physical

factors to consider when assessing the availability of the compounds to microbial degradation and physical analysis. Additional R&D effort is needed toward the development of an optimal extraction method for TNT metabolites that are strongly bound to clay or organic soils.

5 SUMMARY

Explosives represent a threat to human health and to the surrounding environment. They can be spread in the environment all along their life cycle from production to use in training to disposal at the end of their service life. The characterization of potentially contaminated ranges should be conducted; this guide is dedicated to that specific purpose. The unusual properties of explosives and their by-products require special treatment for the effective and safe characterization of explosives-contaminated sites. Characterization of explosives-contaminated ranges must include all aspects of a standard sampling and analysis plan, along with an appropriate amount of quality assurance and quality control. This protocol has been written to cover specific and critical aspects related to the characterization of explosives-contaminated sites. It will serve as a reference to assist the effective characterization of these sites by both minimizing the associated cost and risk and optimizing the information gained.

Site characterization is not intended to hinder the operational activities of defense forces, but rather is meant to assess the environmental impact of such activities. It is hoped that this activity will lead to the implementation of appropriate remedial action and safety precautions during testing and training exercises, thereby lessening the potential for future environmental impacts.

LITERATURE CITED

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APPENDIX A: SAFETY PROCEDURE

In sampling operations undertaken at all sites potentially contaminated with explosive waste, safety precautions must invariably be taken. The first step when planning a sampling campaign on a potentially explosives-contaminated site is to review all the historical information available at the site and to perform a visual inspection of the range. At many potentially contaminated sites, such as firing ranges, there is a high probability that unexploded ordnance is present in addition to soil contaminated by explosives residues. Unexploded ordnance that becomes fractured or ordnance that fails to detonate properly is likely to be one of the main sources leading to leaching of energetic materials (EM) into the environment. Both fractured and unfractured duds present a high risk when carrying out any site investigation or remediation projects. In particular, unfractured duds pose a safety concern since they often are still fused and armed, so they are highly unpredictable.

Specially trained personnel such as ammunition specialists that have the proper expertise are needed to identify and handle unfractured duds. These same specialists are needed to perform a safety clearance. Safety clearances can be performed at three different levels. Level 1 clearance consists of identifying only the surface duds by visual observation of the site. Level 2 clearance consists of screening the top 30-45 cm of soil for duds with the help of a magnetic detector. Level 3 clearance involves completely checking the area of the site to any required depth and establishing that no munitions or explosives at concentrations exceeding 10% are present.

Ideally, a level 3 clearance of a contaminated area should be performed before a soil characterization program or remedial action plan is undertaken. This high-level clearance ensures the greatest safety and also allows the drilling of wells directly on the site. However, this operation is generally uneconomical and physically unfeasible in large firing ranges such as battleruns whereas level 1 or 2 clearance may still provide a safe working environment. In addition, level 3 clearance disturbs the soil profile and it is impossible afterwards to accurately characterize the depth distribution of explosives. No drilling operations should be conducted until level-2 clearance is obtained with the help of the proper equipment such as an electromagnetometer.

Cautious surface sampling can still be achieved after level-1 or 2 clearance operations, but an ammunition specialist or a field engineer must be present at all times during the sampling operation to ensure that proper procedures are followed. When shoveling or implanting grids on the site, the verification by a

specialist of the absence of metallic debris underneath the surface soil must be made with the help of a portable metal detector.

Once site clearance has been granted, several safety precautions still must be observed, because highly contaminated soils can propagate a detonation. The United States has developed a sensitivity testing protocol for determining whether soils contaminated with explosive waste are likely to initiate and propagate, and, if so, how to best handle them. Such sensitivity testing protocol involves many tests; including impact tests, friction and shock gap tests and the deflagration-to-detonation test (capable of measuring the shock of an explosive reaction). The drawback of this protocol is that these tests require relatively large volumes of soil to be excavated and shipped to specially qualified laboratories, often at great expense. In addition, shipping of soils containing reactive levels of explosives is prohibited.

The experience gained by conducting sensitivity tests on many contaminated sites containing different levels of contamination revealed that explosives-contaminated soils could often be treated as normal soils. However, they have also determined that soils containing more than 12% (120,000 mg/kg) secondary explosive by weight are likely to initiate and propagate. As a conservative limit, it is considered that a soil containing more than 10% secondary explosives by weight (100,000 mg/kg) must be considered as explosive and a number of safety precautions must be implemented when sampling and treating these soils and they must not be shipped off site.

It should be noted that concentrations as high as 100,000 mg/kg of secondary explosives are rarely encountered and often a visual inspection will identify the presence of pure explosives in the soil. Recent experience has shown that these high levels are not to be expected in training ranges, since present day military activities tend not to lead to high levels of explosive contamination. Such high levels have, however, been found at old explosive production sites, where production waste was dumped directly in the ground or in lagoons or in areas where open burning of off-spec material was conducted. The slow evaporation of these lagoons may have allowed the accumulation of high levels of explosives in the sediment.

When a site is suspected of being contaminated with high levels of explosives, a preliminary sampling of the worst contaminated area should be carried out. Surface soil samples (0-15cm) only should be taken and no drilling should take place. If shallow depth subsurface sampling is necessary this task should be performed with extreme caution using nonsparking hand augers. Representative composite samples of the worst area should be built and analyzed. This is a good example of where the field methods can be very helpful. Since these tests can be

performed on-site, they provide immediate results to assess any potential risks. The colorimetric method should be employed first, since it is relatively easier to estimate initial concentrations and it is not as selective as the immunoassay tests. High levels of contamination will lead to intensively colored extracts that give an approximation of the dilution factor required to reach the analytical range. A specific protocol for use of the colorimetric methods for high-level samples has been developed (Jenkins et al. 1996b, Hewitt et al. 2001b).

If levels higher than 10% by weight are encountered, additional safety precautions must be implemented. The most important safety precaution is to minimize exposure, which involves reducing the number of workers exposed to the hazardous situation and limiting the duration of exposure on site. To reduce the hazard at explosives-contaminated sites, all mechanical operations should be carried out on materials that have been diluted to a wet slurry. If necessary, water should be added to the soil to achieve the desired moisture content. Water desensitizes the explosive by phlegmatizing it and reducing heat and friction. The drawback of adding water is the possibility of leaching more explosives to the groundwater. However, this is of minimal environmental impact compared with the leaching created by rainfall that has already occurred and ensures the safety of the personnel who will have to manipulate these soils. Other safety precautions that must be taken include the use of non-sparking tools (i.e., non-sparking beryllium tools), conductive, grounded plastics, and no-screw-top bottles that have been developed for the handling of explosives.

If operations involving mechanical shoveling are required, remotely controlled operations offer the best protection. If this is not possible, armored safety glass must be installed in the operator compartment. Drilling operations should only be permitted after removing the soil layer that is contaminated above the safety level. Drilling operations may then be performed. Equipment used during treatment of explosives must have sealed bearings and shielded electrical junction boxes. Finally, the equipment must also be decontaminated frequently to prevent the build-up of explosive dust.

If contamination is above the 10% limit in the soil samples, the contaminated material should be blended and screened to dilute and produce a homogeneous mixture below the limit. This dilution is not a remedial action by itself but a safety measure that will allow the safe handling, storing and shipping of samples. Blending should be carried out precisely in order to calculate the initial concentration that was present in the sample. If the soil were not diluted, the transport of the samples would require the same safety waiver as that required for transporting pure secondary explosive material.

Toxicity Associated with Explosives

In addition to the many hazards associated with energetic compounds, the toxicological aspects of explosives must also be taken into consideration. Secondary explosives are considered carcinogenic and mutagenic. The toxicity of explosive chemicals has been studied extensively by the U.S. Army Biomedical Research and Development Laboratory, and a summary of these investigations has been published (Rosenblatt 1986, Burrows et al. 1989). For an indication of the toxicity of explosives on human health, Table A1 presents drinking water criteria for six explosive compounds at a lifetime exposure cancer risk level of 10^6 (Walsh et al. 1995). The low acceptable threshold criterion for explosives in drinking water indicates high levels of toxicity.

Compound	Criteria (ppb, µg/L)
TNT	1.0
RDX	2.0
HMX	400
2,4-DNT	0.17
2,6-DNT	0.0068
1,3,5-TNB	1.0

For EM-contaminated soils, no general recommendations concerning relevant toxicological properties have been issued. In the United States, the threshold levels in soils are evaluated on a site-by-site basis, depending on factors such as the proximity of the contaminated soils to other locations and the use of surrounding groundwater. Future use of the site is also taken into account. On the other hand, generic criteria for soils and groundwater have been calculated by Daniels and Knezowitch (1994). The same human health-based criteria were calculated using a Canadian model under a DREV contract in 1997 (Rouisse 1997).

As mentioned previously, explosive compounds are not volatile, with the exception of NG, so no specific precautions must be taken to prevent the inhalation of explosive vapor. If NG is a possible contaminant, a strong organic odor will be detected on the site. If this is encountered, an organic vapor protective respiratory mask should be worn at all times during sampling and manipulation of these soils or water samples. For all other energetic compounds, this protective equipment is not needed. However, explosive crystals dispersed in the soil may

be carried away with soil dust, and so a dust mask must be worn by the sampling team when dry sandy or clay type soils are encountered. Protective clothing, gloves and glasses should be worn in all situations to avoid possible dermal contacts with the contaminated media. These recommendations should also be followed in all field screening and laboratory manipulations of samples involving pure explosives or stock solutions.

APPENDIX B: SOIL SAMPLING

Guide:

1. Review of historical records
2. Site clearance
3. Composite sampling of surface soils
4. Vertical profile sampling beneath surface hot spots

Sample Collection

After the sampling site has been cleared to the appropriate safety level, sampling of potentially EM-contaminated soil can proceed. For each discrete or composite sample, a minimum of 500 g of soil should be collected and stored at a low temperature (typically less than 4°C) until it is processed for analysis. Soil samples can be collected using clean metal or rigid plastic tools. The collection tool used often depends on the cohesiveness, coarseness, and moisture of the soil. In general, when sampling a surface, hand-held scoop-shaped devices work well, but a hammer and chisel may be needed for consolidated materials. When shallow-depth sampling is necessary, a metal corer (stainless steel hand corer) that is manually pushed or driven into the ground can be used. Often mechanically driven sampling equipment will be necessary when sampling at depths greater than a meter. All of the equipment that comes into contact with the soil should be carefully wiped with a clean paper towel, washed with acetone, and air dried between sampling locations.

Sample Containers and Storage

Polyethylene bags or glass jars can be used as containers when collecting soil samples in the field and for storage prior to preparing (i.e., drying, sieving, and thoroughly mixing; see Soil Sample Mixing and Subsampling below) for subsampling, since these materials are resistant to adsorption of explosives. Immediately after sample collection, the bags should be cooled and stored in the dark (e.g., in ice coolers). Polyethylene bags are more practical than glass jars during field activities because they decrease the space needed for storing samples, reduce shipping costs, and impart lower risks of breakage during sample transport. Soil subsamples (a portion removed from a well-mixed sample) should be stored in wide-mouth 4-oz amber glass jars with polypropylene- or Teflon-lined caps. Amber glass prevents photodegradation of light-sensitive TNT and other nitroaromatic compounds. The holding time for soil samples is addressed in Appendix E.

Soil Sample Mixing and Subsampling

Because only a small portion (subsample) of the 500-g or larger sample is taken for analysis, the bulk sample has to be thoroughly mixed to allow for representative subsampling. This can be achieved by air-drying, sieving, grinding, and mixing the bulk sample, after subjectively removing vegetation (organic debris) and pebbles. The degree to which a sample is ground (the most time-consuming step) should meet the data quality objectives of the sampling plan. Past experience has shown that soil samples collected in areas contaminated by explosives carried in liquid waste stream may not have to be ground to as fine a particle size as soils collected from an impact range (Jenkins et al. 1996a, 1997b; Walsh and Ramsey, in press).

To air dry at room temperature, the bulk sample should be spread out on a clean flat surface and left in the dark. Typically this step takes about 24 hours, after which the sample should be passed through a sieve. The initial sieving often is based on the definition of soil, which encompasses particles of 2 mm and less, in size. Method 8330 specifies a 2-g subsample, which requires that the bulk sample be ground using a mortar and pestle until it passes through a 30-mesh sieve (0.60-mm). Before grinding it is advisable to screen the bulk sample for high levels of EM. Sample grinding is not recommended when screening results have indicated EM concentrations greater than 1,000 mg/kg. Even when a 20-g or larger subsample is taken, grinding is still recommended to obtain a representative subsample. Before collecting a subsample the ground sample should be thoroughly mixed. Furthermore, it is recommended that the ground sample be spread out in a thin layer and multiple units (30 or more) be taken from random locations to build a subsample (place sample container on scale, add units until desired weight is obtained) of the appropriate weight for the intended method of analysis. Care should be taken when collecting each unit so that particles of all sizes are represented in the same proportions, that is, a visual inspection should establish similar particle size distributions for both the subsample and the bulk sample. An alternative method of obtaining subsamples following grinding is to use a rotatory sample divider.

Analysts are cautioned that subsamples removed from bulk soil samples collected from impact ranges that were air-dried, ground with mortar and pestle, passed through a 30-mesh sieve, and thoroughly mixed, but were not ground to a fine powder, were found to be highly variable in analyte concentrations (Walsh and Ramsey, in press). Walsh and Ramsey (in press) determined that the percent relative standard deviations (%RSD) were typically greater than 50% for sets of twelve subsamples ranging in size from 2 to 50 g. The range in absolute analyte concentration for these subsamples often was on the order of a magnitude, and in

a couple of cases for TNT was two orders of magnitude. It is believed that soil samples collected in impact ranges are very susceptible to segregation error due to the random nature of contaminant dispersion size and shape (i.e., explosions). When portions of these same bulk soil samples from impact ranges were ground to a fine powder (200 mesh) using a ring and puck mill and taking precautionary measures not to generate high temperatures (mill runtimes not exceeding 1 minute), the %RSD for sets of 12 subsamples were frequently below 5%, a level of variation that is not easily separated from the random variation associated with the method of instrumental analysis (i.e., Method 8330 [Walsh and Ramsey, in press]).

Sampling Strategy

The major objective of any sampling plan is to obtain representative samples. This implies that the concentration determined for the sample be representative, i.e., provide a valid estimate of the average concentration for the specified area of concern. Therefore, it is imperative that the area of concern be defined prior to designing a sampling plan. Two typical scenarios are the identification of a suspected surface hot spot and the average surface concentration of EM over a specified area, e.g., a given area within a training range. In the past, sampling plans were written for the collection of discrete samples at a specified number of sampling locations, for each of these cases. However, several studies have shown the futility of this practice, due to extreme short-range spatial variability that often exists for explosives in surface soils (Walsh et al. 1993; Jenkins et al. 1996a, 1997a, 1997b, 1997c; Thiboutot et al. 1997a, b).

Therefore, composite sampling is strongly recommended when characterizing the ground surface at a potentially explosive-contaminated site. In a small area (1 m × 1 m) multiple units (30 or more, each of the same approximate amount) should be randomly collected and placed into a single container. For large-scale areas systematic gridding is useful for establishing sampling nodes, at which, an area of between 3 and 10 m square, should be randomly sampled, by obtaining 50 or more individual increments. Consult *Statistical Methods for Environmental Pollution Monitoring* (Gilbert 1987) for selecting the appropriate sampling design, i.e., grid spacing, to meet various the projects data quality objectives.

With the exception of coupling soil profile sampling with the installation of groundwater sampling points, subsurface (vadose zone) sampling should only occur after the identification of a surface hot spot. Beneath a hot spot it is recommended that a continuous vertical profile be collected over the first meter, with the profile broken into several (five or more) increments, and each incre-

ment processed (dried, sieved, and mixed) for analysis. Beneath 1 m, samples should be collected at least at meter intervals until the groundwater table is reached. The mechanics of subsurface drilling is covered in Appendix D.

APPENDIX C: GROUNDWATER SAMPLING

Guide:

1. Review of historical records
2. Site clearance
3. Monitoring well installation
4. Groundwater sampling for the detection of EM
5. If EM are detected, groundwater contaminant monitoring

When a military range extends over a very large area, sampling the groundwater on a potentially contaminated site can help establish whether an environmental impact exists. Therefore, a sampling plan involving the collection of groundwater samples during the initial phases is not only prudent but may help limit the costs associated with sampling and analysis. When contamination is found in the groundwater, a more detailed sampling plan to identify sources in the surface and subsurface (vadose zone) should be undertaken. All related work concerned with the installation of wells should be conducted with the participation of a hydrogeologist and after explosives clearance has been granted.

In general, there are two principle reasons for sampling groundwater: to detect the presence of a contaminant or to monitor contaminant concentrations on temporal and spatial scales. When sampling groundwater for energetic materials (EM), dedicated or disposable systems are more suitable for a surveillance program than the re-use of equipment following extensive cleaning procedures. When the principle objective is to establish the presence or absence of explosives, sampling can be performed using a variety of fairly simple techniques. One of the most common and economical methods is to use a dedicated or disposable bailer. However, when groundwater sampling is being used to monitor spatial and temporal trends within a contaminant plume, the sampling protocol needs to enhance the representativeness of the samples taken from the formation. Low-flow (or low-stress) sampling is recommended to meet this more stringent objective (U.S. EPA Region 1 1996, Pennington 1996).

Purging of the wells is necessary for all groundwater sampling activities because the water within the well casing may be stagnant, degassed, influenced by the screen or casing material, or chemical oxidation may have occurred due to contact with air. It is therefore necessary to purge a sufficient volume of water from the well to ensure that the sample collected for analysis will be composed of water from the formation. Purging may be accomplished using either a pump or a bailer, depending on the objective of the sampling plan (i.e., contaminant detection or temporal and spatial monitoring). When using a bailer, this task is subject-

tive. Typically, three well volumes should be removed before sampling. This volume may or may not be exceeded when using the low-flow procedure that requires that stabilization parameters be used to judge if a sufficient amount of water has been purged from the well. The water retrieved from the purging of the well should be stored until analysis reveals the presence or absence of explosive contaminants. Uncontaminated water can be disposed of directly on the site, but contaminated groundwater should be treated by passing it through an activated charcoal filter prior to disposal.

The low-flow procedure for groundwater sampling requires that groundwater be purged from the well using a pump until specific parameters are stabilized. Moreover, while purging groundwater the flow rate should be controlled so as to limit a water-level draw down. When the sampling depth is less than 25 ft (7.6 m), a suction lift pump can be used; a submersible pump is recommended for greater depths. The stabilization parameters include temperature, conductivity, pH, turbidity, redox potential, and dissolved oxygen levels. Measurements are taken at time intervals (3 to 5 min) or after successive half-well volumes. When three or more of the parameters have stabilized (agree within 10% of each other for three consecutive measurements), sufficient water has been purged from the well and a groundwater sample can be taken. The positioning of the sample inlet (collection point), water quality stabilization parameters, and flow rate should be recorded for each sampling event. Moreover, the sampling team should strive to match each of these parameters during all subsequent sampling events. For monitoring wells where parameter stabilization cannot be obtained, no more than five well volumes should be purged prior to sampling.

A minimum volume of 2 L water should be collected from each well and poured into two 1-L amber glass containers. Groundwater samples should be collected first from the wells expected to be the least contaminated to minimize any cross-contamination when disposable or dedicated equipment is not used. Since concentrations are unknown during the initial stages of a surveillance program, only disposable or dedicated equipment should be used. When a bailer or pump is reused for sampling, it should be decontaminated by rinsing it three times with acetone and three times with distilled water between each well, and a rinsate blank should be taken.

Samples suspected of being contaminated by TNT or TNT derivatives should be stabilized by adding sodium bisulphate (e.g., 1.5 g/L), acidifying the aqueous solution to pH 2 (Jenkins et al. 1995b). If samples are to be preconcentrated using the salting-out solvent extraction method, they must be first neutralized prior to extraction, or incomplete recovery of the amino compounds will result. If preconcentration is to be achieved using solid-phase extraction, neutralization is not

necessary. Depending on the preconcentration method used, a sufficient volume of water must be collected to obtain the required number of replicates and to ensure quality assurance/quality control. The salting-out method requires 770 mL per sample, and the solid-phase extraction requires 500 mL per sample.

APPENDIX D: BOREHOLE DRILLING

Guide:

1. Review of historical borehole records
2. Site clearance
3. Mechanical drilling

Borehole Drilling and Soil Sampling

The local stratigraphy of the site is first determined by examining the log-book of existing boreholes (typically available from the Department of Environment). The thickness of unconsolidated material can then be assessed. The proposed boreholes and monitoring wells are located taking into account the geology and the topography of the site. Hydrogeologists should be involved at this step to evaluate the direction of groundwater flow and the likely extent of the potential contaminant plume. Once drilling locations have been sited, a level 2 clearance must be obtained prior to positioning the equipment. The drilling depth of the boreholes is defined on-site depending on the observations made from the first drilling.

For soil sampling, a hollow-stem auger or geoprobe is used to drill a borehole. These drilling devices are often equipped with a split spoon or lined core barrel sampler to collect a cylindrical segment of the subsurface soil profile. For each borehole, a well log should identify all geologic formations present in the unconsolidated material. Initial borehole diameter in unconsolidated material should be large enough to allow the installation of 5-cm (2-in.) monitoring wells.

A good subsurface sampling procedure consists of collecting soil cores at intervals of 1.5 to 2.0 m and analyzing the soils using the colorimetric test kits (Appendix H). If contaminated, further analysis by US EPA Method 8330 or 8095 should be carried out. This way, a three-dimensional map may be constructed and a more comprehensive understanding of the contamination on the site is obtained. The down-hole equipment is decontaminated by immersing it in a hot water barrel and by cleaning it with high-pressure steam. In addition, acetone should be sprayed on the core barrel sampler to remove the last traces of explosives, followed further by spraying with distilled water.

Monitoring Well Installation

Wells required for subsurface sampling should be drilled by contractors who specialize in contaminated site assessment. Nested wells with 2–4 m depth levels can be used to establish the contaminant profile, but frequently only a single

observation well equipped with a 1.5- to 2.0-m screen is installed at each monitoring point. The maximal depth of drilling is related to the depth of the groundwater at the specific site. The well's components (well casing, joints, screen, filtering pack, expansive cement, cement/bentonite mix or bentonite silt, protective casing), its dimensions, and its installation must be in accordance with ASTM-D5092-90. Installation of the wells is also described in the Natural Attenuation Protocol (Pennington 1996). No other seal material than those required by the guideline or by the standards should be used in the space between the permanent well casing and the borehole wall. The permanent casing and screen of the well should be made of PVC with 1.5- to 2.0-m well screens. Well elevation must be established from the top of the PVC permanent casing. The borehole locations, depth of drilling, local geological stratigraphy (drilling log), identification of the drilling method used, and the specifications related to the installation of the well are then recorded. A protective casing with locks should be installed on each well. This is intended to protect the well from outside contamination as well as from mechanical shock. Additional protection can be gained by installing a concrete pad at the surface around the wellhead.

APPENDIX E: SAMPLE CONSERVATION: MAXIMUM HOLDING TIMES

Soil/Sediment Samples

For soil samples, Method 8330 specifies a maximum pre-extraction holding time (MHT) of 7 days in the dark at 4°C for nitramines and nitroaromatics. However, studies have shown that nitramines are stable over an eight-week period when held at 4°C in the dark, and that nitroaromatics were stable for the same period when frozen (Grant et al. 1993a, Jenkins et al. 1994). Therefore, if agreed upon by the parties involved, soil samples can be held beyond 7 days; if stored in the dark and frozen, for an additional 7 weeks prior to extraction.

Water Samples

For water samples, Method 8330 specifies a maximum pre-extraction holding time (MHT) of 7 days in the dark at 4°C for nitramines and nitroaromatics. Studies have evaluated the pre-extraction holding times for nitroaromatic and nitramine explosives (Maskarinec et al. 1991, Grant et al. 1993b) and the preservation of water samples (Jenkins et al. 1995b). The first two studies demonstrated that an MHT of 50 days could be used for both nitramines and nitroaromatics in many types of water samples when refrigerated at 4°C. However, water with active microbial populations (such as surface water) showed significant losses of TNB and TNT within a day or two when refrigerated at 4°C. The preservation study concluded that the MHT for water samples containing nitroaromatics such as TNT, TNB, and tetryl can be extended to at least 28 days by acidification to pH 2 using NaHSO₄ (e.g., 1.2 g/L). Furthermore, the acidification did not affect the stability of nitramines that were already stable over a period of 50 days, with or without preservation. Therefore, all water samples should be acidified to pH 2 (or less) soon after collection. Once acidified, they should be stored in the dark at 4°C. Under these conditions, water samples can be held beyond 7 days, if agreed upon by the parties involved, for an additional 21 days prior to extraction.

APPENDIX F: EXTRACTION AND ANALYSIS: EPA METHOD 8330/8095

Method 8330 and Method 8095 can be downloaded in their entirety from the EPA Internet site www.epa.gov.

The following sections were copied from EPA Method 8330 (EPA Method 1994), to support decisions when using this guide. The only change to the text is the inclusion of Note 2.

A. SOIL EXTRACTION

7.1.2 Soil and Sediment Samples

1. Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile-rinsed mortar to pass a 30-mesh sieve.
2. NOTE 1: Soil samples should be screened by Method 8515 prior to grinding in a mortar and pestle (See Safety Sec. 11.2)
3. NOTE 2: Some soil samples may require that the material is ground to a finer particle size (30 mesh) than what is presented in this method to obtain an acceptable level of homogenization (see Appendix B).
4. Sample extraction
 5. Place a 2.0-g subsample of each soil sample in a 15-mL glass vial. Add 10.0 mL of acetonitrile, cap with Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.
 6. After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant and combine with 5.0 mL of calcium chloride solution (Sec. 5.1.3) in a 20-mL vial. Shake, and let stand for 15 minutes.
 7. Place supernatant in a disposable syringe and filter through a 0.45- μ m Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

B. WATER EXTRACTION BY SALTING OUT

Low-Level Method (salting-out extraction)

1. Add 251.3 g of sodium chloride to a 1-L volumetric flask (round). Measure out 770 mL of a water sample (using a 1-L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.
2. Add 164 mL of acetonitrile (measure with a 250-mL graduated cylinder) while the solution is being stirred and stir for an additional 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.
3. Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipette and transfer it to a 100-mL volumetric flask (round). Add 10 mL of fresh acetonitrile to the water sample in the 1-L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.
4. Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100-mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes, followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase to a 10-mL graduated cylinder using a Pasteur pipette. At this stage, the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram, where it could interfere with the HMX determination.
5. Add an additional 1.0 mL of acetonitrile to the 100-mL volumetric flask. Again stir the contents of the flask for 15 minutes, followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10-mL graduated cylinder (transfer to a 25-mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [Vt] in the calculation of the concentration after converting to μL). The resulting extract, about 5–6 mL, is then diluted 1:1 with organic-free water (with pH < 3 if tetryl is a suspected analyte) prior to analysis.
6. If the diluted extract is turbid, filter it through a 0.45-mm Teflon filter using a disposable syringe. Discard the first 0.5 mL of filtrate and retain the remainder in a Teflon-capped vial for RP-HPLC analysis, as in Sec. 7.4.

APPENDIX G: SOLID-PHASE CARTRIDGE EXTRACTION

Solid-phase cartridge extraction was developed as an alternative preconcentration method for explosives in water (Jenkins et al. 1995a). Briefly, prepacked cartridges of Porapak RDX Sep-Pak, 6 cc, 500 mg (Waters Corporation) are cleaned by placing them on a Visiprep solid-phase extraction manifold (Supelco) and passing 15 mL of acetonitrile through each cartridge at gravity flow. The acetonitrile is then flushed from the cartridges using 30 mL of reagent-grade water. Care is taken to ensure that the cartridges are never allowed to dry after the initial cleaning. A connector is placed on the top of each cartridge and fitted with a length of 0.635-cm (1/8-in.)-diameter Teflon tubing. The other end of the tubing is placed in a 1-L flask containing 500 mL of the sample. The vacuum is turned on and the flow rate through each cartridge is set at 10 mL/min. If the flow rate declines significantly due to partial blocking from suspended material, it is readjusted. After the sample is extracted, the top plug containing the fitted tubing is removed from each cartridge, and 10 mL of reagent-grade water is passed through the cartridge under gravity flow, unless the cartridges are sufficiently blocked to require vacuum. A 5-mL aliquot of acetonitrile is used to elute analytes from the cartridges under gravity flow. The volume of recovered acetonitrile is measured and diluted (1:1) with reagent-grade water prior to analysis.

Solid-phase cartridge extraction (SPE) has several advantages over the salting-out method, including the speed at which a sample can be concentrated and extracted. It is a technique that brings excellent recovery and reproducibility and requires less solvent than the salting-out method. Furthermore, it is inexpensive and easy to use. However, this method does require that the extraction cartridge be cleaned prior to use, and water samples with a lot of suspended solids may need to be filtered. Recently, the SPE alternative has been given preliminary approval for use by the US EPA Office of Solid Waste; it will be issued as Method 3535 (A).

APPENDIX H: COLORIMETRIC FIELD METHODS

There are several field colorimetric methods for detecting explosive contaminants that are present on most military sites. This document covers a visual screening method (Mistral Security, Inc., Expray Kit, Israel) and two spectrophotometric methods (Jenkins 1990, Grant et al. 1991, Walsh and Jenkins 1991, Jenkins and Walsh 1992, Walsh et al. 1993, Myers et al. 1994, Ampleman et al. 2000). All of these EM detection methods result in colored end products that can be easily monitored by visual inspection or with the use of a portable spectrophotometric device. TNT, 2,4-DNT, TNB, RDX, HMX, NG, PETN, tetryl, and picric acid are all detected by using one or a combination of these techniques. This document will focus on the determination of TNT and RDX, because these explosives are the major ingredients in nearly all military munitions. Most sites can be adequately evaluated by employing this approach (Walsh et al. 1993, Table H1). One exception, however, is the investigation of production facilities, where these methods could be used to characterize for 2,4-DNT, TNB, DNB, tetryl, picric acid, and HMX. Moreover, a greater emphasis is placed on the on-

	Total
Installations	46
Samples analyzed	1,155
Samples with detectable explosives	319
Analytes detected:	
HMX	37
RDX	87
1,3,5-TNB	108
1,3-DNB	53
Tetryl	28
NB	0
TNT	209
4-ADNT	21
2-ADNT	54
2,6-DNT	23
2,4-DNT	143
2-NT	0
3-NT	0
4-NT	0

site determination of explosives in soil as compared to water, because of the time and equipment necessary to extract and concentrate explosives from an aqueous matrix.

All of these methods are simple, portable, rapid (especially for soils), use only low-toxicity solvents, work over a large linear analytical range, and have low detection limits. Moreover, the two spectrophotometric field colorimetric analytical methods have shown strong correlations when compared to standard laboratory methods. The major attribute of the visual method is its ability to rapidly screen for the presence and estimate the concentration of EM in soil or on surfaces. The following sections will separately discuss the visual screening methods and the spectrophotometric colorimetric methods.

Visual Colorimetric Screening Method

Simple qualitative and semi-quantitative visual colorimetric tests to screen for explosive residues on-site can be performed using the Expray kit (e.g., available from Plexus Scientific, Silver Spring, Maryland). The Expray kit comes in a small, lightweight (less than 1.4 kg) case that contains three aerosol cans for dispensing chemical reagents and some test paper. To screen surfaces, e.g., range scrap, the first step is to wipe (rub) exposed surfaces with a white sheet of paper (100 test sheets are supplied with the kit, or any white filter paper or cotton swab could be used). For direct analysis of soils (or other materials comprised of small particles), a small quantity (0.5 to 1 g) is placed in the middle of 47-mm glass fiber filter paper and soaked with acetone (approximately twice the volume as weight). The filter paper is folded over and placed on a clean white paper surface. For soil or water sample extracts, a small aliquot (5 μ L) of solvent extract (acetone or ACN) is transferred to a test sheet. Actually, several (6 to 12) sample extracts can be screened simultaneously by carefully arranging the placement of each aliquot on the test sheet.

The next step is to spray the surface of the test sheet, wipe, or folded filter paper, following the kit instructions. If a color appears after application of the first aerosol, then polynitroaromatics (e.g., TNT, TNB, DNT, picric acid, tetryl, etc.) are present. Some of the colors that may appear upon the application of this first aerosol are blue, red, or orange. A bluish color appears when 2,4-DNT or 2,6-DNT is the dominant compound, a reddish-brown color appears for TNT and TNB, and an orange color for tetryl and picric acid. After application of spray from a second aerosol can, the formation of a pink color indicates the presence of nitramines or nitrate esters (e.g., RDX, HMX, NG, PETN, NC, NQ, and tetryl). Application of the first two aerosol cans allows for the sequential detection of both polynitroaromatics and nitramines. If no color has appeared, the sample is

then sprayed with the third aerosol can. If a pink color appears only after applying the third aerosol, then the presence of an inorganic nitrate (ammonium, potassium, sodium, barium, strontium nitrate, or black powder) is indicated.

To estimate the explosives concentrations in soil or water sample extracts, a visual calibration scale can be prepared by spraying 5- μ L aliquots of 10, 100, and 1000 mg/L standards of TNT and RDX that have been placed on separate test sheets (all six aliquots can be placed on the same sheet, but the TNT standards need to be covered when applying the second aerosol). This screening method can detect the presence of 0.05 μ g of explosive analyte when concentrated in a discrete location (5 μ L) on a white surface (test paper or filter paper). Screening sample extracts using this method complements the on-site spectrophotometric colorimetric, immunoassay, and GC methods of analysis (see the following sections and Appendixes I and J) by alerting the analyst to when sample extract dilution is necessary.

Spectrophotometric Colorimetric Methods Extraction

To characterize EM in soil, a 20-g portion of undried or dried material is mixed with 100 mL of acetone containing 3% distilled water. Extraction is performed over a 30-min period facilitated by 3-min intervals of vigorous shaking. Typically, this extraction procedure is sufficient to achieve complete recovery of the EM (Jenkins et al. 1997c). After extraction, the sample is allowed to settle and is then filtered with a syringe filter. Very heavy clays might need more time to settle, but sandy and loamy soils require as little as 3 minutes to settle. To prepare a water sample for analysis, see Appendix G, Solid-Phase Cartridge Extraction. The extracts are then subjected to TNT and RDX screening procedures (see below). It should be noted that these acetone extracts can also be analyzed by Methods 8330 (Jenkins et al. 1997b) and 8095 (Walsh and Ranney 1998, 1999).

TNT On-Site Determination

In the TNT procedure, the initial absorbance of the acetone extract at 540 nm is obtained using a portable spectrophotometer. Potassium hydroxide and sodium sulphite are added to the extract, it is agitated for 3 minutes, and then filtered. Extracts are evaluated visually. If the extract has a reddish or pinkish color, it contains TNT; if it has a bluish color, it contains 2,4-DNT; if it is orange, it contains tetryl; if it has a reddish-orange color, it contains picric acid. The absorbance peak at 540 nm is used to verify the presence of TNT and represents the optimal wavelength to minimize interference from humics. The field spectrophotometer recommended is the HACH DR/2010 Portable Data Logger. The

results of the TNT screening, which often reflect the sum of TNT and TNB concentrations, correlate well with results obtained in the laboratory with Method 8330.

RDX On-Site Determination

On-site analysis for RDX is similar to the TNT colorimetric method. The acetone extract is passed through an anion exchange resin to remove any nitrate and nitrites (this step may be avoided when the site is not suspected of containing detectable levels of these ions). Zinc and acetic acid are then added to the extract; this converts the RDX to nitrous acid. Note that the same reaction will occur with HMX, NG, or PETN because they are all degraded to nitrous acid using this treatment. The test can therefore be used to estimate if any one of these four explosives is present, or their sum. The extract is then filtered and placed in a vial with a Hach Nitriver 3 powder pillow. If the extract develops a pinkish color, it contains at least one of the analytes. Similarly for the TNT detection procedure, quantitative analysis of RDX, HMX, PETN, or NG can be obtained from absorbance measurements. The maximum absorbance of the colored reaction end product is at 507 nm, so the reading should be done at that wavelength. The results of the RDX on-site analysis, which often reflects the sum of RDX and HMX, also correlate well with results obtained in the laboratory.

Advantages and Limitations of Colorimetric Methods

The colorimetric field methods have several advantages. They are rapid (35 min or less per soil sample), use only inexpensive solvents, are very simple to apply, and have shown a strong correlation with results obtained by Method 8330. These methods have a low incidence of false negative responses and low detection limits for most analytes (Table H2).

The main limitation of the spectrophotometric colorimetric method for TNT is that the procedure is subject to positive interference from humic materials (often a yellow hue), particularly if the requirement to visually detect only a reddish hue in the extract after base addition isn't followed. Compared to the immunoassay field screening method, the spectrophotometric colorimetric method requires more in-field manipulations. However, the spectrophotometric colorimetric methods produce more precise results and have a larger analytical range (0–200 ppm) as compared to the immunoassay field screening methods. In addition, the reagents used for the colorimetric methods have a much longer shelf life and are far less sensitive to temperature. Lastly, because of the larger sample size (even larger than 20-g samples could be handled, if desirable) for soils, heterogeneity, especially when dealing with a moist material, is not as large a

variable as compared to the immunoassay method (i.e., 2 g is used for immunoassay).

Compound	Minimum sensitivity (mg/kg)*
2,4,6-trinitrotoluene (TNT)	1
1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX)	1
2,4-dinitrotoluene (2,4-DNT)	0.5
2,6-dinitrotoluene (2,6-DNT)	2.1
2-nitrotoluene (2-NT)	>100
3-nitrotoluene (3-NT)	>100
4-nitrotoluene (4-NT)	>100
4-amino-2,6-dinitrotoluene (4-ADNT)	>100
1,3,5-trinitrobenzene (TNB)	0.5
Nitrobenzene (NB)	>100
Tetryl	0.9
1,3-dinitrobenzene (DNB)	ca. 0.5

*The lowest concentration at which the analyte is distinguishable from a matrix blank by two standard deviations.

APPENDIX I: GAS CHROMATOGRAPHY FIELD METHOD

Gas chromatography has not received wide use for quantitative explosives analysis due to the thermal instability of several of the important analytes. However, Hable et al. (1991) demonstrated that by using a short-fused silica macro bore column (0.53 mm) and a deactivated injection port, and setting high linear velocities for the carrier gas, explosives analysis is possible. Recently a field-transportable gas chromatograph that has many of these features and is equipped with a thermionic ionization detector (TID) was found to be well suited for the estimation of explosives (Hewitt et al. 2001a, b). This detector is selective for compounds containing nitro functional groups, which are present in most explosives. Indeed, all of the explosives cited in Method 8330 (Table 2), plus NG, 3,5-DNA, and PETN, can be detected by GC-TID. The dynamic ranges of detection are analyte-specific and extend over two to four orders of magnitude (e.g., 10–0.01 mg/L) with detection limits often below 0.1 mg/kg (Table 2). Lastly, because this detector is selective, hardware-store-grade acetone can be used, eliminating the need to ship large quantities of this solvent to the field.

Sample Preparation

Water samples are prepared following the guidelines provided in Appendix G, and soil sample preparation follows the guidelines presented in Appendix H. Following extraction, an aliquot of the acetone is then drawn into a disposable plastic syringe and filtered by passing through a 25-mm Millex FH (0.45- μ m) filter that attaches via a Luer-Lok fitting. The filtered extract is directly transferred to a 2-mL amber deactivated glass vial.

Instrumentation

A field-transportable SRI Model 8610C gas chromatograph equipped with a heated (250°C) TID detector, a heated (225°C) on-column injection port, and an internal air compressor can be used on-site for the detection of explosives (Hewitt et al. 2001a, b). Separations were performed on a Crossbond 100% dimethyl polysiloxane column (DB-1), 15 m \times 0.53 mm i.d., 0.5 μ m (coating thickness). Injections of 1 μ L were made manually with a 10- μ L glass syringe (SGE) equipped with cone pointed needle. The oven temperature program, carrier gas and flow rate, detector voltage, and the use of a supply of air to the detector are optimized for the explosives analytes of concern. When the analytes of concern include nitroaromatics, nitramines, and nitrate esters explosives, ultra-high purity nitrogen should be used for a carrier gas with the TID potential set at -3.40 V (Hewitt et al. 2000).

Calibration Standards

Analytical standards containing all of the explosive analytes listed for Method 8330 can be purchased as a mixed stock standard (each analyte 1.00 mg/mL) from AccuStandard, Inc. (New Haven, Connecticut). These commercially prepared stock standards need to be specially prepared using acetone as the solvent. Additional standards, e.g., PETN, NG, and 3,5-DNA, are also commercially available from the same vendor.

Instrument Calibration

Initially a five-point calibration curve should be established. This number of standards allows a nonlinear model (quadratic through the origin) to be used when a linear regression through the origin fails to establish a correlation coefficient (r) of greater than 0.990. Continuing calibration checks should be made after every five samples. If the calibration model fails to establish a concentration within +20% of the expected value for a working standard, recalibration should be performed.

Advantages and Limitations of GC-TID On-Site Analysis

This on-site method can be used to measure several explosives at concentrations well above and below current action levels. Presently this task cannot be achieved using current on-site colorimetric techniques because they lack adequate selectivity, and the enzyme immunoassay methodologies measure exclusively TNT and RDX. The cost of this instrument (less than \$9K), a personal computer (\$1K) for controlling oven temperature and data processing, auxiliary support (tank of nitrogen and electrical power), and initial training makes this method less economical than the colorimetric or immunoassay methods for small projects. However, the GC-TID is economical for larger projects, particularly when knowledge of identity of the explosives is critical.

APPENDIX J: ENZYME IMMUNOASSAY FIELD METHOD

The immunoassay field method is an immunochemical detection method based on a reaction between target analyte and a specific antibody that is quantitated by monitoring a color change or by measuring radioactivity or fluorescence. Immunochemical methods use predominantly antibodies obtained from rabbits, sheep, or goats (for polyclonal preparations) or rats and mice (for monoclonal preparations). The D-Tech enzyme (EIA) test kits for RDX and TNT are commercially available from Strategic Diagnostics, Inc. The test kits are named D-Tech Environmental Detection Systems and were developed in 1994-95 (Teany and Hudak 1994, Teany et al. 1995). The components of the EIA include RDX- and TNT-specific antibodies covalently linked to small latex particles that are collected on the membrane of the cup assembly. A color-developing solution added to the surface of the cup assembly reveals a color inversely proportional to the concentration of RDX or TNT in the sample. RDX and TNT are best measured in the ranges between 0.5-6 ppm and between 0.5-5 ppm, respectively. In the case where concentrations are higher than these upper working range limits, a dilution of the extracts can be made to obtain a result within the effective range of the test.

Extraction

Using the D-Tech system, soils are extracted using an equivalent ratio of soil/acetone (1:5) as for the colorimetric procedure. However, the weight of the soil sample is limited to approximately 2 g of material.

TNT and RDX Screening

A 1.0-mL aliquot of clear acetone extract is transferred into a bottle of buffer solution (bottle 2 in the extraction pack). Then prescribed volumes of the buffered soil extracts are added to the vials containing enzyme-labeled RDX or TNT and antibody-coated latex particles. The mixtures are allowed to stand for 2 min (TNT) and 5 min (RDX) to allow the explosive molecules to interact with the binding sites of the antibodies. A control reference is processed with each analysis. Samples and references receive identical treatment, and both solutions are poured into their respective sides (test or reference) of the porous membrane of the cup assembly. The conjugate solutions are allowed to pass through the membranes, washed and treated with a color-developing solution. The reference side of the cup is used to determine the end-point of the color development, with all readings done at room temperature. The time for complete color development is less than 10 min for TNT and 15 min for RDX, respectively.

The results from the test kits are determined with the DTECHTOR environmental field test meter (EM Science). This device, a hand-held reflectometer powered by a 9-V plug-in battery, measures the amount of light reflected from the surfaces of the color-developed test and reference sides of the cup assembly. Readings are given in percentages and are then translated into TNT- or RDX-equivalent concentrations. This procedure is well documented in the field test kit package.

Advantages and Limitations of EIA Field Screening

The EIA field screening method is excellent for use as a positive/negative field test to discriminate between which samples are to be sent to the laboratory for extraction and analysis and for discriminating between high and low levels of contamination. However, the requirement for multiple tests per sample, particularly for highly concentrated explosives, increases the amount of manipulations and cost per sample. Moreover, the use of a reference test and the reflectometer also represent a limitation since the operator must be very attentive in order to take an accurate reading at the correct time. Erroneous results can easily be obtained if all procedures are not followed carefully. However, this technique does have the advantage of being easy to perform in the field, requiring minimal space to operate. Lastly, the method was designed only for RDX and TNT; therefore, the EIA field testing methods are more selective than the colorimetric methods covered in Appendix H.

REPORT DOCUMENTATION PAGE

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14. ABSTRACT <p>One consequence of the development, testing, and firing of ammunition is the potential contamination of test sites by high explosives, propellants, and pyrotechnics. These energetic compounds pose particular environmental concerns because of their unusual chemical, physical, and toxicological properties. For this reason there is a need to scrutinize past and current defense activities to ensure that they have had no adverse effect upon the surrounding environment. The need for environmentally sound policies, especially within the context of base closures and demilitarization, makes studies of the environmental impact of munitions an increasingly important issue. Moreover, in the future the implementation of environmentally benign defense activities should be encouraged.</p> <p>All aspects of the life cycle of munitions can affect the environment or human health. Production and firing of munitions, demolition procedures, and destruction of outdated ammunition can all cause dispersion of energetic compounds into the environment. These various scenarios lead to different patterns of contamination, thereby creating a need for a general protocol that is applicable in all circumstances. The goal of this guidance document is to collate information relevant to the characterization of sites contaminated by energetic materials. This guide will serve as a reference for future sampling campaigns on sites potentially contaminated with explosives. The characterization of training and firing ranges, demolition, and open burning/open detonation ranges will allow assessment of the environmental impacts of these various operational activities. In addition, it will provide information critical to the establishment of future operational requirements and procedures that minimize environmental damage.</p>					
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