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The Technical Cooperation Program

**SUBCOMMITTEE ON NON-ATOMIC MILITARY RESEARCH AND
DEVELOPMENT**

**WPN GROUP
CONVENTIONAL WEAPONS TECHNOLOGY**

**TECHNICAL PANEL WPN/TP-4
ENERGETIC MATERIALS AND PROPULSION TECHNOLOGY**

**KTA 4-28 FINAL REPORT
DEVELOPMENT OF A PROTOCOL FOR EM CONTAMINATED SITES
CHARACTERISATION
SEPTEMBER 2003**

VOLUME II

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THE TECHNICAL COOPERATION PROGRAM

WPN GROUP – CONVENTIONAL WEAPON TECHNOLOGY

TECHNICAL PANEL 4

ENERGETIC MATERIALS AND PROPULSION TECHNOLOGY

FINAL REPORT Volume II

**PROTOCOL FOR ENERGETIC MATERIALS-CONTAMINATED
SITES CHARACTERIZATION**

September 2003

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ABSTRACT

Military readiness involves the production of energetic materials, their load and pack into weapon systems and the use of these weapons in training and testing exercises. Therefore, one potential consequence of these activities is the contamination of soils or groundwater by energetic materials, either in production sites or in military training or testing area. These energetic compounds pose particular environmental concerns because of their unusual chemical, physical and toxicological properties. All TTCP countries, therefore, face the need to implement environmentally benign defence activities, and this involves the scrutiny of all defence activities to ensure that they have no adverse effects upon the surrounding environment. The needs 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 in each of the TTCP Countries.

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 out-dated 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 the present protocol is to collate all of the information relevant to characterization of sites contaminated by energetic materials. This protocol will serve as a reference guide for future sampling campaigns on sites potentially contaminated with explosives. The characterization of production sites, training and firing ranges, and demolition and open burning/open demolition ranges will allow assessment of the environmental impacts of these various operational activities. In addition, characterization will provide information critical to the establishment of future operational requirements, remediation needs and procedures that minimize environmental damage.

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ABBREVIATIONS

2-ADNT	2-Amino-4,6-dinitrotoluene
4-ADNT	4-Amino-2,6-dinitrotoluene
CGS	Canadian Geotechnical Society
CRREL	Cold Regions Research and Engineering Laboratory
2,4-DANT	2,4-Diamino-6-nitrotoluene
2,6-DANT	2,6-Diamino-4-nitrotoluene
3,5-DNA	3,5-Dinitroaniline
DNB	1,3-Dinitrobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
DRDC	Defence Research and Development Canada
ECD	Electron capture detector
EIA	Enzyme immunoassay
EM	Energetic Materials
EPA	Environmental Protection Agency
EOD	Explosive Ordnance Disposal
ERDC	Engineering Research and Development Laboratory
EL	Environmental Laboratory
FAC	Field analytical chemistry
GC	Gas chromatography
HMX	1,3,5,7-Octahydro-1,3,5,7-tetranitrotetrazocine
HPLC	High pressure liquid chromatography
IAH-CNC	International Association of Hydrogeologists, Canadian National Chapter
ID	Internal diameter
INRS	Institut national de la Recherche scientifique
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
SERDP	Strategic Environmental Research and Development Program
SPE	Solid phase extraction
Tetryl	2,4,6-Trinitro-phenylmethylnitramine
TID	Thermionic detector
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
TTCP	The Technical Cooperation Programme

1. BACKGROUND

One possible consequence of munitions production, 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. Data defining the quantities, transport properties, and outcomes of energetic materials and their by-products in the environment are limited. 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, particularly when unexploded ordnances are also present.

The end of the Cold War has resulted in the worldwide closure of many military bases and munitions production sites. At the same time, a growing awareness of environmental issues has led to the adoption of R&D programs related to the environmental impact of energetic materials. It is within this context that KTA 4-28 was proposed to develop a protocol for the characterization of sites contaminated by energetic materials. In the TTCP countries, 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, 1993). The explosives contamination in some ranges have been assessed and the reader may find more detailed information in the following: Ampleman *et al.*, 1998, 2000, 2001; Dubé *et al.*, 1999; Jenkins *et al.*, 1997b, 2000, 2001; Latreille *et al.*, 2001; Martel *et al.*, 2001; Thiboutot *et al.*, 1998a, 1998b, 2000, 2001a, 2001b, 2002; Walsh *et al.*, 2001. In general, anti-tank and grenade ranges show higher

levels of contamination than wider area such as artillery impact area or batterruns (Jenkins *et al.*, 1997b, 1998, 2001; Thiboutot *et al.*, 1998a). Former explosive manufacturing sites are also likely to be highly contaminated with energetic compounds (Hains *et al.*, 2001). The handling of wastewater during manufacturing is one major source of contamination. For example, a single TNT manufacturing plant can generate over 1.8 megalitres of wastewater per day (Yinon, 1999).

To assess the extent of explosive contamination, it is necessary to detect and identify explosives and their degradation products in groundwater and soil. The establishment of a sampling protocol for explosives-contaminated sites must, therefore, include all of the currently accepted practices for sampling, analysis and management of environmental data (Canadian Council of Ministers of the Environment, 1991 and 1993). In addition, this protocol also 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. These include 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine or research development explosive (RDX), 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine or high melting

explosive (HMX) and 2,4,6-trinitro-phenylmethylnitramine (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 I (Walsh *et al.*, 1995).

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 (NC), double based (NC and NG) or triple based ((NC, NG) and nitroguanidine (NQ)). Single based propellants may also contain 2,4-dinitrotoluene (2,4-DNT). Recently in the USA, AP contamination in the ground water has been a high concern since the Environmental Protection Agency (EPA) might lower the accepted threshold criteria to 1 ppb in drinking water. This mandates that perchlorates should be included in the analytes of concern in the ground water analysis for training area

Pyrotechnics include illuminating flares, signalling flares, coloured 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. Signalling flares contain barium, strontium or other metal nitrates. Smoke generators are mainly composed of red and white phosphorous, and coloured 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. However, characterization of primary explosives, propellants and pyrotechnics will not be covered in this protocol. Polymeric substances such as NC or nitrate esters such as NG found in propellants require special sampling and characterization techniques. Protocols for propellant contamination will, therefore, be addressed when future R&D work has identified appropriate sampling and characterization methods for these particular compounds. However, NG and 2,4-DNT can be analyzed with other high explosive compounds via both the GC and HPLC method. On the other hand, sampling and analytical methods for pyrotechnics compounds already exist and no specific protocol is needed in that instance. One important aspect of soil contamination by pyrotechnics is that the white phosphorous present in flares will be eventually oxidized into phosphoric acid and phosphates that are harmless to the environment at low concentration. However, when white phosphorous is dispersed in a wetland environment, particles can be extinguished and resist oxidation. This pyrotechnic can then become a significant problem because it has a long residence time in water and is very toxic to waterfowl (Racine *et al.*, 1992) that selectively ingest it when feeding upon tubers.

The protocol is, therefore, targeted at the characterization of secondary explosive compounds in soil and groundwater, because they represent the major environmental threat. Pertinent information related to the safe and effective sampling specific to explosive compounds such as TNT, RDX and HMX has been assembled in this document. More recent information regarding the new explosive CL-20 can be found in Larson *et al.*, 2001. 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 munitions formulations, including 2,4-DNT, HMX, tetryl and 1,3,5-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 towards biotic and abiotic transformations.

This protocol 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 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. Furthermore, this document can be viewed as a literature review since more than 150 references are cited.

Range Types Classification

Various types of ranges present the potential of being contaminated by EM. Activities such as production, firing exercises, demolition procedures and the destruction of out-of-date or faulty ammunition lead to the dispersion of energetic compounds in the environment. These various scenarios lead to different patterns of contamination and, therefore, define a need for a general protocol that is applicable in all cases. We have identified the following general types of ranges that are potentially contaminated by energetic materials within the TTCP Countries.

- Firing ranges
 - Small arms ranges
 - Artillery ranges
 - Anti-tank ranges

- Tank/armoured personnel carrier (APC) ranges (battleruns)
- Grenade ranges
- Air to soil bombing ranges
- Mortar ranges
- Explosive 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
- Load assemble and pack 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, burning or high-rate decomposition. Care must also be taken to avoid ingestion or inhalation of explosive particles or vapours, since 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 Annex 1.

Most firing ranges cover large areas, making a comprehensive soil survey of the site an extremely costly and time-consuming exercise. An alternative approach to site assessment 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 that 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 Annex 4). An outside approach for well location is recommended first since it is hazardous or sometimes impossible to drill through a source zone containing high duds or high explosives concentration in soil. 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 must be implemented. Moreover, the installation of wells is considered as a long term investment since they can be used afterward to monitor the quality of the ground water on an annual or semi-annual basis.

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 variously sized particles; they dissolve slowly and sparingly in aqueous solution and possess low vapour pressure (Table I). 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 inactive 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 define the stratigraphy of geologic material and to evaluate as a first approximation the depth of the water table. Subsurface soil sampling allows estimation of the extent (vertical and lateral) of the contamination in soil and the number of samples required to get accurate results, and the mass of contaminants in soil (e.g. in source zone). 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. Therefore, the sampling protocol must include testing procedures that are not biased by the degree of sample heterogeneity. Information regarding soil sampling, spatial heterogeneity and groundwater sampling can be found in Annex 2 and 3.

Subsurface Sampling

As discussed above, explosives will slowly solubilize and then migrate toward the groundwater, leading to the formation of a subsurface plume. Therefore, subsurface sampling of the range should be conducted whenever possible, given the history of the site and the probability of finding unexploded ordnances. There are two situations where the risk level will be higher for subsurface sampling: if levels of pure explosives are suspected to be higher than 10% by weight or if underground UXOs are suspected in the drilling area. In the first case, more details on specific precautions will be addressed later on in this protocol. In the second scenario, the use of an electromagnetometer (type EM-61) will be critical to insure that no high caliber UXO is located on the drilling site. Moreover, locations where there is a low expected probability of UXO present should be selected such as access roads or in dry zones. This will insure the appropriate safety of the drilling team. 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). Subsurface soil sampling should also be conducted whenever contamination is found on or near the surface to establish a depth profile of contamination. Annex 3 provides additional information related to groundwater sampling procedures and Annex 4 addresses subsurface drilling operations.

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 required to characterize a site and, hence, the total cost of the analysis. Nevertheless, laboratory-based instrumentation generally provides more precise and accurate analysis 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.

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 – the colorimetric test (Annex 5) or GC method (Annex 7) is recommended;
- 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. In addition, the precision of the gas chromatography and the colorimetric methods are given in Tables II and VI. These field analytical methods are described in detail in Annexes 5, 6, 7 and 8.

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 (typically aluminium, lead, chromium, cadmium, strontium 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. Activities such as open burning of obsolete ammunition may also lead to the accumulation of polyaromatic or metallic compounds (Thiboutot *et al.*, 2001a). In

some ranges, the past use of depleted uranium will involve the necessary addition of this specific analyte. In some other ranges, radioactive materials might have been used in the past. One example is the MILAN German missile, which included thorium 232 as a tracer. In these cases, the radioactive analytes should also be included. Consequently, based on a historical review of the range record, it may be necessary to monitor for additional analytes. It is, therefore, critical to review all historical data and to interview the sites users (range control, military users) to include all pertinent analytes.

Atmospheric Impact

The atmospheric impact caused by firing munitions in training exercises or destroying energetic materials by OB/OD will not be covered in this report. However, a reader interested in this subject is referred to the following documents: Headquarters U.S. Army Armament Test Series (1992a and 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 non-toxic 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 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) should be observed. The MHT is essentially the maximum retention time for preserved soil/sediment/aquatic samples before loss of the analyte is detected. Detailed information of the MHT under various conditions is critical for determining the shipping requirements, storage time and conditions of the samples in the laboratory. Details related to the sample preservation and MHTs of soil/sediments/aqueous samples are listed in Annex 9.

Because explosives-contaminated sites may contain various energetic compounds, the methods and techniques used in the extraction and analysis of samples must be carefully chosen. Numerous studies have addressed the optimization of the extraction of explosives from water and soil matrices (Jenkins *et al.*, 1986; Bauer *et al.*, 1986, 1989; Liquid Chromatographic Method, 1986; Jenkins and Grant, 1987; Jenkins *et al.*, 1988a, 1988b, 1989, 1993; Army Environmental Sciences, 1989; Walsh, 1990; Bouvier and Oehrle, 1995).

The accepted soil extraction procedure is the EPA Method 8330A (EPA 1998), a sonication method which is described in Annex 10. 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-billion ($\mu\text{g/L}$) range. Two methods are available for the groundwater extraction: the salting out method (EPA Method 8330A) that can be found in Annex 10 and the solid-phase cartridge extraction method (EPA Method 3535A (EPA 2000c)) that is described in Annex 11. In the past, the preconcentration method of choice was the EPA salting out technique; however more recently, the SPE technique (Annex 11) is preferred because of its speed, reproducibility and ease of use.

For a rapid, precise and sensitive determination of the analytes in a wide range of matrices, the EPA Method 8330A is preferred (Grant *et al.*, 1993a; EPA 1998; Annex 10). When analyzing samples suspected of being contaminated with trace levels of energetic materials in both soil and water matrices, gas chromatography coupled with an electron capture detector (GC-ECD, EPA Method 8095 (EPA 2000a)) provides greater sensitivity than EPA Method 8330A (Walsh and Ranney 1998, 1999). Detection limits for EPA Method 8095 are typically two to three orders of magnitude lower than EPA Method 8330A for comparable sample extracts (Table II). Furthermore, EPA Method 8095 is applicable to all of the analytes covered by EPA Method 8330A along with NG, PETN, and 3,5-DNA.

4. ENVIRONMENTAL FATE OF EXPLOSIVES

The behaviour 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:

- Molecular structure
- Water solubility
- Interactions with soil particles.

For instance, TNT is a nitroaromatic that is readily subject to photolysis (Spanggord *et al.*, 1980b, Mabey *et al.*, 1983), while the nitramines, RDX and HMX, undergo photolysis more slowly (Spanggord *et al.*, 1980b; 1982b; 1983b; Burrows, Chyrek, and Noss, 1984; Sikka *et al.*, 1980). TNT is also more soluble than RDX or HMX (HMX being the least soluble). However, the rate of dissolution, especially from formulations of explosives that are frequently used in munitions, cannot be predicated on solubility (Lynch, Brannon, and Delfino, 2002; Lynch *et al.*, 2002). For example, in laboratory tests under the same experimental conditions of particle surface area, temperature, and mixing rate, the order of dissolution rates (fastest to slowest) was TNT, HMX, RDX (Lynch, Brannon, and Delfino, 2002). Furthermore, dissolution rates of explosives compounds are suppressed when the explosives are present in formulations such as LX-14, Composition B, and octol (Lynch *et al.*, 2002). TNT can degrade to products with various solubilities and toxicities. Prominent among these products are 2- and 4-aminodinitrotoluene (ADNT), 2,4- and 2,6-diaminonitrotoluene (DANT), and under strictly anaerobic conditions 2,4,6-triaminotoluene. The aminodinitrotoluenes that result from the photolysis, chemical reduction, or biotransformation of TNT are much more soluble than the parent compound (Layton *et al.*, 1987; Rosenblatt *et al.*, 1989; Spanggord *et al.*, 1980a). All of the aminonitrotoluenes can covalently bind to functional groups on soil organic matter forming variously stable imines and heterocyclic compounds (Thorn *et al.*, 2002; Thorn and Kennedy, 2002; and Thorne and Leggett, 1997). Moreover, in soils containing clays, sorption mechanisms are stronger for TNT

and its metabolites than for RDX and HMX, which adsorb very poorly to clay minerals (Pennington and Patrick, 1990; Haderlein et al. 1996 and Townsend and Myers, 1996).

Therefore, the relative rates of soil leaching of TNT, RDX, and HMX can be explained in terms of their relative water solubility, dissolution rates, and adsorptive properties. RDX leaches faster than TNT or HMX. TNT and its transformation products are more soluble than RDX, but their migration is attenuated by interactions with soil constituents. Consequently, RDX is often found in groundwater to the exclusion of TNT when both were initially introduced at the soil surface. HMX has a tendency to remain at the surface of the soils, because it is almost insoluble in water.

These properties can also explain discrepancies observed in the analysis of samples taken from a site contaminated by Octol (HMX/TNT 70:30). A high concentration of HMX was detected at the surface, but only very low levels of TNT were found (Mailloux *et al.*, 2000). Based upon the discussion above, one could hypothesize the following: TNT is solubilized faster than HMX and can undergo biotic and abiotic transformation to various products. Many of these products cannot be extracted because of their strong association with humic organics present in soils (Thorne and Leggett, 1996; and Thorn *et al.*, 2002). However, HMX being much less soluble in water (6 mg/L versus 130 mg/L for TNT; see Table 1) remains at the surface where it is detected. There is, of course, the possibility that the site was contaminated with additional HMX, further increasing the concentration of HMX at the soil surface, which is quite unlikely. In addition, for high-order detonations, RDX and HMX tend to deposit on the soil more easily than TNT, which seems more readily consumed by the blast (Pennington *et al.*, 2001a and 2001b; Jenkins *et al.*, 2000).

The nature and extent of contaminant adsorption to soils is an important factor influencing EM extraction and migration as well as toxicity and contaminants bioavailability to degrading microorganisms. However, adsorption of explosives is less significant than certain other transport properties. TNT can be reversibly adsorbed by soils (Haderlein, Weissmahr, and Schwarzenbach, 1996; Pennington and Patrick, 1990).

However, reactions that remove TNT from solution and bind TNT transformation products to soil in an unextractable manner can be mistaken for adsorption (Pennington *et al.*, 1995a; Brannon, Price, and Hayes, 1997; Price, Brannon, and Hayes, 1997). Several investigators have reported batch-determined equilibrium sorption coefficients whose isotherms were typical of existing models (Leggett, 1985, Pennington and Patrick, 1990, Ainsworth *et al.*, 1993; Xue, Iskandar, and Selim, 1995; Comfort *et al.*, 1995; Haderlein, Weissmahr, and Schwarzenbach, 1996). However, recent experiments have shown that TNT in batch tests for some soils may not reach nonzero steady-state concentrations in either soil or dissolved phases due to transformation (Price, Brannon, and Hayes, 1995; Myers *et al.*, 1998). Some investigators have tried to eliminate the effects of transformation by using (a) short equilibration times (Myers *et al.*, 1998), (b) poisoning of microbes (Ainsworth *et al.*, 1993; Brannon, Price and Hayes, 1997) and (c) short equilibration times coupled with poisoning of microbes (Pennington and Patrick, 1990). Analysis of solution phase in batch tests may reflect TNT disappearance from solution by both sorption and transformation. Therefore, isotherms based only on solution phase analyses may be misleading. Steady-state conditions for TNT are more likely to be attained in low organic carbon soils, such as those typical of aquifer, than in typical surface soils (Pennington *et al.*, 2001a). Adsorption coefficients for RDX and HMX in soils range from 0 to 8.4 L/Kg (Pennington *et al.*, 1999; Ainsworth *et al.*, 1993; Tucker, Dose, and Gensheimer, 1985; Brannon *et al.*, 1992; Xue, Iskandar, Selim, 1995; Myers *et al.*, 1998; Singh *et al.*, 1998; Sheremata *et al.*, 2001; Townsend and Myers, 1996; Price *et al.*, 2000) and from 0 to <1 L/Kg (Pennington *et al.*, 1999; Price *et al.*, 2000; Brannon *et al.*, 1999; McGrath, 1995), respectively. These low adsorption coefficients suggest that adsorption will not significantly attenuate RDX or HMX during transport through soils. Adsorption and desorption are a function of soil parameters such as organic carbon content, the proportion of clay, sand and silt, cationic exchange capacity, iron, and the porosity of the soil (Pennington and Patrick, 1990; Shaw *et al.*, 2001. Detailed information related to adsorption tests can be found in Annex 12.

Bioremediation of HMX-contaminated soils have been addressed by Dubois *et al.* (2001). RDX is relatively stable under aerobic conditions, but is transformed under

anaerobic conditions (McCormick, Cornell, and Kaplan, 1985; Spanggord *et al.*, 1982; 1983a, Price *et al.*, 2001). Boopathy (2001) reported degradation of HMX to methanol and chloroform under sulfate-reducing, nitrate-reducing, fermenting, methanogenic, and mixed-electron-accepting conditions using an anaerobic digester sludge enrichment culture. Additional studies of the fate of RDX, TNT and its metabolites in sterile and nonsterile soils have been reported (Brannon, Price, and Hayes, 1997; Sheremata *et al.*, 1999, and 2001). Annex 13 provides additional information on microcosm tests used to assess the biodegradation of EM.

The environmental fate of explosives can be easily and rapidly visualized using conceptual models that help to understand the behaviour of the groundwater flow and of the contaminants in soil and groundwater (Hains *et al.*, 2001; Mailloux *et al.*, 2000, 2001a, 2001b). Every characterization study of an explosives-contaminated site should focus on the realisation of a conceptual model. They are also very useful to plan future work or to point out the information needed to better understand the site. They can also be used for numerical modeling purposes (Mailloux *et al.*, 2001a), as well as for scientific and public meetings. Some examples of conceptual models are given in Annex 14.

5. CONCLUSION

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 in TTCP Countries; this protocol 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 a 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 in 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 defence forces, but rather it 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. The large volume of collaborative R&D work described in this report will better help TTCP members to pursue operational activities in an environmentally responsive manner.

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ANNEX 1**SAFETY PROCEDURES**

In sampling operations undertaken at all sites 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 any 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 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 are often still fused and armed; they are, therefore, highly unpredictable.

Specially trained military personnel, such as ammunition specialists that have the proper expertise, are needed to identify and handle unfractured duds. The same specialists are needed to perform a safety clearance. Level 1 clearance consists of screening only the surface duds by visual observation of the site. Level 2 clearance consists of clearing the top 30-45 cm of soil for duds with the help of a magnetic detector. Level 3 clearance involves completely cleaning 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 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 careful proofing is obtained with the help of the proper equipment such as an electromagnetometer (EM-61).** The following steps **must always be followed when drilling is conducted in a live fire training area:**

1. Hiring of an expert consultant for conducting electromagnetic surveys with the help of EM-61 electromagnetometer.
2. Location of the drilling site downgradient of the potential source area while trying to find the nearest location outside of the high risk area (nearby access road, in dry zone).
3. Proofing of the drilling site (5m x 5m grid).
4. In the case where a unexploded ordnance is suspected within the 5m x 5m perimeter, move the drilling location elsewhere outside of the grid to another representative location.
5. No live fire is allowed in the range between the proofing and the actual drilling of the proofed location.

Cautious surface sampling can be achieved after level 1 clearance operation, 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 and the safety of the sampling team. When shovelling for depth profiling 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 prior to digging.**

Once site clearance has been granted, several safety precautions must still 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 requires the same expense and handling procedures as required for the explosives without the soil.

The experience gained by conducting sensitivity tests on many contaminated sites containing different levels of contamination revealed that explosive-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 that must not be shipped off site, except as high explosives.

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 such 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. It is also well established that when explosives are buried, they either remain intact or slowly biodegrade. These effects will primarily be observed in highly concentrated areas such as factory and waste sites. The colorimetric screening methods have been shown to be particularly useful in characterizing these highly contaminated soils on-site (Jenkins *et al.* 1996b).

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. Only surface soil samples (0-15 cm) 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 non-sparking 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 test. High levels of contamination will lead to intensively coloured 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. The risks are, however, minimized if the explosives are not confined or if no explosive chunks bigger than the critical diameter (the critical ratio length/diameter below which detonation does not occur) are present. For example, TNT chunks of less than approximately 2.5 cm will burn violently instead of detonating. As the critical diameter varies with the type of explosive and the surrounding conditions to which it is exposed, the sampling team should consult a specialist such as a detonation scientist or an ammunition specialist to make the best possible evaluation of the risks involved with the sampling of the site.

To reduce the hazard at explosives-contaminated sites, all mechanical operations should be carried out on materials that have been diluted to a slurry. If needed, water should be added to the soil to achieve the desired moisture content. Water desensitizes the explosive by phlegmatizing it and by reducing heat, friction and sparking that could ignite TNT. 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 already occurred and ensures the safety of the personnel who will have to manipulate these soils. Once wet, the soil can be safely excavated if minimize leaching is necessary. Moreover, it is recommended that firemen be present on the site at all times both to water the soil and to intervene in case of an emergency.

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 shovelling are required, remotely controlled operations offer the best protection. If this is not possible, armoured 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, and no drilling or excavation should be done without a remote system if NG is detected in the soil. Equipment used during treatment of explosive 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 soils 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 and Burrows *et al.*, 1989). For an indication of the toxicity of explosives on human health, Table III 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 criteria for explosives in drinking water indicate high levels of toxicity.

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 DRDC Valcartier contract in 1997 (Rouisse, 1997). Human health criteria for soils calculated by both teams are shown in Table IV. The latest threshold criteria are very severe, taking into account all possible intakes of explosive compounds by humans. Typically, many of the exposure pathways considered in the calculation of the criteria are not encountered in real-site situations and thus, the levels recommended are probably too severe. The evaluation of site-by-site threshold criteria as it is performed in the U.S., appears to be the best choice to obtaining threshold criteria that are realistic and capable of protecting human health. This can be achieved by a detailed site risk assessment that considers all possible exposure pathways relative to the site.

In most countries, no generic threshold criteria have been published for explosives. However, an important effort being conducted under the auspices of KTA 4-28 is to establish ecotoxicological-based threshold criteria, or environmentally acceptable end-points. To date, accepted health risk or ecotoxicological criteria are not available for explosives in soil and groundwater. A site risk assessment approach will probably be the

best choice for addressing this problem in the future, but is costly if performed at each site, thus the use of ecotoxicological-based threshold criteria would be more readily available and easier to use on Defence properties.

As mentioned previously, explosive compounds are not volatile, with the exception of NG. Therefore, no specific precautions must be taken to prevent the inhalation of explosive vapour. If NG is a possible contaminant, a strong organic odour will be detected on the site. If this is encountered, an organic vapour 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 hence 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.

ANNEX 2

SOIL SAMPLING

Spatial Heterogeneity and 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. However, several studies have shown the futility of this practice, due to the extreme short-range spatial variability that often exist for explosives in surface soils (Walsh *et al.*, 1993; Jenkins *et al.*, 1996a, 1997a, 1997b, 1997c; Thiboutot *et al.*, 1997a, 1997b, 1998c). The heterogeneous dispersion of explosives in soil matrices has also been noted when taking samples from biopiles (Dubois *et al.*, 1997). Even with extensive homogenisation of the treated soil, high spatial heterogeneity of explosive concentrations has been observed.

Therefore, composite sampling is strongly recommended when characterizing the ground surface at a potentially explosive-contaminated site. In a small area, (1 m x 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 between 3 and 10 m square should be randomly sampled by obtaining 50 or more individual increments. See *Statistical Methods for Environmental Pollution Monitoring* (Gilbert 1987) for selecting the appropriate sampling design, i.e., grid spacing, to meet the various projects data quality objectives.

The short and medium-range heterogeneity of HMX dispersion pattern has been studied by the characterisation of the spatial distribution of HMX on an active anti-tank firing range site (Jenkins *et al.*, 1997b and 1997c; Thiboutot *et al.*, 1998a). On this particular sampling campaign, a strategy involving an "area integrated sampling", in field sample homogenisation, compositing to produce representative grid samples, and on-site analysis was used. Depth of contamination and dimensions of the sampling grids were determined by using on-site methods. The seven discrete samples pattern was also applied to the anti-tank firing range in order to compare the heterogeneous nature of HMX dispersion with other explosives. To overcome heterogeneity problems, a combination of collecting an area-integrated sample and a simple compositing approach within defined geographic (grid) boundaries was studied.

To assess the large-scale heterogeneity of such a site, the area between two tanks targets was divided into fourteen 6-m x 6-m grids, then each grid was further subdivided into four 3-m x 3-m subgrids. The samples within each subgrid were obtained as follows: a spading shovel was used to scrape the top 5 cm of soil from a circle of medium radius of 77 cm in the centre of each subgrid. The soil scraped from the surface was piled in the centre of the circle and mixed thoroughly with the spading shovel and a small hand shovel. Pieces of metallic and ceramic debris from munition detonation were removed by hand and a subsample of about 1 kg of soil was collected from random locations in the pile. Duplicate portions of soil from these soil piles were collected in nine randomly selected subgrids. In these same nine subgrids, a duplicate was prepared from a separate sampling circle in the subgrid, in a manner identical to that described above except that the sampled area was offset from the initial one. Weighed portions from each of the four area integrated subgrid samples from within a grid were combined and homogenised in duplicate to prepare two composite samples to represent each grid.

Statistical analysis revealed that the concentration estimates for the grid composites (6 m x 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 homogenisation 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 costs. More details on effective sampling grids that should be used on specific ranges can be found in annex 15.

Sample collection

After the sampling site has been cleared to the appropriate safety level, sampling of EM-contaminated soil can proceed. If no clearance operations were conducted prior to sampling, an explosive ordnance expert must be involved in the sampling campaign to ensure the safety of the sampling team. For each discrete or composite sample, a minimum of 500 g of soil must 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, non-sparking metal or rigid plastic tools. The choice of collection tools often depends on the cohesiveness, coarseness and moisture content 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, after previous proofing of the location. Often mechanically driven sampling equipment will be necessary when sampling at depths greater than a meter. All the sampling equipment that comes into contact with the soil should be carefully washed between each sample to avoid cross-contamination. It is accomplished by brushing the excess soil and then, acetone is sprayed on the surface of the tools to remove the traces of explosives followed by spraying with distilled water. These last steps should be done twice. If the metals are also a concern at the site and chemical analysis have to be done another washing/rinsing step with nitric acid 10% and distilled water is added. However, if nitrates analysis in groundwater is needed, the nitric acid

must be replaced by hydrochloric acid (HCl 10%). Annex 14 will present in more depth which sampling pattern is recommended based on what type of activity was conducted on the sampled site.

Sample Containers and Storage

Polyethylene bags or amber 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) for extraction, since these materials are resistant to adsorption of explosives. Amber glass prevents photodegradation of light-sensitive TNT and other nitroaromatic compounds. Immediately after sample collection, the containers 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. Anti-static polyethylene bags are available if minimizing static is desirable. The holding time for soil samples is addressed in Annex 8 and Table VII.

Soil Preparation

Soil preparation methods were developed to improve the availability and to minimize the heterogeneity problem of nitroaromatic and nitramine residues in soil. To obtain representative results, soil samples need to be thoroughly homogenized before extraction and analysis by EPA Methods 8330A (EPA 1998) or 8095 (EPA 2000a). Various methods have been studied over the past few years to reduce the high heterogeneity pattern in soils. The following method represents the best approach and should be carefully followed to insure that representative sub-samples will be collected from the 500 g composite sample.

First, soil or sediment samples (~500 g) are visually inspected to ensure that no chunks of solid explosive are present. Soil samples are then spread out on a clean flat surface and air-dried to a constant weight at room temperature. The air-drying process

should be protected from sunlight to minimize photodegradation of TNT and its metabolites. Typically, this step is conducted under a hood and takes about 24 hours, after which the sample is saturated with lab-grade acetone to minimize contaminant heterogeneity and to optimize the availability of the contaminants within the sample. This solubilisation step is critical and ensures a homogeneous dispersion of the explosive contaminant in the soil matrix. Care should be taken to ensure that acetone does not draw the contaminants out of the sample matrix, as over saturation with acetone could cause contaminants to leach to the edge of the sample container. The soil is then ground with a mortar and the soil/acetone slurry is thoroughly mixed. The sample with acetone is air-dried again until no traces of acetone are perceptible (24 hours). The soil is then ground to pass through a 30 mesh sieve (0.60 mm). During soil preparation, care should be taken to avoid cross-contamination between the samples from dust deposition, especially when some samples are suspected to be highly contaminated. Ideally, background samples should be processed first, followed by the lowest contaminated soils to the highest contaminated ones. Finally, the soil sample is covered with aluminium foil and is ready for analysis by EPA Method 8330A (Annex 9). If soil samples are processed in a commercial laboratory, this procedure should be provided to the laboratory, which should follow it carefully.

QA/QC

A quality assurance and a quality control program must be included in any sampling campaign. A representative number of background samples must be collected off ranges. A minimum amount of 20 background samples must be collected when sampling is performed in large area such as live fire training ranges. These background samples are used to insure that no explosives are detected off limits of the potential contaminated area and also they can be used to determine a mean background value for all metals analytes. Statistical treatment of the results for each parameters allows the comparison of the results obtained in the sampled area versus the mean value for each analyte.

In the laboratory, analyses of each sample can be done in duplicates to insure laboratory reproducibility. Moreover, 10 % to 15% of field replicates must be collected

and analyzed to verify the field reproducibility. The contracted laboratory for metals and other parameters must present their QA-QC including surrogates and blanks, detection limits and quantification limits. Trip blanks and field blanks should also be included in the

ANNEX 3**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

Generally, military ranges are very large areas for which systematic gridding and soil characterization results in large expenditure outlays. Sampling the groundwater plume of a potentially contaminated site is often the best way to monitor the environmental impact. This is particularly true for non-volatile explosives. Thus, an adequate sampling plan involving the collection of groundwater samples during the initial phases can minimise the costs associated with sampling and analysis. If contamination is not found in detectable levels in the groundwater on-site, nor in the down- and up-gradient wells, the implication is that explosives do not leach from the site and do not present a threat to the groundwater quality. However, if contamination is found in the groundwater, a more detailed sampling plan to identify sources in the surface and subsurface (vadose zone) must be undertaken. All related work concerned with the installation of wells, pumping and sampling must be conducted with the participation of a hydrogeologist and after explosive clearance has been granted.

In general, there are two main reasons for sampling groundwater, i.e., to detect the presence of a contaminant or to monitor contaminant concentrations on temporal and spatial scales. When sampling groundwater for 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

of explosives, sampling can be performed using a variety of 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 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 (USEPA Region 1, 1996; Pennington *et al.*, 1996).

Sampling of explosives-contaminated groundwater is described in the Natural Attenuation Protocol (Pennington, 1996). Purging of the wells is necessary for all groundwater sampling activity 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. For low permeability geologic material like clay, till or rock, only one well volume is purged prior to sampling because of the low recovery of the water table. Depending on the objective of the sampling plan (i.e., contaminant detection or temporal and spatial monitoring), purging may be accomplished using either a submersible pump, a peristaltic pump (for water table depth less than 8 m), an inertial pump (Waterra) or a bailer. The material of the pumping system that comes in contact with groundwater must not affect its chemical composition. The preferred materials for groundwater sampling for energetic material are: glass, PTFE, stainless steel 304 or 316, PVC and HDPE. The choice of purging system will be based on the water table depth, the volume of water to be purged and the permeability of the aquifer. 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 the analysis reveals the presence or absence of explosive contaminants. Uncontaminated water can be disposed of directly on the site, but contaminated groundwater must be treated by passing it through an activated charcoal filter prior to disposal.

The low-flow procedure for water sampling requires that groundwater be purged from the well until specific parameters are stabilized. Moreover, while purging groundwater the flow rate should be controlled to limit a water-level draw down. 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 each successive half well volumes (a well volume being the water in the casing, the screen and the sand pack). 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 in order to collect a representative formation sample. 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 parameters stabilization cannot be obtained, no more than five well volumes should be purged prior to sampling. If the equipment needed for monitoring these parameters is unavailable or would increase the cost, then we recommend purging the well of three well volumes before sampling.

Immediately upon completion of purging, samples should be collected for analysis using either a polytetrafluoroethylene (PTFE)-coated bailer on a PTFE-coated stainless steel cable or via the output of the PTFE well tubing when using a Waterra pumping system. A minimum volume of 2 L water should be collected from each well and poured into two 1-L amber glass containers. The groundwater samples do not need to be filtered in the field or in the laboratory prior to energetic material analysis. However, if the metals need to be analysed in groundwater a field filtration of the sample immediately after it was collected is required with a 0.45 µm filter. A proper acid (HNO₃ 8N) is added in the sample bottle before transferring the sample in order to lower the pH at less than 2. Groundwater samples should be collected from the least contaminated wells first to minimise any cross-contamination. Dedicated systems are more suitable for groundwater monitoring program because concentrations are unknown during the initial stages of a surveillance program. However, all non dedicated sampling or purging systems (like bailer) or instruments (electric water level tape) that come into contact with

groundwater should be decontaminated by washing and rinsing alternatively two times with acetone and distilled water between each well. If the metals are also a concern at the site and chemical analysis has to be done, a further washing/rinsing step with nitric acid 10% and distilled water is added.

Samples suspected of being contaminated by TNT or TNT derivatives should be stabilized by adding sodium bisulphate (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, neutralisation is not necessary. Depending on the pre-concentration method used, a sufficient volume of water must be collected in order to obtain the required number of replicates and to insure quality assurance/quality control by the selected analytical laboratory or a separate laboratory. The salting-out method requires 770 mL per sample, while the solid-phase extraction requires 500 mL per sample. The water samples should be extracted and analyzed in the shortest timeframe as possible, especially when low levels are suspected. For low levels ground water samples, we recommend to use the GC-ECD method (US EPA 8095) which provide lower detection limits.

Quality Control

A minimum of 10% to 15% of the wells must be sampled in duplicate. These samples are analysed by the same laboratory in order to verify the reproducibility of the samples. In addition, a field blank and a trip blank for the sampling campaign must be provided by the analytical laboratory to control, respectively, the contamination of the bottles during the sampling and the transportation of the samples. Blanks contain distilled water from the laboratory and the stabilizing agent. The trip blank must never be opened whereas the field blank is open in the field for the same period as a sample bottle is opened during the sampling of a well. These samples are carried with the other bottles before, during and after the sampling and are shipped to the laboratory with the other

samples. The washing equipment blanks are taken to verify the efficiency of equipment decontamination and to ascertain that the groundwater in wells is not contaminated by equipment. This sample is made by collecting the purified water from the last rinsing of the equipment. If water is used during the drilling, it is also recommended to take a water sample from the tank truck or the reservoir in order to verify the quality of the water injected in the formation.

ANNEX 4**SUBSURFACE SAMPLING****Guide:**

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

Wells required for subsurface sampling should be drilled by contractors specialized in contaminated site assessment. Nested wells with 2–4 m depth levels must be installed to establish the contaminant profile and boreholes must be equipped with observation wells with a 1.5–2.0 m screen interval. The installation of only one well per borehole is recommended in order to avoid any vertical cross-contamination in multilevel wells. To make a concentration profile many wells with different depths are drilled beside each other (3-5 m apart). The maximal depth of drilling is related to the depth of the groundwater table at the specific site. Generally, energetic materials are present in the first 6 m of the water table but can be diluted by recharge in the upper part of a water table aquifer.

Boreholes Drilling and Soil Sampling

The local stratigraphy of the site is first determined by examining the logbook 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 contaminant plume. The drilling depth of the boreholes is defined on-site depending on the observations made from the first drilling.

Boreholes for soil sampling are drilled using a hollow-stem auger (vibrasonic method) or geoprobe equipped with a split spoon or a lined core barrel sampler to collect a cylindrical segment of the subsurface soil profile. No drilling fluid should be used. If the vibrasonic method is selected for sampling, any ODEX type drilling method can be used to drill boreholes designed for the observation of wells installation. For each borehole, a well log should identify all geologic formations present in the unconsolidated material. Initial borehole diameter in unconsolidated material should be sufficiently large to allow the installation of 5- cm (2-inch) 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 (annex 5). If contaminated, further analysis by EPA Method 8330A (EPA 1998) or 8095 (EPA 2000a) 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 and brushing its surface in a hot water tub with non-phosphate detergent and by cleaning it with high-pressure steam. Acetone is then sprayed on the split spoon to remove the last traces of explosives, followed by additional spraying with distilled water. This last step is done twice. The same decontamination procedure is also done with the auger and the pilot bit of the drill rig to avoid cross-contamination between boreholes.

Monitoring Well Installation

Each borehole should be equipped with a monitoring well. The well depth is defined in the field, depending on the information obtained from the first drilling. The well's components (well casing, joints, screen, filter pack, expansive cement, cement/bentonite or bentonite grout and protecting casing), dimensions and installation of the well 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 annular space between the permanent well casing and the borehole wall. In permeable porous

media, naturally development is recommended. In that case, the screen of the well must have a slot size appropriate to the grain size of the formation (d_{20} of the finest sample along the screen). For wells installed in finer porous media, a filter pack is recommended. The filter pack must be appropriate to the grain size of the formation (3 to 4 times d_{30} of the finest sample along the screen and a uniformity coefficient (d_{60}/d_{10}) of 2 to 3) and the screen must be appropriate to the grain size of the filter pack (d_{10} of the filter pack). The filter pack should be made of round or sub-round quartz sand. A secondary filter pack is recommended to prevent cement or bentonite grout from migrating into the primary filter pack. The d_{10} of the secondary filter pack should be between one-third and one-fifth of the d_{10} of the primary filter pack (Nielson, 1991). The permanent casing and screen of the well should be made of PVC or other inert material with 1.5 to 2.0 m well screens. Well elevation must be established from the top of the PVC permanent casing. The boreholes 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 to protect the observation well from outside contamination as well as from mechanical shock that could permanently damage the well. Usually, the protective well casings are installed 15 cm above the top of the PVC tubing and extend 2 m below the ground surface (cold region). In ranges and OB/OD sites, it is recommended that the protective well casings be flush-to-ground-surface completions. Additional protection can be gained by installing a concrete pad at the surface around the wellhead.

For the new wells installed in the porous media, well development must be performed one time prior to water level measurement or groundwater sampling. Wells are developed by surging with the Waterra pump, a surge block connected to the foot valve at the end of the tubing, or pumping/recovering/pumping the water in the well. In all cases, the dewatering of the screened interval and the sand pack must be avoided in order to prevent air entrapment and changing redox conditions around the sampling point.

ANNEX 5

COLORIMETRIC FIELD METHODS

Several field colorimetric methods can be used to detect and identify the type of explosives that contaminate a specific site. This protocol covers a visual screening method (ExprayTM, Plexus Scientific, Silver Spring, MD) and two spectrophotometric methods (Walsh and Jenkins, 1991; Jenkins, 1990; Grant *et al.*, 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 coloured 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 protocol will focus on the analysis of TNT and RDX, because these explosives are the major ingredients in nearly all military munitions. Most sites can, therefore, be adequately assessed by employing this approach (Walsh *et al.* 1993, Table V). One exception, however, is the investigation of production facilities, where these methods could be used to characterize 2,4-DNT, TNB, DNB, tetryl, picric acid and HMX. Moreover, a greater emphasis is placed on the on-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 methods have shown strong correlations 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 (available from Plexus Scientific, Silver Spring, MD). This method is particularly useful in the field when chunks of unknown material are suspected to be energetic material based. 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 fiberglass 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 µL) of solvent extract (acetone or acetonitrile) 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 colour appears after application of the first aerosol then polynitroaromatics (e.g. TNT, TNB, DNT, picric acid, tetryl, etc.) are present. Some of the colours that may appear upon the application of this first aerosol are blue, red, or orange. A bluish colour appears when 2,4-DNT or 2,6-DNT is the dominant compound, a reddish-brown colour appears for TNT and TNB, and an orange colour for tetryl and picric acid. After application of spray from a second aerosol can, the formation of a pink colour 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 polynitroaromatic and nitramines. If no colour has appeared the sample is then sprayed with the third aerosol can. If a pink colour 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 μL 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 μg of explosive analyte when concentrated in a discrete location (5 μL) 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 following sections, and Annexes 6 and 7) by alerting the analyst to when sample extract dilution is necessary. More details on the ExprayTM method can be retrieved in annex 8.

SPECTROPHOTOMETRIC COLORIMETRIC METHODS

Extraction

A simple extraction process is used to extract the explosives from the soil matrix. A 20- g portion of dried or undried soil from the site 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 contaminants (Jenkins *et al.*, 1997c). After extraction, the sample is allowed to settle and is then filtered with a syringe filter. Sandy and loamy soils require as little as 3 minutes to settle, but very heavy clays might need more time. To prepare a water sample for analysis, see Annex 10, 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 EPA Methods 8330A (Jenkins *et al.*, 1997b; EPA 1998) and 8095 (Walsh and Ranney, 1998, 1999; EPA 2000a). Some on-site methods recommend using very small amounts of soil

and extracting solvent. We do not recommend this approach because of the large heterogeneity of explosives even over very short distances.

TNT On-Site Determination

In the TNT screening 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 that is agitated for 3 minutes, and then filtered. Extracts are evaluated visually. If the extract has a reddish or pinkish colour, it contains TNT; if it has a bluish colour, it contains 2,4-DNT; if it is orange, it contains tetryl; if it has a reddish-orange colour, it contains picric acid (Janowsky reaction). The absorbance peak at 540 nm is used to verify the presence of TNT, and represents the optimal wavelength to minimize interference from humic species. The field spectrophotometer recommended is the HASH 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 EPA Method 8330A.

RDX, HMX, NG and PETN On-Site Determination

On-site analysis for RDX is similar to the field screening for TNT colorimetric method. In addition, 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, converting RDX, HMX, NG or PETN to nitrous acid. The test can, therefore, be used for any of these four compounds, and the results correspond to the sum of these analyte's concentrations. The extract is then filtered and placed in a vial with a Hach NitriVer 3 powder pillow. If the extract develops a pinkish colour (Griest reaction), 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 coloured reaction end products is at 507 nm, and, therefore, the reading should be done at that wavelength. The results of the

RDX on-site analysis also correlate well with results obtained in the laboratory. EPA Method 8510 (EPA 2000b) gives additional details about the use and performance of the method.

Advantages and Limitations of Colorimetric Methods

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

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 and the use of a field spectrophotometer. However, the spectrophotometric colorimetric methods produce more precise results, and cover a larger analytical range (0-200 mg/kg) 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 as with the immunoassay method (i.e., 2 g is used for immunoassay).

ANNEX 6

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 colour 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 by Teany and Hudak (1994) and 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 colour-developing solution added to the surface of the cup assembly reveals a colour inversely proportional to the concentration of RDX or TNT in the sample. RDX and TNT are best measured in the range between 0.5 – 6 mg/L and between 0.5 – 5 mg/L, 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. More details concerning the precision and reproducibility of the D-Tech™ kit as well as the matrix effects and potential interferences are given in EPA Methods 4050 (EPA 1996a) and 4051 (EPA 1996b) for TNT and RDX, respectively.

Extraction

Using the D-Tech™ system, soils are extracted with 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). Prescribed volumes of the buffered soil extracts are added to the vials containing enzyme-labelled 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 colour developing solution. The reference side of the cup is used to determine the end-point of the colour development, with all readings done at room temperature. The time for complete colour development is less than 10 min for TNT and 15 min for RDX.

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 colour-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 carefully followed. 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 Annex 5.

ANNEX 7

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 macrobore 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 GC that has many of these features and is equipped with a thermionic ionization detector (TID) was found to be well suited for the analysis of explosives (Hewitt *et al.*, 2001a, 2001b). This detector is selective for compounds containing nitro functional groups, which are present in most explosives. Indeed all of the explosives cited in EPA Method 8330A (Table II), 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/kg) with detection limits often below 0.1 mg/kg (Table II). 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 Annex 10 and soil sample preparation follows the guidelines presented in Annex 5. Following extraction an aliquot of the acetone is 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, 2001b). Separations are performed on a Crossbond 100% dimethyl-polysiloxane column (DB-1), 15 m x 0.53 mm ID, 0.5 μm (coating thickness). Injections of 1 μL were made manually with a 10- μL 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 EPA Methods 8330A or 8095 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 non-linear model (quadratic through the origin) to be used when a linear regression through the origin fails to establish a correlation coefficient (r) greater than 0.990. Continuing calibration checks should be made after every five samples. If the calibration model fails to establish a concentration within $\pm 20\%$ 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, since they lack adequate selectivity, while the enzyme immunoassay methodologies measures 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 very economical for larger projects, particularly when knowledge of the identity of the explosives is critical.

ANNEX 8

Explosives Detection Field Test Kits

[Expray](#) | [Drop-Ex](#) | [Detection Chart](#)



Expray is a unique, aerosol-based field test kit for the detection and identification of Group A explosives (e.g. TNT, TNB, etc.), Group B explosives (e.g. Semtex H, RDX, C4, etc.) and compounds containing inorganic nitrates that are used in improvised explosives (e.g. ANFO). Expray is commonly used as a pre-blast, analytical tool, post-blast investigative tool, screen against potential terrorist elements and as a technical evaluation test in soil remediation on hazardous material "clean-up" sites. When used as a post-blast investigative tool, the product is field proven to speed up crucial investigations.

The level of sensitivity (20 nanograms) surpasses that of other currently available products. The testing process is fast and efficient. No glass ampoules, spatulas or waiting period required. Results appear in seconds. No additional tools or equipment required. The identification/detection process requires no special training and testing can be performed "on the spot".

For both law enforcement and investigative personnel, Expray is a proven tool for increasing the accuracy, efficiency and number of interdictions. For forensic and environmental laboratories, it has proven to reduce the number of samples submitted for testing, saving both time and money.

Expray is sold in a kit configuration, which provides all three aerosol sprays, collection papers, and an RDX-impregnated verification pad (verification pad is useful for ensuring that the spraycan still contains active reagents and for demonstrating how a positive reaction will appear) in a convenient plastic carry case. Expray kits are available in both regular size (100 tests) and mini-size (50 tests).

Mistral is proud to say that Expray provides a low "per test" cost and poses no risk to you or the environment

"E": Expray-1 for Group A

Expray-1 is used to search for GROUP A type explosives which include TNT, Tetryl, TNB, DNT, picric acid and its salts. To use, wipe suspected surface with special collector test paper. Spray with Expray-1. If a dark brown-violet color appears, this indicates the presence of TNT; An orange color indicates the presence of Tetryl and other GROUP A explosives.

"X": Expray-2 for Group B

Expray-2 is used to search for GROUP B type explosives which include Dynamite, Nitroglycerine, RDX, PETN, SEMTEX, Nitrocellulose and smokeless powder. If after spraying Expray-1 there is no color change, spray Expray-2. The almost immediate appearance of a pink color change indicates the presence of GROUP B explosives. Most plastic types of explosives belong to this group, including C-4 and Semtex.

"I": Expray-3 for Nitrates

Expray-3 is used to search for nitrate-based explosives which includes ANFO (ammonium nitrate-fuel oil), commercial and improvised explosives based on inorganic nitrates, black powder, flash powder, gun powder, potassium chlorate and nitrate, sulfur (powder), and ammonium nitrate (both fertilizer and aluminum). If there is still no reaction after using the Expray cans 1 and 2, but presence of explosives is still suspected, spray the same paper with Expray-3. A pink reaction indicates the presence of nitrates, which could be part of an improvised explosive.

Drop-Ex

Drop-Ex is our newest Explosive Detection and Identification Kit. This system is based on the same reagents in Expray, but in a drop tube deliverable system, for ease of use during field and laboratory investigation. This kit is also able to detect an additional category of explosives: chlorates. When using drop # 4 for detection of chlorates (also for bromides) this drop is used by itself and does not require drops # 1, 2, or 3 to precede it. If you are not sure what type of explosive you are testing for, you will need two samples. The first sample can be tested using Drop-Ex 1, 2 and 3. The test for chlorates and bromides must be a separate test using Drop-Ex 4.

Drop-Ex-1 is used to search for GROUP A type explosives which include TNT, Tetryl, TNB, DNT, picric acid and its salts. To use, wipe suspected surface with special collector test paper. Drop with Drop-Ex-1. If a dark brown-violet color appears, this indicates the presence of TNT; An orange color indicates the presence of Tetryl and other GROUP A explosives.

Drop-Ex-2 for Group B

Drop-Ex-2 is used to search for GROUP B type explosives which include Dynamite, Nitroglycerine, RDX, PETN, SEMTEX, Nitrocellulose and smokeless powder. If after Drop-Ex-1 there is no color change, use Drop-Ex-2. The almost immediate appearance of a pink color change indicates the presence of GROUP B explosives. Most plastic types of explosives belong to this group, including C-4 and Semtex.

Drop-Ex-3 for Nitrates

Drop-Ex-3 is used to search for nitrate-based explosives which includes ANFO (ammonium nitrate-fuel oil), commercial and improvised explosives based on inorganic nitrates, black powder, flash powder, gun powder, potassium chlorate and nitrate, sulfur (powder), and ammonium nitrate (both fertilizer and aluminum). If there is still no reaction after using the Drop-Ex 1 and 2, but presence of explosives is still suspected, drop the same paper with Drop-Ex-3. A pink reaction indicates the presence of nitrates, which could be part of an improvised explosive.

Drop-Ex-4 for Chlorates and Bromides

Drop-Ex-4 is used to search for chlorates (such as potassium chlorate and sodium chlorate) and bromides. If you suspect a chlorate or bromide, use Drop-Ex-4. If there is a dark blue reaction, there is the presence of chlorates or bromides. If you have already tested with Drop-Ex 1, 2 and/or 3, you must use a fresh sample for Drop-Ex-4.

Detection Chart

Product :	EXPRAY - 1 / Drop-Ex 1		EXPRAY - 2 / Drop-Ex 2		EXPRAY - 3 / Drop-Ex 3		Drop-Ex 4 (used alone)	
Detects:	Polynitro Aromatics		Nitrate-esters Nitramines		Inorganic Nitrate Compounds		Chlorates	
	Group A		Group B		Group C		Group D	
#	Substance	Color	Substance	Color	Substance	Color	Substance	Color
1	TNT	Dark Brown	Semtex	Pink	Ammonium Nitrate	Pink	Potassium Chlorate	Dark Blue
2	TNB	Dark Brown	RDX	Pink	Potassium Nitrate	Pink	Sodium Chlorate	Dark Blue
3	DNT	Blue Green	HMX	Pink	Sodium Nitrate	Pink	Bromides	Dark Blue
4	Picric Acid	Yellow	PETN	Pink	Barium Nitrate	Pink		
5	Tri Nitro Naphthalene	Violet	EGDN	Pink	BlackPowder	Pink		
6	Lead Styphnate	Yellow	Nitro Glycerin	Pink				
7			Nitro Cellulose	Pink				
8			Tetryl	Pink				
9			Smokeless Powder	Pink				

ANNEX 9**SAMPLE CONSERVATION: MAXIMUM HOLDING TIMES***Soil/Sediment Samples*

For soil samples, EPA Method 8330A (EPA 1998) 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 and Jenkins *et al.*, 1994). Therefore, soil samples can be held for 8 weeks if stored in the dark and frozen. And if nitroaromatics are no concern, the MHT for soil samples can be extended for up to six months at -20°C, based on their stability at 4°C (Table VII).

Water Samples

For water samples, EPA Method 8330A (EPA 1998) 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 and 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 for up to 28 days prior to extraction. Data are not available on the MHT of explosives in water when the samples are frozen, but considering that at -20°C almost all microbial activity has stopped, the MHT can be safely extended to 6 months (Raymond, 1995). If the solution is frozen, it is necessary to ensure that the analytes re-dissolve before analysis. However, some explosives such as HMX are slow to dissolve. The MHT for explosives in water samples at both temperatures are reported in Table VII. Another way of extending the MHT for water samples is to extract them with SEP-Pack cartridges and keep the extracts at 4C in the dark. It was demonstrated that these extracts are stable for at least 14 days in these conditions.

ANNEX 10**EXTRACTION AND ANALYSIS: EPA METHODS 8330A/8095**

EPA Methods 8330A (EPA 1998) and 8095 (EPA 2000a) can be downloaded in their entirety from the EPA internet site <http://www.epa.gov>.

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

WATER EXTRACTION BY SALTING-OUT**7.1.1. Aqueous Low-Level Method (salting-out extraction)**

7.1.1.1. 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 and stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.1.1.2. Add 164 mL of acetonitrile (measured with a 250 mL graduated cylinder) while the solution is being stirred and stir for an additional 15 min. Turn off the stirrer and allow the phases to separate for 10 min.

7.1.1.3. Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100 mL volumetric flask (with a round bottom). Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 min followed by 10 min 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.

- 7.1.1.4. 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 min, followed by 10 min for phase separation. Carefully transfer the acetonitrile phase to a 10 mL graduated cylinder using a Pasteur pipet. 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.
- 7.1.1.5. Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 min, followed by 10 min 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 reagent water (with $\text{pH} < 3$ if tetryl is a suspected analyte) prior to analysis.
- 7.1.1.6. 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.

SOIL EXTRACTION

7.1.4 Soil and Sediment Samples

7.1.4.1. Sample homogenization

Dry soil samples in air at room temperature (or less) to a constant weight, being careful not to expose the samples to direct sunlight. Follow the homogenization step described in annex 2. Grind and homogenize the dried sample thoroughly in an acetonitrile-rinsed mortar to pass a 30-mesh sieve.

NOTE 1: Soil samples should be screened by EPA Method 8515 prior to grinding in a mortar and pestle (See Safety Sec. 11.2).

NOTE 2: Some soil samples may require grounding to a finer particles size (30 mesh) than what is suggested in the method to obtain an acceptable level of homogenization (see Annex 2).

7.1.4.2 Sample extraction

7.1.4.2.1. 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.

7.1.4.2.2. After sonication, allow sample to settle for 30 min. 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 min.

7.1.4.2.3. Place supernatant in a disposable syringe and filter through a 0.45 μm Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Sec. 7.4.

ANNEX 11**SOLID PHASE CARTRIDGE EXTRACTION**

Solid-phase cartridge extraction was developed as an alternative pre-concentration method for explosives in water (Jenkins *et al.*, 1995a; EPA 2000c). 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 with reagent-grade water (1:1) 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. This technique allows 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 EPA Method 3535A (EPA 2000c).

ANNEX 12**PROTOCOL FOR ADSORPTION TESTS***Objectives*

1. Specify the adsorption kinetic of energetic materials;
2. Evaluate the partition coefficient (K_d) of EM;
3. Evaluate the retardation factor (R) of EM.

Assumptions

1. The biodegradation of the energetic materials is negligible during the tests. Otherwise, 2% of sodium azide (NaN_3) has to be added to the aqueous solution containing the EM.
2. The analytical method has quantification and detection limits low enough to observe adsorption of the EM on soil.

GENERAL PROCEDURE

Before performing the adsorption tests two preliminary steps are necessary. The first step specifies the soil to water ratio to be used in the adsorption test with both an empirical and an experimental method. This ratio can greatly affect the test and needs to be precisely evaluated. The second step defines the equilibration time corresponding to the time required for the chemical equilibrium of the system. The adsorption tests are realised following these two preliminary steps. This protocol is adapted from EPA (1992) and Hains (2002).

DETAILED PROCEDURE

Experimental Soil

The soil sample comes from the contaminated site or close to the site. It must be representative of the soils of the contaminated area, but is not contaminated. Before it is used for the tests, it must be dried at 43°C for 48 hours, and sieved to remove soil particles larger than 2 mm. It may be also be important to characterize the soil by determining the grain size curve (% sand, % silt, % clay), the organic carbon content, the cationic exchange capacity, the iron content and the porosity (Pennington and Patrick, 1990). It may also be interesting to evaluate the proportion of clay and to determine the mineralogy of the clay size particles because adsorption of EM depends mainly on these two parameters (Haderlain *et al.*, 1996).

Contaminants

The energetic materials used for the adsorption tests either can be extracted from the contaminated soils of the site or be obtained from the owner of the site or the Defence Department.

1. From Contaminated Soils

The extraction is made with acetone. This solvent is mixed with the contaminated soil to dissolve the explosives, and then recovered and evaporated to obtain an extract of energetic materials. A chemical analysis of the extract by the EPA method 8330 is needed to evaluate the type and the concentration of the energetic material in this solid. The extract must be carefully and gently grinded in a fine powder with a non-sparkling mortar and pestle pillar and a crucible. This procedure makes the powder more easily dissolvable in water. In addition, for safety only small amount of extracts should be ground. Acetone can also be added to the extract to make it less sensitive during the

grinding step. However, the powder must be completely dried (no acetone) before the powder is mixed with water.

2. From the Owner of the Site or the Defence Department

The sample of EM must be in a fine powder. If not the sample must be carefully and gently ground to a fine powder with a non-sparkling mortar and pestle . This procedure makes the powder more readily dissolvable in water. In addition, for safety only small amount of extract should be ground. Acetone can also be added to the extract to make it less sensitive during the grinding step. However, the powder must be completely dried (no acetone) before the powder is mixed with water.

Aqueous Solution

The concentration of energetic materials in the aqueous solution that is put in contact with the experimental soil must be as high as possible. This solution is made in 4 L amber glass bottles. The pure energetic materials supplied or the powder of energetic materials extracted from the soil at the previous step is mixed with distilled water. The water must be supersaturated with energetic materials. For example for a TNT aqueous solution, 2 g of powder is mixed with 3.5 L of distilled water. The aqueous solution is stirred for 72 hours or up to the equilibrium of the energetic material with water. The aqueous solution is filtered through a funnel and a fine glass paper filter or a glass syringe with a 0.45 μm filter (Millex HV or FH). 2% of sodium azide has to be added to the aqueous solution if biodegradation is likely during the adsorption tests. Ideally, the concentration of the solution should be close to the solubility limit of the energetic materials in water. For example the TNT concentration should be in the range of 25 to 50 mg/L. This concentration is required to follow the behaviour of the EM in the subsequent adsorption tests.

Identification of the Soil:Water Ratio

EPA (1992) suggests two methods to identify the soil:water ratio. The experimental protocol is described below.

The percentage of adsorption of energetic materials by the soil is evaluated for eight soil-water ratios (1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200 and 1:500). The percentage of adsorption must be between 10% and 30% for a statistically valid test (EPA, 1992). The adsorption tests are made in reactor cells made of 250 mL amber glass bottles, closed with Teflon septum lids. The incubation time is 24 hours and the temperature is maintained at the average groundwater temperature. The solution and the soil are gently shaken or stirred during the time period of the test. At the end of the test, 30 mL of supernatant are taken in each reactor and centrifuged for 30 min at 15 000 rpm. Approximately 10 mL of each centrifuged sample is taken, filtered (0.45 μ m, Millex HV or FH) and combined with 10 mL of acetonitrile that acts as a preservative and a solvent for the chemical analysis. The preserved samples are put in 40 mL amber glass bottles, closed with Teflon septum lids, and stored at 4°C. All 8 samples are sent to the analytical lab for energetic materials concentration determination and the selection the appropriate soil:water ratio is made based upon an adsorption of EM by the soil between 10% and 30%. A typical example of an adsorption test in a sandy soil is given in Table VIII and (Figure 1).

Identification of the Equilibrium Time

The equilibrium time is an important factor for the adsorption tests because the system tested must have reached the equilibrium. Seven samples of the selected soil:water ratio are prepared in a 250 mL amber glass bottles closed with Teflon septum caps. For example 50 g of soil and 200 mL of aqueous solution should be taken to prepare a soil:water ratio of 1:4. The incubation time of these different reactors are fixed

at 1, 6, 12, 24, 48, 72 and 96 hours. The reactors are stirred for the period of incubation time. A volume of 30 mL of the supernatant is then removed from the reactor and centrifuged for 30 min at 15 000 rpm. Approximately 10 mL of each centrifuged sample is filtered (0.45 μm , Millex HV or FH) and the filtrate combined with 10 mL of acetonitrile that acts as a preservative and a solvent for the chemical analysis. The preserved samples are put in 40 mL amber glass bottles, closed with Teflon septum lids, and are stored at 4°C. All the 7 samples are sent to the analytical lab for energetic materials concentration determination. The appropriate equilibration time is selected from the plateau of adsorption of EM by the soil (Table IX, Figure 2).

Adsorption Tests

After the selection of the appropriate soil:water ratio and the equilibrium time (for example a soil:water ratio of 1:4 and an equilibrium time of 24 hours), it is possible to perform the adsorption tests. The original EM aqueous solution is diluted and placed into contact with the soil in the reactor. Nine dilutions were made as follow: 1:1, 1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200 and 1:500. All the tests are duplicated and one control reactor with distilled water and soil is introduced. The reactors are stirred for the period of incubation time. A volume of 30 mL of the supernatant is then removed from the reactor and centrifuged for 30 min at 15 000 rpm. Approximately 10 mL of each centrifuged sample is filtered (0.45 μm , Millex HV or FH) and combined with 10 mL of acetonitrile that acts as a preservative and a solvent for the chemical analysis. The preserved samples are put in 40 mL amber glass bottles, closed with Teflon septum lids, and are stored at 4°C. All 19 samples are sent to the analytical lab for energetic material concentration determination. The results are evaluated from a plot of the mass of energetic materials adsorbed on soil ($\mu\text{g/g}$) as a function of the concentration of energetic materials at equilibrium in the aqueous phase (Figure 3). For detailed instructions on the construction of adsorption isotherms (curves) and the selection of adsorption equation see EPA (1992). Table X gives values of partition and adsorption coefficients of some nitroaromatics and nitramines found in the literature. Moreover, a detailed study was recently published that covers this topic in details (Brannon and Pennington, 2002).

ANNEX 13**MICROCOSM TESTS: BIODEGRADATION OF NITROAROMATICS***Objective*

Evaluate the transformation of TNT or other energetic material in soil under representative conditions of the site.

GENERAL PROCEDURE

This type of test allows the quantification of the biological transformation processes of TNT by using soils from the source of contamination (adapted from BRI, 1999 and Hains, 2002).

Soil Sampling

The soil samples are taken from the source zone. All the sampling equipment and the bottles must be clean prior to sampling. The field equipment used to sample the soil must be washed between sampling locations with three successive wash/rinse cycles with acetone and water and can be sterilize with three wash cycles with ethanol. The bottles used to collect the samples have to be clean (analytical lab standard cleaning procedure applied), and sterile. The sterilization of the bottles or the equipment can be done by heating them in an autoclave for 15 minutes at 121°C or for 2 hours in a Pasteur oven at 180°C. The sampling of soil can be done with a stainless steel scoop. Sampling at shallow depth requires a shovel or a backhoe. Prior to sampling, a small layer of soil must be scraped off the wall of the excavation with a scoop. The samples are collected from the walls of the excavation and put directly in 500 mL amber glass bottles. We recommend combining 20 subsamples of soil taken at the selected depth intervals to make a composite sample. The bottles are filled to the top and sealed with a lid and a Teflon-lined septum. For safety, the soil samples at depth can be taken directly from the bucket of the backhoe. Care must be taken in selecting subsamples that were not in direct

contact with the bucket and a small soil layer must be scraped off the exposed soil in the bucket. The soil samples are homogenised and stored in the dark at 4°C until their use in the microcosm tests.

Microcosm Test (Aerobic or Anaerobic Conditions)

Small 20 g soil samples are taken from the amber bottles and put in serologic bottles of 120 mL. A series of 5 bottles is prepared in triplicate for each depth of soil (15 bottles per soil) and another series of 5 bottles is used for the abiotic control of each soil. An abiotic control is prepared for each of the two soils by autoclaving the soil in a serologic bottle 2 times for 30 minutes at 24 hours intervals or by adding 0.2% w/w (40 mg) of sodium azide (NaN_3) in the soil of the microcosm for aerobic condition tests. For anaerobic condition tests, the abiotic control is prepared by adding 0.2% w/w (40 mg) of HgCl_2 . Each soil is brought to humidity according to the field conditions: fully saturated for soil from the saturated zone, or at field capacity or less for soil from the unsaturated zone. Each serologic bottle is closed with a butyl grey lid and an aluminium seal (Fisher Scientific) or with a mininert valve with septum (Supelco). Under anaerobic conditions the bottles are flushed with Ar or N_2 and the head space is analysed for O_2 by gas chromatography to assure anaerobic conditions (absence of oxygen). All microcosms, initially under aerobic or anaerobic conditions, are incubated without agitation (static), in the dark at the average soil temperature. The three triplicates and the abiotic control are sacrificed for each soil at the 5 times selected for the evaluation of the biodegradation. Each sacrificed serologic bottle is frozen in the dark. At the end of the test the nitroaromatics in all soil samples are extracted and analysed with the EPA Method 8330 or 8095. The chemical analysis can also be performed immediately after the sacrifice of each series of samples instead of having the samples frozen and stored.

Oxygen Level in Aerobic Microcosms

The soil samples collected at shallow depths can be studied under aerobic conditions. The level of oxygen in the microcosm can be analysed by gas

chromatography. Hence, oxygen levels can be maintained and increased if necessary by injecting 60 mL of filtered air with a syringe. The excess air of the bottle can leave by another syringe needle insert in the lid of the bottle.

The soil samples studied under anaerobic conditions must not be opened and injection of air must not be carried out.

ENUMERATION OF THE TOTAL HETEROTROPHIC POPULATION

Objective: To evaluate the total heterotrophic bacterial population in the unsaturated zone of soil (adapted from BRI, 1999 and Hains, 2002).

The enumeration of the total heterotrophic population of bacteria is made with the spreading method on agar-agar. The dilutions are made with sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$, 0.1% (p/v), pH 7.0). The spreading is done on agar-agar made on a culture medium with a low nutrients content named YTS₂₅₀ (yeast extract, tryptone, and soluble starch: 250 mg per litre of water from municipal supply each). Municipal water is used to provide mineral salts. The spreading of many dilutions are made in triplicate, the incubation is made at the average soil temperature and the counting of bacteria colonies is made after 7 and 14 days.

Generally, a healthy soil has a bacterial population between 10^6 and 10^7 bacteria/g of soil (Chapelle, 1992). However, this number is a function of depth and can reach 10^5 bacteria/g of soil at 1 m depth.

ANNEX 14**THE CONCEPTUAL MODEL OF A SITE**

A conceptual model should show in a cross-section the hydrostratigraphy of the site (aquitards and aquifers), the groundwater flow direction, the source zone and the plume with the transport and attenuation mechanisms of the contaminant in groundwater and in soil. A model should be presented for each contaminant or group of contaminants and should also indicate the receptors that can be potentially affected. The development of the conceptual model is an iterative process that can evolve with time and with the knowledge of the site acquired by the different characterization studies. Figure 4 illustrates the conceptual model developed for the behaviour of a dissolved HMX plume in a porous sand aquifer. The source of contamination is ammunition of an anti-tank range. Examples of a conceptual model for TNT can be found in Volume 4.

ANNEX 15

SITE DESCRIPTION AND SAMPLING STRATEGY

Introduction

Many different ranges can be found in training areas. Each service uses ranges specific for their related activities. Depending on the type of ranges related to the activities, the calibre and uses of different munitions, the approach and the sampling strategy for all sites will have to take into account these different situations and be adapted to the specific activities. As an example, a rifle range is not sampled the same way as an anti-tank range since the contaminants are different and the impacts on the ranges are also different. Another problem encountered in assessing range contamination is the fact that range use has often changed over the years. It is important to get the history of the site before evaluating the potential problems of each site. Some sites have a long legacy behind them and strange situations can be encountered such as an anti-tank range installed on a forgotten old burial site. All of this complicates the evaluation of the site, but in some cases, the history of site usage over the last 30-50 years is available. This annex describes most of the different ranges that can be encountered in the tri services and the most appropriate approach that can be used to characterize these sites.

Type of Ranges

Here are the main types of ranges that can be found in the different army, navy and air services.

Army: Anti-tank, hand grenade, 40-mm grenade, cratering, wood cutting, concrete cutting, steel cutting, demolition, explosive ordnance disposal pits, artillery, mortar, open burning, open detonation, rifle, rocket, missile, battleruns, refuelling areas, land mine field and old burial sites.

Navy: Artillery (ex: Kaho'olawe), underwater explosion, munition sea dumping, munition wrecked ships, torpedoe range (ex: Coral at Kaho'olawe), missile range (tomahawk), ship to ship shooting (Harpoon).

Air: Air to ground (CRV-7), bombing area (Tracadie), missile range (cruise), refuelling area, small arms (20 mm).

Categories of ranges

Ranges can be classified according to their size:

Size of the ranges: Small: 20-30 x 20-30 m,
 Medium: 50-150 x 50-150 m
 Large: 0.5-2 x 0.5-20 km
 Extra-large: 2-20 x 2-20 km

In general, two main categories can be encountered in live firing ranges: Ranges that are free of unexploded ordnances (UXO) and ranges that are know to be impacted with them. The ranges containing UXO are of particular concern since they are unsafe to the users and can lead to dangerous situations including death. Depending on the particular range, UXO clearances may have been done on a regular basis to keep the amounts of UXO as low as possible, increasing the safety of the site. At other ranges, no regular maintenance may have been conducted. For ranges that are subjected to regular maintenance, only level 1 clearance is usually done on large areas, meaning that UXO at the surface are located, identified and disposed of by C-4 detonation or deflagration. During these operations, second (low) order detonation or deflagration sometimes occurs. These events may lead to explosive particles projected far away from the UXO and thus to soil contamination, and with time, to groundwater contamination following the dissolution and infiltration of the explosives to the water table. This behaviour is also true for second (low) order detonations of ammunition that did not function properly. On these sites, much shrapnel is observed. Once in a while the metal is recovered, assessed

for explosive presence, and disposed of by sending to a scrap metal dealer. Other sites that do not contain UXOs are much safer for on-site workers.

Sites Containing UXOs

Army: Anti-tank, grenade, artillery, rocket, missile, battlerun, land mine fields and old burial sites.

Navy: Artillery (ex: Kaho'olawe in Hawaii), munition sea dumping, munition wrecked ships, torpedo range (ex: Coral at Kaho'olawe), missile range (Tomahawk). All navy ranges can contain UXO and this is an important problem encountered in Canada, USA, UK, Netherlands, etc. For underwater explosion ranges, there could be UXO produced by a malfunction of the ammunition, but most of the time, since they are quite large weapons, disposal by detonation is done in each case.

Air: Air to ground (CRV-7), bombing areas (Tracadie, Trenton) that are also air to ground ranges and missile ranges can contain important amounts of UXO especially the bombing areas that can contain very large UXO deeply buried in the ground (1000 pounds up to 30-45 feet deep).

Range Description and Problem

In general, use of training ranges by the military for their operational activities leads to low contamination with explosives. These low levels of explosives are the result of second (low) order detonation or deflagration, malfunction of the ammunition leading to UXO production, casing perforations leading to the spreading of their content into the environment, and incomplete destruction of live ammunition using blow-in-place techniques. When a detonation occurs as designed (high-order detonation), results indicate that this situation leads to no or very little contamination by explosives. For example, high levels of contamination with HMX were found at anti-tank ranges due to malfunction of the M-72 rockets.

The more we learn about explosive contamination, the more we realize that this is coupled with heavy metal contamination that is more strictly regulated. So, in future research efforts, more work will have to be dedicated to the understanding of this unique mixed contamination problem.

Army Ranges

1. Anti-Tank (small to medium size (hundreds of hectares))

On this type of site, rockets are launched from a firing point hundreds of meters from the targets. Targets are usually old tanks. Carl-Gustav type M-72 rockets, which contain shape charges, are launched using a shoulder-mounted tube launcher. The explosive charge of this rocket is octol, which is a mixture of 60% HMX, 30% TNT, and 10% RDX (an impurity in industrially produced HMX). These rockets are powered by double-based propellant containing 2,4-DNT, NG and NC. Many M72 rockets do not explode on impact, but are propelled intact close to the targets leading to UXO presence on the site. Alternatively, the rockets are broken into pieces upon impact on the tank and their explosives contents spread on the ground. Therefore, when broken casings are observed, the EM contained in these unexploded broken rockets are spread on the ground, dissolved by rain and water from snowmelt, and eventually infiltrate to the water table through the soil, contaminating the groundwater. Since rockets are propelled all the way to the target, there is residual propellant present when the rockets detonate or are left on the site as UXO. Moreover, propellants can also be found behind the firing points once expelled by the launching system. Since these propellants contain NG, this compound is generally found at these ranges as well. Level 1 clearance is occasionally done and the metallic debris are removed, but particles of explosives and propellants cannot be removed as easily so, the environmental problems on these sites persist.

Usually, systematic sampling can be done and the wheel sampling pattern is applied to collect soils near targets on these sites (Figure 5). Systematic sampling such as

a grid was undertaken at anti-tank ranges in Valcartier and mapping of the HMX contamination was achieved. Concentrations were quite high around targets, but decreased rapidly with distances. Two approaches may therefore be used in antitank ranges: Sampling using the wheel pattern around all targets in all directions or collecting composite samples around the targets in various radius from the target (1 to 5 m radius at each meter). Drilling of boreholes for hydrogeology study can be done following a strict clearance process using an EM-61 or a magnetometer detector, and only outside of the target area boundary. The proofing is done down to 8-10 feet and this is considered safe enough for drilling. If depth profiling is conducted on antitank ranges, the digging location should be proofed with the help of a metal detector prior digging to insure the safety of the operator of the auger or the shovel.

2. Grenade Range (small size)

On this type of site, soldiers throw grenades from behind a protective barrier and they wait for the explosion. Grenades can contain TNT or Comp B; so, RDX and TNT can be found on these sites if an incomplete detonation occurs. Usually when no detonation occurs after a throwing, the grenade is destroyed using C-4 plastic explosive after waiting a designated period of time for safety purposes. This can also lead to the spreading of RDX on the soils if an incomplete destruction is achieved with the C-4. The probability of encountering UXO on grenade ranges was initially thought to be very low since the grenades are thrown only a short distance and the concussion of the grenade would indicate that a detonation occurred. Sometimes, though, two soldiers from adjoining grenade pits throw grenades simultaneously. Thus, when a single concussion occurs, both think that their grenade detonated when only one did so. Undetonated grenades can roll into detonation craters and be covered by sand/soil thrown by subsequent detonations leaving a very dangerous situation for EOD personnel called into the range to detonate duds. Consequently, even if grenade ranges are considered free of UXO, care must be taken if subsurface sampling or drilling is done on site.

Metal fragments are widely distributed at hand grenade ranges potentially leading to heavy metals problems. For example, some German grenades contain a cadmium liner from which cadmium is spread into the environment upon explosion. Since these sites are small, systematic sampling such as compositing can be applied (Figure 6). Drilling to install monitoring wells can be done directly in the explosion area following the clearance of the drilling spot, but usually, since the sites are small and the wells could be damaged by detonations, the drilling is done just beside the area and down gradient to catch any contamination coming from the site.

Results obtained up to now on grenade ranges show a pattern of multi-contamination by various explosives and heavy metals. The contamination is always distributed all over the range, even at distances as high as 50 meter from the bunker. The grid should therefore encompass the overall range area plus some sampling lines in the outer limit of the range.

3. Artillery Range (large to extra-large size) (square kilometres)

On this type of range, gunners are shooting large calibers ammunition such as 105-155 mm artillery projectiles from firing points in a very wide field.. Sometimes fixed firing points are used, but more recently the importance of being able to set up the guns, fire, and move before the enemy can respond has become important. This had led to the use of random firing points at some ranges.

Firing of large calibers rounds leads to UXO when the ammunition does not explode on impact. The ammunition used contains Comp B, TNT, RDX and sometimes HMX. Close to the firing points, nitroglycerine and 2,4-DNT contamination can be found coming from propellant residues expelled at the gun muzzle. These large impacted areas can contain more or less UXO depending on the environmental conditions, the type of ammunition, and the use of the range. Low levels of contamination by explosives are encountered randomly at these ranges, but the main problems are the presence of UXO and high concentrations of explosives (sometimes in the % level) in soil next to low-order

detonations. Systematic sampling is not appropriate because of the size of the sites, but localized, judgmental soil sampling can be done on suspected areas, for example, near targets, using the compositing approach. Furthermore, a linear transect strategy could be applied and leads to a broad assessment of the whole area (Figure 7). EOD personnel conduct clearance of these large sites once in a while, and they usually detonate the UXO upon identification. Drilling of boreholes for well installation is done close to the road access down gradient from the range following the usual procedure of clearance. No well installation is done directly in the impact areas for safety reasons and also to avoid the destruction of the wells by subsequent detonations in the area. Nevertheless, hydrogeological studies can be accomplished because most of the time, there are access roads that cross the impact areas and the drilling rig can be brought very deeply in these areas allowing the installation of wells to intercept the groundwater coming out of the impact areas.

4. Rocket and Missile Ranges (large to extra-large size (square kilometres))

These sites are dedicated to the firing of mortars, rockets, and wired or wireless missiles. Presence of UXO is typical of the sites, and low concentrations of explosives are encountered resulting from second-order detonations or leaching of explosives from UXO. Propellant residues are also encountered near firing points due to deposition from firing or from burning of excess propellant. In some cases, radioactive contamination has been observed. As an example, radioactive Thorium-232 used as a tracer in MILAN missiles can be spread into the environment if the protective casing is broken during the impact of the missile. For these reasons, these missiles are now forbidden in Canada. Systematic sampling is not appropriate because of the size of the sites, but judgmental soil sampling can be done on suspected areas using the compositing approach. Systematic sampling can be done near targets and the compositing sampling strategy should be applied. EOD personnel conduct clearance of these large sites occasionally and they detonate the UXO upon identification. For Thorium-232, collection of the suspected missile debris and pieces is done using a procedure to avoid radioactivity contamination.

Again, as for the artillery ranges, boreholes are drilled close to the road access following the usual procedure of clearance.

5. Battleruns (large to extra-large size (square kilometres))

On this type of site, armies conduct tank manoeuvres, fire at pop-up targets, and simulate war field conditions. Contamination by explosives is low and is not concentrated close to the targets, because tanks often fire penetrators that do not contain high explosives. Pop-up targets do not provide sufficient resistance to cause detonation of HE containing shells; therefore, the ammunition often skips along the ground resulting in UXOs. So, the problems characteristics of UXO fields are observed in battleruns. However, target sites are often contaminated by heavy metals since pop up targets are used for tank mounted machine guns. Systematic sampling is not optimal because of the size of the sites, but nevertheless, can be done. The compositing approach can be used to characterize a large portion of the width of the site (linear transect strategy, Figure7). This systematic sampling can show trends in the concentrations of contamination, but does not provide reliable estimates of mean concentrations over the whole area. In general this approach consist of collecting two soil samples A and B in linear patterns of approximately 500 m perpendicular to the firing line at various percentages of the range length. This pattern was proven useful in battleruns where residues of gun powder were detected more frequently in the 0 to 40 % length area while the explosive residues where detected more frequently in the 80% and more transepts. In specific suspected areas, the compositing approach for the soil sampling can be used especially around pop-up targets, or where debris from low-order detonations is observed. The circular sampling strategy is appropriate for these pop-up targets and consists in collecting composite samples at defined distances around the targets (Figure 8). EOD technicians conduct clearance of these large sites occasionally, and they detonate the UXOs upon identification. Boreholes are drilled close to the road access following the usual procedure of clearance. No well installation is done directly in the impact area for safety reasons and also to avoid the destruction of the wells by subsequent detonations in the area or simply by a tanks running over them. Nevertheless, the hydrogeological study can be accomplished

since most of the time, there are access roads that penetrate the impact areas. Drilling rigs can be brought far into these areas allowing the installations of wells to sample the groundwater coming out of the impacted areas.

6. Land Mine Field (small to medium size)

Land mine fields are built during wartime to retard troop movements. Even if there are no such ranges in Canada, USA, UK and Australia, this is a very important worldwide problem and many efforts have been dedicated to this problem. In Canada and the United States, research minefields were constructed to evaluate various types of mine detectors. One type of detector is based on the detection of vapour signatures from these mines. As a part of this work, analysis was conducted on soils near buried mines. Very low concentrations of explosives are typically encountered around land mines and in the end, land mines can be considered as vicious UXO. Neither sampling nor drilling is allowed in a live land mine field.

7. Old Burial Site (small to medium size (hectares))

At this type of site, obsolete ammunition was disposed of by burial. This was an old practice, no longer acceptable for safety and environmental reasons. Burial led to large amounts of UXO at the same location. These sites are very dangerous because of the obsolete character of the UXO and also because of the large amount at the same location. In addition, in many cases the geographic locations of the sites are unknown. Since most of these sites are very old, some of the UXOs may be perforated, their content leaching into the surrounding environment. This could represent a large source of contaminants similar to an industrial waste site, but with more dangerous characteristics. Sometimes these sites, filled with everything from small arms to chemical warfare rounds, are found accidentally. The usual approach consists of determining the perimeter of the UXO contamination using a magnetometer. The site is then slowly and carefully excavated to allow the identification of the UXO. Sampling for residues can be done using the compositing approach once safety is ensured. Usually, soils are collected

around the ammunition. Depending of the size of the site, open detonation can be done using sand bags to contain the fragmentation of the UXO, but the absence of chemical warfare must be ascertained first. Drilling is not allowed close to the burial site, but it is done outside the area to sample the groundwater flow and ascertain whether explosive contamination is present. At these sites everything can be discovered from small arms to radioactive contaminants or mustard gases, etc, so, extreme care must be taken.

8. Cratering Range (small size (hectare))

The purpose of these ranges is to practice the art of making craters in airfields or in roads to stop tanks, truck convoys, or any motorized vehicle passing through areas of concern. Trigran, a mixture of TNT and RDX containing small amounts of HMX, or C4 are mainly used for this purpose. The soils are generally strongly disturbed in these sites with craters as deep as 6-10 ft. There are no UXO present; so, the sites are relatively safe for sampling and drilling. Usually a compositing strategy is used to sample walls, bottom and surroundings of craters. Low concentrations of TNT and RDX are found, probably due to poor high-order detonations. Drilling can be done on these sites or around them with no necessary proofing.

9. Wood, concrete and steel Cutting ranges (small size (hectare))

The purpose of these ranges is to practice the art of cutting trees in order to block roads, or to cutting concrete in order to attack buildings or bridge foundations or to practice the art of cutting steel in order to attack steel construction or bridges. C4 is the explosive of choice for these purposes and RDX contamination should be expected. . There are no UXO in these sites; therefore, sampling and drilling are allowed. The sampling patterns that should be used in these ranges should take into account the craters that are to be found there. All craters should be sampled in the center and on the outer circle around the crater. A systematic grid could also be used (10 m x 10m) with the random collection of 30 sub-samples in each grid.

10 Demolition Range (small size (hectare))

The purpose of these ranges is to practice the art of destroying pieces of equipment such as trucks, cars, etc., or to stop terrorist acts. In these cases, C4 is also the explosive of choice and RDX contamination should be expected. There are no UXOs in these sites; therefore, sampling and drilling are allowed.

11 Explosive Ordnance Disposal Pits (small size (hectare))

These pits are used to destroy obsolete ammunition that is considered safe enough to be moved, or other types of ammunition that contains explosives but without primers to initiate the explosion. Damaged ammunition still containing explosives, but with their casing ruptured are destroyed, can result in incomplete destruction of the explosive content. Low to medium contamination can be observed in these pits. C4 is usually the explosive chosen to destroy the ammunition, so RDX contamination can be observed in these pits. There are no UXOs; therefore, sampling and drilling are allowed. In general, composite samples should be collected in the bottom and in the walls of the pits.

12 Open Burning (small size (hectare))

In this type of site, obsolete propellants and dangerous explosive residues are burned at atmospheric pressure usually on a concrete slab or metal pan. In the past, burning was often done directly on the ground, which we now know, causes substantial contamination. This activity leads to environmental pollution by explosives and, in many cases, high levels of nitroglycerine and nitrocellulose were found. In addition, since the temperature of burning is less than the temperature of detonation, complete combustion is not achieved and the gaseous emissions contain more toxic gases. Melting of high explosives followed by recrystallization with depth in the soil has been observed at one site. Moreover, high heavy metals concentrations were found around the open burning area. Some propellants contain lead to lubricate the gun interior plating avoiding gun erosion. The burning of these specific propellants on the soil surface builds up a

contamination by lead of the surface soils. In the past, small arms were also disposed of by incineration under less than optimal conditions leading to the spreading of heavy metals around the incinerator. In general, open burning is a dirty process and should be avoided. Controlled incineration equipped with afterburner and dust collector is more appropriate for the destruction of obsolete ammunition. There are no UXO and sampling and drilling are allowed. In these sites, surface and subsurface sampling should be conducted. When appropriate, wells are installed down gradient of the burning location.

13 Open Detonation (small to medium size (hectares))

In this type of site, obsolete explosives, ammunition containing high explosives, and other high-energy components are detonated at atmospheric pressure in the field. In some cases, this technique has proven to be a clean process for the disposal of explosives. No contamination or very low concentrations of explosives were detected on extensively used open detonation sites in Canada. A large study conducted in USA demonstrated that the gaseous emissions coming from an open detonation were harmless for the environment and that the main components were carbon dioxide, nitrogen and water. Providing adequate donor charge to sustain a complete afterburn is critical to eliminating harmful residues or emissions. This activity is a very cheap way of disposing obsolete munitions, but nearby communities often complain of the noise made by these large detonations. Quenching of the noise, however, increases the potential for undesirable emissions. There are no UXO on these sites; therefore, sampling and drilling are allowed. Grid pattern should be used (10 m x 10m) with collection of at least 30 random sub-samples within each grid.

14 Rifle Range (small to medium size (hundreds of hectares))

These sites are dedicated to practice with small arms. Usually, the targets are installed on a stop butt (or berm), which is heavily contaminated by heavy metals, but not by explosives. Since the users are skilled marksmen, the contaminated area is largely restricted to the stop butt. Occasionally, the manager of these sites must remove the

metals from the butt, and the recovered metals are sent for disposal to a scrap metal dealer. If the sifting of the berm is not done on a regular basis, the metals can slowly dissolve and contaminate the groundwater. This is particularly true when acidic or basic soils are encountered, since metals are more soluble at high or low pH. However, dissolution of these metals is slow and groundwater contamination can be avoided by the periodic cleaning of the butt. There are no UXO on these sites; therefore, sampling and drilling is allowed without the need for proofing. Systematic sampling can usually be done using various composite sampling patterns depending on the number of targets. If biomass is present on the berm, it should be also collected and analyzed since many plants are known to phytoextract metals (Figure 9). Subsurface sampling should also be conducted with the help of a manual auger. Both total metal (soil digestion) and leachate testing should be conducted to assess the total amount of metals present and their leachability towards the ground water.

15 Refuelling Areas (small size)

In the areas where the militaries refuel their vehicles, petroleum contamination can be encountered if spillage occurs. Even if the procedures are excellent in the training areas, the possibility of contaminating the environment with petroleum products is present. No major problems were observed in these areas; therefore, sampling and drilling is allowed. Monitoring of volatile organic compounds (VOCs) can be done in soils and groundwater at these locations.

Navy Ranges

1. Artillery (large to extra-large (square kilometres))

Navy is using large areas to practice their artillery firing. The firing points in these cases are ships and the targeted area, a piece of land close to the shore or an island such as the Kaho'olawe Island in Hawaii. The problems of naval artillery ranges are similar to those encountered for Army artillery ranges. The ammunition that the navy

fired is also similar in calibre, except on old ranges where larger caliber rounds from battleships and cruisers were fired. This also leads to the production of UXOs when the ammunition does not explode on impact. The ammunition used contains Comp B, RDX, TNT, HMX, and sometimes picric acid coming from old vintage munitions. These large impacted areas can contain more or less UXOs depending on the conditions, the type of ammunition, and the use of the ranges. Low levels of contamination by explosives are encountered, but the main problem is the presence of UXOs. Systematic sampling for contamination with explosives is not appropriate because of the size of these ranges, but judgmental sampling can be done on suspected areas using a compositing approach. Clearance of these large sites is occasionally done by EOD technicians, and they detonate the UXO upon identification. In the case of the Kaho'olawe Island, extensive UXO identification, destruction, and disposal are being conducted to clear definitely the island from the presence of UXO. Similarly to the Army sites, boreholes are drilled close to the road access following the usual procedure of clearance. No well installation is done directly in the impact area for safety reasons and also to avoid the destruction of the wells by subsequent detonations in the area. Nevertheless, hydrogeological study can be accomplished, since most of the time, there are access roads that penetrate the impact areas and the drilling rig can be brought far into these areas allowing the installations of wells to sample groundwater.

2. Underwater Explosion Range (small to extra-large size)

In this type of range, the Navy conducts experiments to evaluate the bubble formation, the pressure of detonation, the impact of the detonation on submarines, etc. Most of the time, the ammunition functions properly; but, when malfunction occurs, divers using C4 for clearance. Explosive contamination is difficult to evaluate in these instances. However, the greater pressure suggests that the detonation should be more complete and leads to cleaner products. Sampling water is not appropriate since the dilution factor is too big in the open sea. When underwater detonations are done in closed vessels, contamination can be evaluated by collecting water samples. This was

done at Eglin Air Force Base, and no or low contamination by explosives was found. When detonations were done in lakes, sediment sampling can be appropriate.

3. Munition Sea Dumping (extra-large size)

This is the marine equivalent of old terrestrial burial sites. In the past, obsolete ammunition was disposed of by sea dumping and in some cases, extremely large quantities were dumped at the same location. These munitions cannot be compared to UXOs, since they were never fired and they can be seen as obsolete munitions. As for the burial site, the problem is similar. The presence of a large amount of explosives in one location increases the danger related to an unplanned explosion. These large amounts can be looked at as very big potential sources of explosives leaching slowly into the oceans. Some experiments done by Sandia National Laboratory demonstrated that obsolete World War II ammunition sitting at the bottom of Halifax harbour is slowly leaching explosives into the ocean. Over time, corrosion will breach the casings and all the ammunitions dumped at the same time will perforate and release their contents together leading to an important explosive contamination problem. Some scientists in the Netherlands stated that a period of 200 years may be required for the corrosion to compromise the munitions, but this was not corroborated. Today, this activity is no longer allowed, but some efforts of sediments and water sampling should be made to address this important problem.

4. Munition Wrecked Ships (small size)

This situation is like a mini sea dumping site with an additional difficulty; there is a steel shell surrounding the ammunition that was deposited at the bottom of the sea. The problem is identical to the sea dumping problem, but the solution is different. In order to remove this contamination, methods to get the ammunition out of the wrecked ship will have to be identified. Sediment and water sampling can be done near the wrecked ships using divers or remotely controlled apparatus.

5. Torpedo Range (small size)

In these sites, the Navy uses old ships or island or continental shores to practice the shooting of torpedoes. As an example, the coral barrier around the Kaho'olawe Island was used as a target and some of these torpedoes did not function and are still there plugged into the coral barrier. This situation is like underwater UXOs and the safety issue is also of great concern. The same problems of underwater sea dumped or wrecked ammunitions are encountered with these torpedoes. For now, there is no technology to remove them except detonation and in some cases, this is not an acceptable solution. To detect underwater UXOs, some technologies are available, the most promising one is MUDS system that uses sonar and infrared sensors.

6. Missile Range (tomahawk) (large size)

In some cases, the Navy is assessing tomahawk technology and needs sites for the impact of the missiles. The problem is similar to the one encountered on Army missile ranges.

7. Ship-to-Ship Ranges (extra-large size)

Old ships can be used as practice target. For example, harpoon technology can be used to fire on these targets. Missing or malfunction can result in an UXO. This problem is similar to a torpedo range except that the munition will be recovered at the bottom of the sea and depths will be greater in these cases. The impact to the environment would be similar to that of an underwater UXO (corrosion, leaching, etc.).

Air Ranges

1. Air-to-Ground (CRV-7) (large to extra-large size (many square kilometres))

At these sites in Canada, F-18 fighter-bombers practice against ground targets at low altitude. Weapons such as sidewinder, CRV-7, or maverick can be used to destroy the targets. Usually, the sites will have metals debris and a possibility of deeply buried UXOs. Soil sampling can be accomplished around targets using a composite circular strategy that takes into account the different problems resulting from weapons launched from the air (Figure 10). The circular pattern is divided in 26 sub-area in which composite samples are collected. Drilling sites will have to be proofed before boreholes are made and wells are installed, down gradient of the target area.

2. Bombing Area (Tracadie) (large to extra-large size)

These sites are used to practice air bombing. During World War II, some islands in Canada and also some ranges such as the Tracadie range were used for such practice. Large bombs, 500 pounders and bigger, were used for this practice. This resulted in areas heavily impacted with debris and UXO, some buried very deeply and still active after 50 years. Levels 1, 2 and sometimes 3 are necessary to render these sites safe, especially if the site is to be given back to the public. Drilling is particularly dangerous on these sites, since large bombs can be encountered 15-50 feet deep. Proofing is possible, but drilling should not be done in the impact areas, but restricted to the outside boundaries. Surface soil sampling is allowed using a compositing sampling strategy, but generally low contamination by explosives is expected, except where low-order detonations have occurred or UXO casings are breached. The sites should therefore be examined visually and any area presenting high levels of shrapnel residues or low-order events should be sampled with the potential use of 10m x 10m grids pattern.

3. Missile Range (cruise) (large to extra-large size)

The problem of these sites is the same as encountered for the Army and Navy missile ranges. The differences reside in the type of missiles used for the practice. Cruise missiles do not lead to the same contamination as MILAN or Tomahawk missiles. If radioactive contamination is possible, specific sampling strategy must be adopted.

Protective clothing is appropriate on these sites. Soil sampling can be done using compositing in the field or close to the targets. Drilling can be done using the proofing technique.

4. Refuelling Area (small to large size)

In these areas, the problem is related to petroleum, methanol and ethylene glycol contamination especially when de-icing activities are conducted at airports. Petroleum contamination typically occurs as aircraft are refuelled. Even if the procedures are excellent and up-to-date, the possibility of contaminating the environment with petroleum products is present. This problem is now well understood and controlled. Monitoring of volatile organic compounds (VOCs) can be done in soils and groundwater at these locations.

5. Small Arms (20 mm)

These sites are dedicated to the firing of small arms and for practice by F-18s. Usually, the targets are installed on stop butts (berms), which are heavily contaminated by heavy metals, but not by explosives. The most contamination by heavy metals coming from F-18 small arms does not come from practice firing, but from the destruction of rounds by incineration. According to regulations, small arms that were subjected to real flight conditions suffered overpressure and must be destroyed after three flights. This leads to the destruction of many small arms rounds. In Canada, incineration was done to destroy these small arms, but this activity was stopped since it was contaminating the environment with heavy metals. In the practice ranges, the contaminated area is restricted to the stop butt. Once in a while, the manager of the sites must remove the metals from the butt and the recovered metals are sent for disposal to a scrap metal dealer. If metals are not removed, they can dissolve and contaminate the groundwater. The dissolution of metals is slow and groundwater contamination can be avoided by the cleaning of the butt. There are no UXO on these sites; therefore, sampling and drilling is allowed. In general, a linear sampling pattern could be used in lines perpendicular to the

firing line at various distances in front and behind the target area to assess the extent of heavy metal contamination.

Production Facilities

The suspected areas of soil and groundwater contamination can be identified based on where washout and other releases were made and/or on results of any previous characterization data. The potentially contaminated areas are not restricted to the suggested list below, but must be adapted to specific site conditions.

Effluent ponds (lagoons) known to hold TNT contaminated wastewater. The legacy production method involved toluene, nitric and sulphuric acids that produced a red water waste containing dissolved TNT and TNT by-products. The evaporation of the water induced the precipitation of TNT in crystalline form. Lagoons with no, or very low, density vegetation may indicate a high level of TNT in the sediment. ; These lagoon water and sediments should be analyzed for the high potential presence of residues of explosives. Care should be taken, since high levels may be encountered.

Burning grounds were used to burn explosives-containing solid wastes generated by the industrial activity. EM and metals contamination can be associated to these areas. Care should be exercised when taking soil sample with depth since lenses of recrystallized explosives are possible in the near surface soils (cm to m depths).

Disposal areas. Industrial wastes were often disposed of in “non-engineered” sites. Such sites can generate organic and inorganic soil and groundwater contamination.

Storage tanks (underground or above ground) and associated piping systems for organic solvents (e.g. toluene) and basic and acidic liquids (e.g. sulphuric or nitric acid) used for explosives production were stored in tanks which may have leaked over the years, resulting in soil and groundwater contamination with the presence of a free phase in groundwater.

Drain outlets. Surface soils or streams receiving drainage from pipe outlets are potentially contaminated and should be sampled. .

Test sites for explosive products can generate dispersion of explosives and metals on soil.

Production buildings. Soil around production buildings may contain explosives, especially in front of doors where the dust of the floor is swept outside the building. Soil under the buildings (via floor drain) may also be contaminated.

Storage and shipping buildings. The handling of packed explosives can contaminate the soil close to loading ramps.

Underground ducts and service ducts may have leaked and contaminated the surrounding soil.

Areas of excavation and fill may indicate waste handling or landfilling and should be tested for soil contamination.

Conclusion

Many different types of sites where different activities are conducted may be contaminated with explosives residues. Depending on the activities, different sampling strategies have to be applied and developed. In general, low explosive concentrations are encountered in training areas with a few exceptions, such as in anti-tank ranges, grenade ranges, firing positions and in hot spots generated by low-order detonations. For metal concentrations, the worse case scenarios are generally found in rifle ranges, scrap disposal and open burning areas. Specific precautions will have to be taken to mitigate the effects of these metals on the environment. An important aspect of training activities in most types of sites is UXOs. These UXOs represent a safety issue and are a worldwide problem. They can also be seen as potential sources of explosives that may leach to

groundwater upon shells breaching by eventual corrosion. When UXOs are generated from fixed firing points, high-density pockets of UXOs can built up in the target area. Incoming high-order detonations can crack the buried shells by sympathetic detonation leading to open sources of explosives. This situation will soon be studied and the problems addressed. The UXO problem is probably the most complex and important impact generated by military activities. Now, the detection, identification, and elimination technologies are addressed, but UXOs will also have to be addressed in the future. A corrosion study was also recently initiated that will try to evaluate the time to failure or time to rupture of various representative munition casings in accelerated corrosion conditions. The development of secondary fuzing systems in munitions should be studied to ensure that the fired munitions would always detonate leading to a zero dud production while being safer to handle.

TABLE I

Physical and Chemical Properties of Nitroaromatics and Nitramines

(Values taken from the Agency for Toxic Substances and Disease Registry

<http://www.atdsr.cdc.gov>) unless otherwise noted

Analyte	Molecular Weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Water Solubility at 20°C (mg/L)	Vapour pressure at 20°C (torr)
TNT	227.13	80.1-81.6	240 (explodes)	130	1.99×10^{-4}
RDX	222.26	205-206	(decomposes)	40-60	4.03×10^{-9} (a)
HMX	296.16	276-286	(decomposes)	6.63	3.3×10^{-14} (b)
TNB	213.11	122.5	315	350	3.2×10^{-6} (b)
DNB	168.11	89.6	300-303	500	3.9×10^{-3} (c)
Tetryl	287.14	132	187 (explodes)	75	5.7×10^{-9} (b, c)
2,4-DNT	182.15	71	300 (decomposes)	300 (d)	1.4×10^{-4} (b)
2,6-DNT	182.15	66	285	180	5.67×10^{-4}
2-ADNT	197.17	176		2800 (b)	4×10^{-5} (b)
4-ADNT	197.17	171		2800 (b)	2×10^{-5} (b)

(a) Rosenblatt *et al.* (1991)

(b) 25 °C

(c) Walsh *et al.* (1995)

(d) 22 °C

TABLE II

Detection Limits for Explosives in Soil by HPLC (EPA Method 8330A), GC-EDC (EPA Method 8095) and GC-TID (Field Analytical Method)

Analyte	Method		
	HPLC mg/kg	GC-ECD mg/kg	GC-TID mg/kg
HMX	1	0,025	0,027
RDX	1	0,0034	0,0094
TNB	0.3	0,0016	0,0024
DNB	0.3	0,00073	0,012
Tetryl	0.7	0,020	0,0017
NB	0.3	0,017	NA
TNT	0.3	0,0013	0,0016
2-ADNT	0.3	0,002	0,0068
4-ADNT	0.3	0,0015	0,0010
2,6-DNT	0.3	0,00069	0,0054
2,4-DNT	0.3	0,00068	0,0016
2-NT	0.3	0,012	NA
3-NT	0.3	0,011	NA
4-NT	0.3	0,010	NA

TABLE IIIDrinking Water Criteria for Munitions-Related Chemicals

(Roberts and Hartley, 1992)

Compound	Criteria ($\mu\text{g/L}$)
TNT	1.0
RDX	2.0
HMX	400
2,4-DNT	0.17
2,6-DNT	0.0068
TNB	1.0

TABLE IVHuman Health Risk Based Criteria in Soils for RDX, TNT and HMX

Compound	Criteria (a) mg/kg	Criteria (b) mg/kg
TNT	0.3	0.0024
RDX	0.3	0.012
HMX	1.7	2.2

(a) Daniels and Knezowich (1994)

(b) Rouisse (1997)

TABLE V

Frequency of Detection of Explosives Residues
in Soil Samples Analysed at Various Sites using EPA Method 8330A
(Walsh et all 1993)

	TOTAL
Installations	46
Samples analyzed	1155
Samples with detectable explosives	319
Analytes Detected	
HMX	37
RDX	87
TNB	108
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

TABLE VI

Detection Limits, Colorimetric Method

Compound	Minimum Sensitivity (mg/kg)*
RDX	1
TNT	1
2,4-DNT	0.5
2,6-DNT	2.1
2-NT	>100
3-NT	>100
4-NT	>100
4-ADNT	>100
TNB	0.5
NB	>100
Tetryl	0.9
DNB	ca. 0.5

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

TABLE VIIMaximum Holding Time (MHT) for Nitroaromatics and Nitramines.

Target analyte	MHT Water (4°C)	MHT Water (-20°C)	MHT Soil (4°C)	MHT Soil (-20°C)
Nitroaromatics	28 days [*]	6 months	7 days	8 weeks
Nitramines	50 days	6 months	8 weeks	6 months

* (Stabilized with NaHSO₄, 1.5g/L)

TABLE VIII

Chemical Analysis Results to Evaluate the Soil/Water Ratio of Adsorption Tests
(Adapted from Mailloux, 2002)

Soil/Water Ratio	Average Real Concentrations		Percentage of the Mass Initially Adsorbed	
	HMX mg/L	TNT mg/L	HMX %	TNT %
Co	1,9830	0,9676	NA	NA
Blank	1,8248	0,9476	NA	NA
3:1	1,5136	0,6578	25,7	32,0
2:1	1,6260	0,7314	19,6	24,4
1:1	1,7057	0,7980	6,5	17,5
1:4	1,7714	0,9113	2,9	5,8
1:10	1,7722	0,9445	2,9	2,4
1:20	1,8324	0,9200	0,0	4,9
1:40	1,7318	0,9404	5,1	2,8
1:60	1,9186	0,9614	0,0	0,6
1:100	1,8494	0,9800	0,0	0,0
1:200	1,8358	0,9404	0,0	2,8

TABLE IX

CHEMICAL ANALYTICAL RESULTS FOR THE EVALUATION OF THE EQUILIBRIUM TIME

for a Soil/Water Ratio of 2:1

Time hours	Average Real Concentrations in the solution phase	
	HMX mg/L	TNT mg/L
B	1,263	0,580
0	1,220	0,551
1	1,017	0,537
6	0,943	0,482
12	0,926	0,487
16	0,918	0,488
24	0,924	0,477
36	0,853	0,412
72	0,864	0,423

TABLE X

Values of partition and adsorption coefficients of Nitroaromatics and Nitramines
(Adapted from Hawari J.A. and A. Halasz (2002))

(Reader should also consult Brannon, J. M. and Pennington, J. C. (2002) for latest data.)

Analyte	Partition coefficients (log Kow)	Adsorption coefficients (Kd) (L/kg)
TNT	1.6, 2.2, 2.7 (b)	4.0 (a), 6.38 (c)
RDX	0.87(g)	1.2 (e), 0.2-7.8 (h)
HMX	0.13 (i)	0.0-1.2 (h)
TNB	1.18 (d)	60000 (e)
DNB	1.49 (d)	4500 (e)
Tetryl	1.65 (f)	5.8 (e)
2,4-DNT	1.98 (d)	7400 (e)

- (c) Pennington and Patrick Jr. (1990)
- (d) ATSDR (1995)
- (e) Sheremata *et al.* (1999)
- (f) Rosenblatt *et al.* (1991)
- (g) Haderlein *et al.* (1996)
- (h) Jenkins (1989)
- (i) Banerjee *et al.* (1980)
- (j) Townsend and Myers (1996)
- (k) Tucker *et al.* (1985)

FIGURE 1

Evaluation of the Soil/Water Ratio for Adsorption Tests
(from Mailloux, 2002)

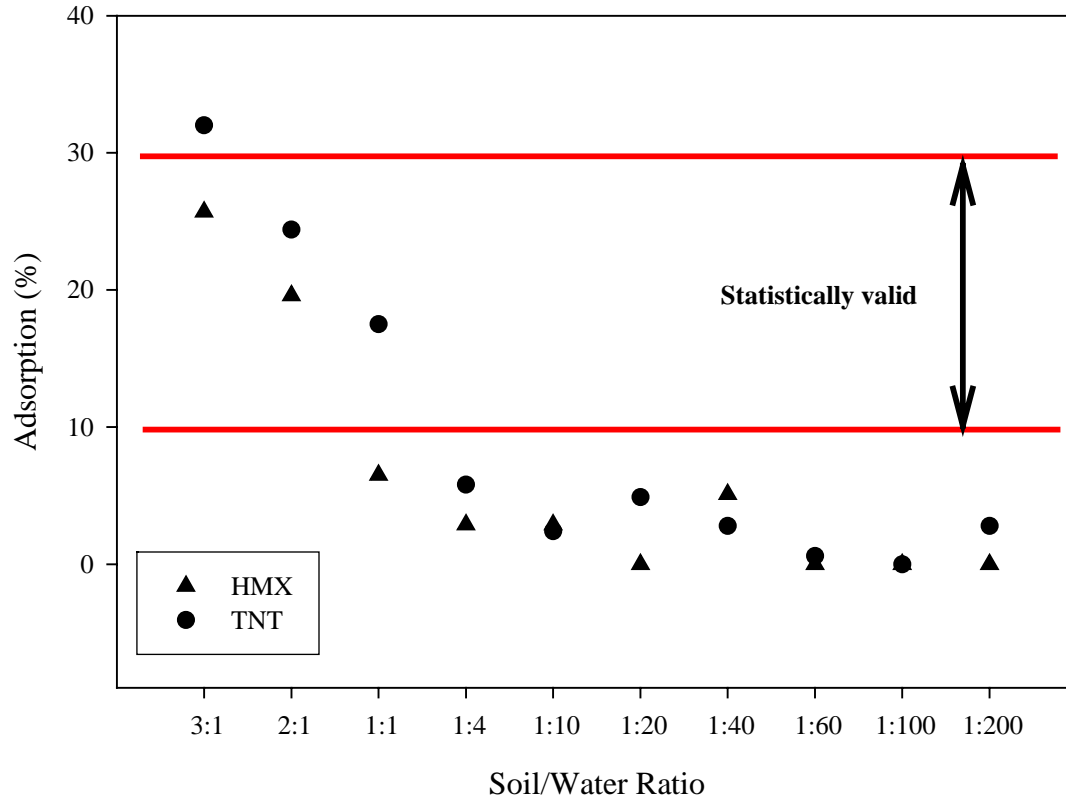


FIGURE 2

Evaluation of the Equilibrium Time for HMX and RDX in Sand
(from Mailloux, 2002)

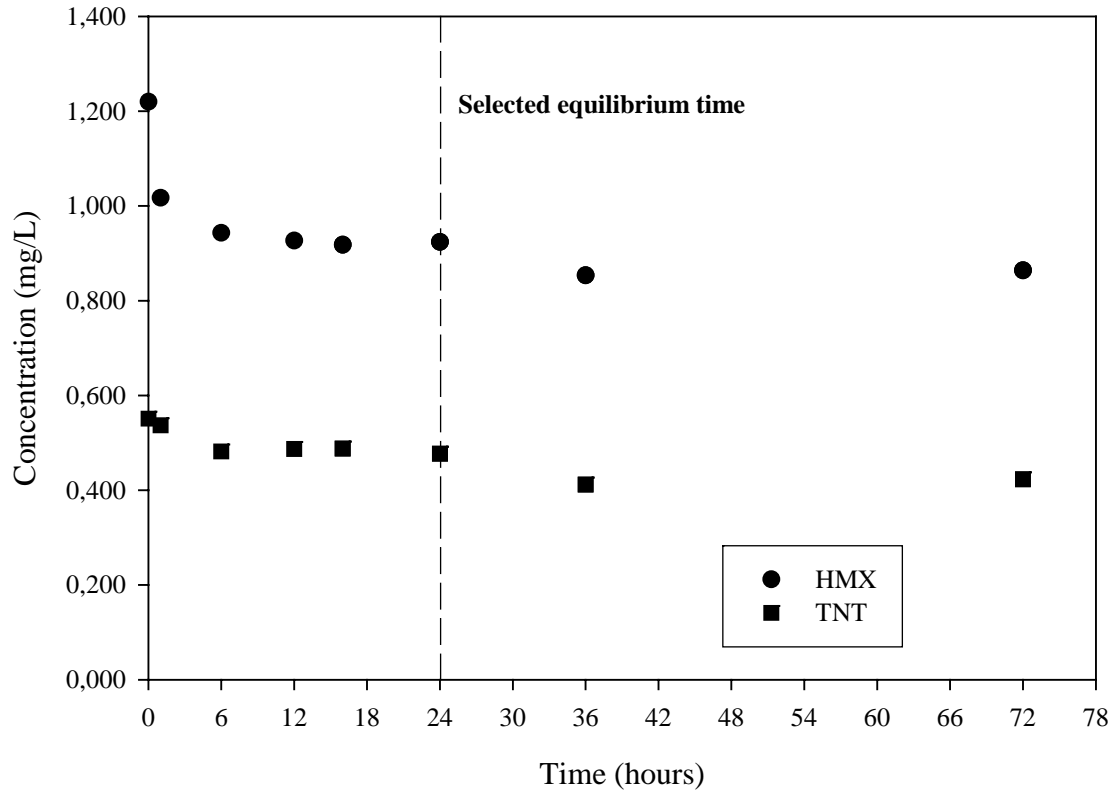


FIGURE 3

Preliminary Adsorption Isotherms for TNT and HMX in Sand
using the Freundlich Model (from Mailloux, 2002)

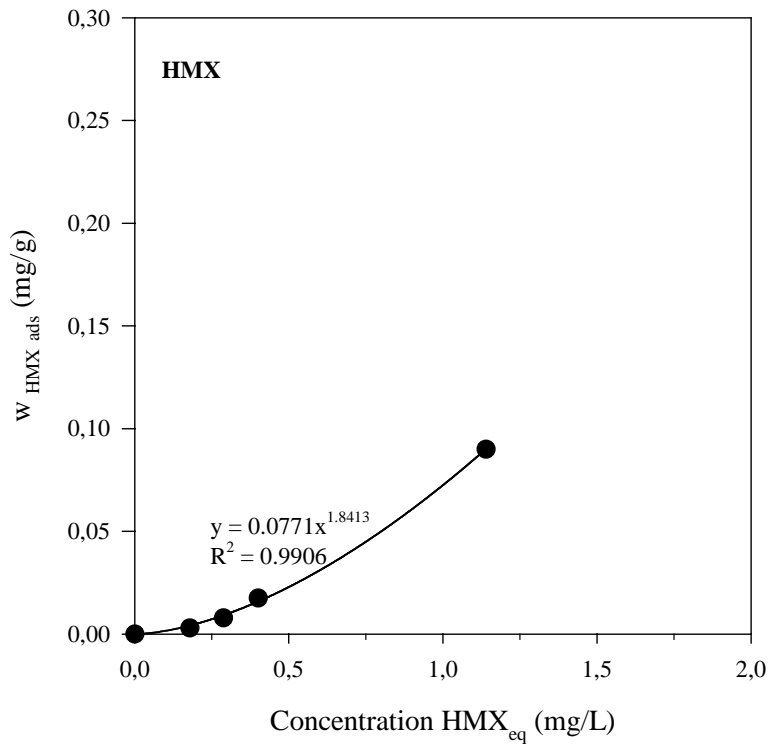
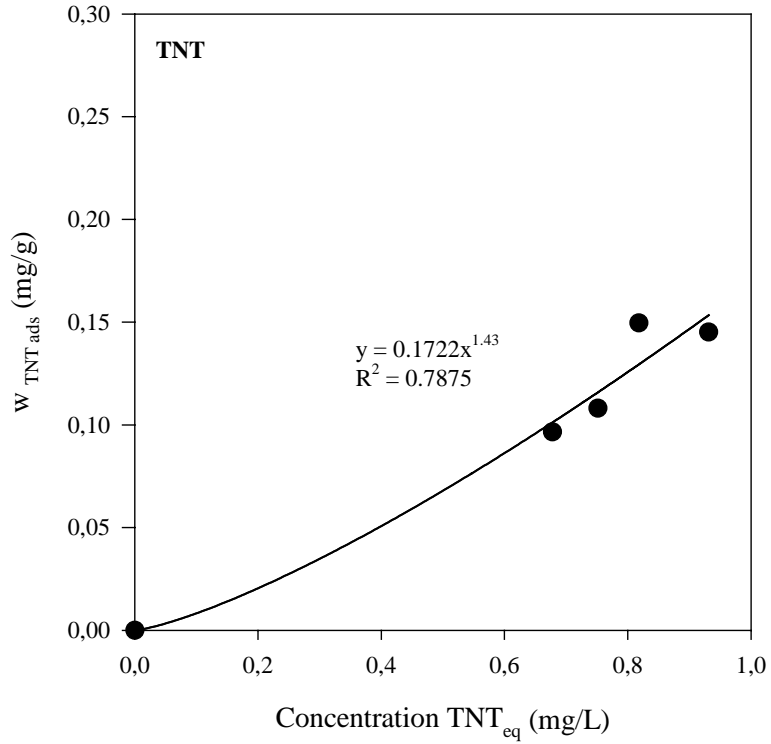
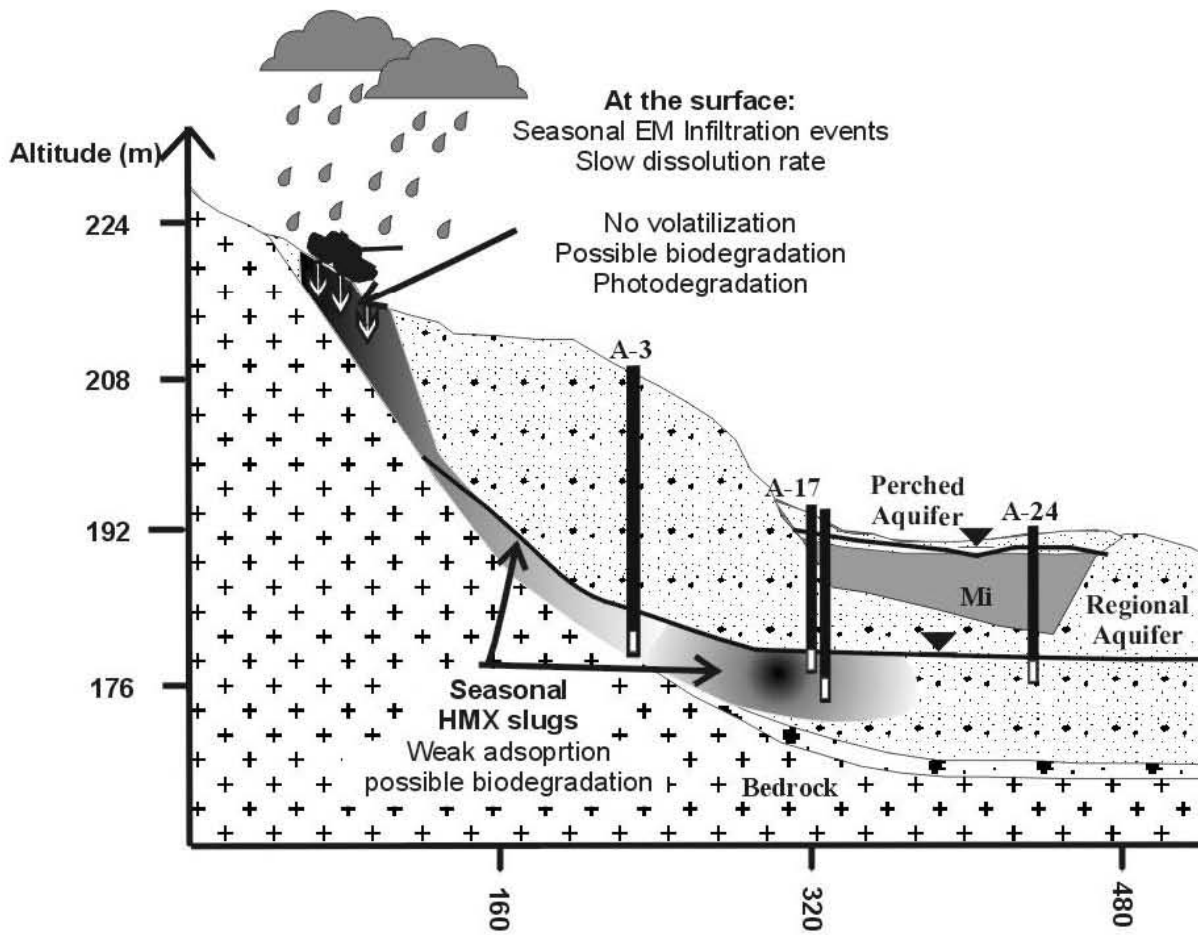


FIGURE 4

Conceptual model of HMX behaviour in an anti-tank range
 (Adapted from Mailloux (2002))



Vertical exaggeration: 5X

FIGURE 5

Wheel Sampling Pattern at anti-tank range

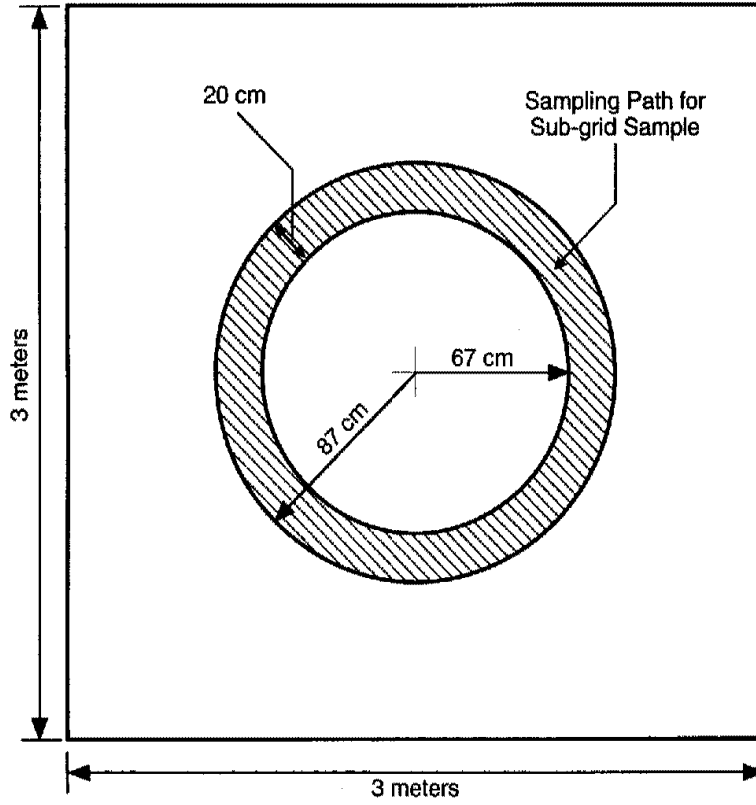


FIGURE 6

Soil Sampling Pattern for Grenade Ranges

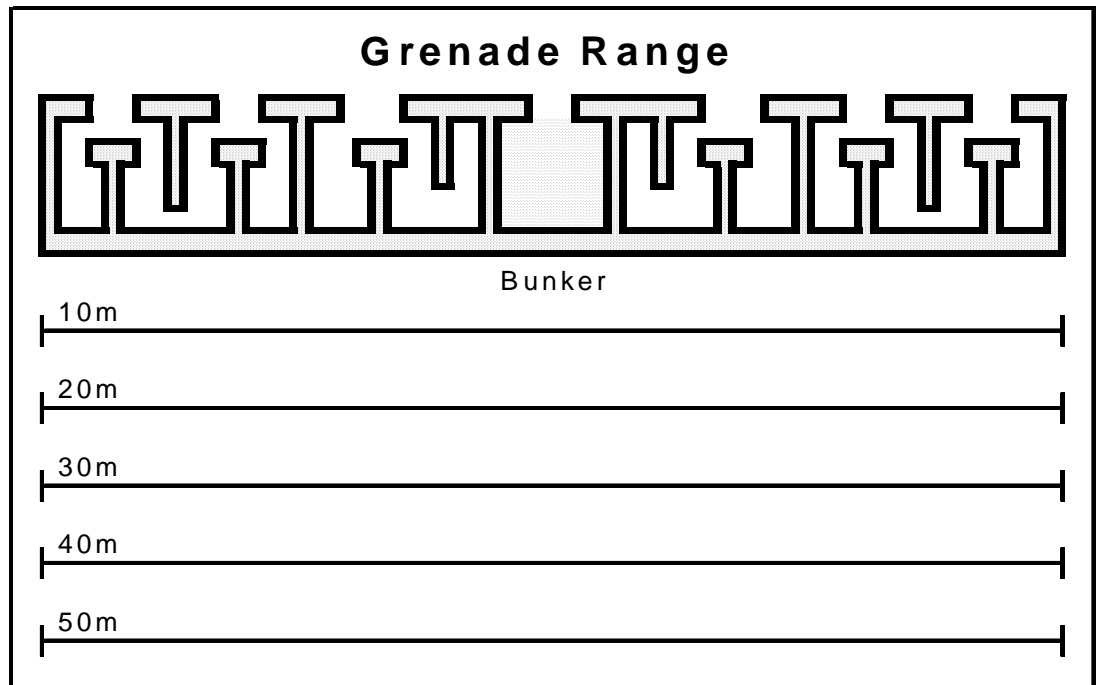


Figure 23. Linear Sampling, NCHGR Range

FIGURE 7

Linear Transect Sampling Strategy for Battleruns

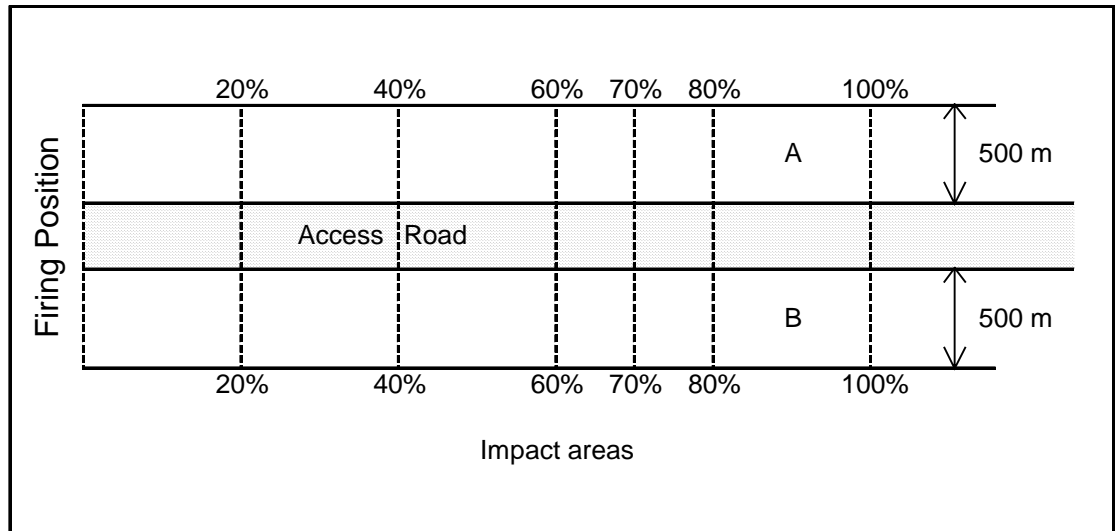


FIGURE 8

Circular Sampling Strategy Around Pop-up Targets

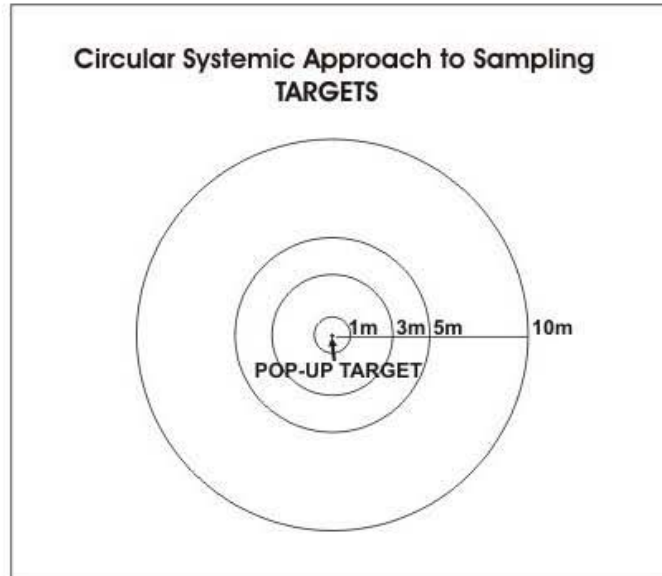


FIGURE 9

Soil Sampling Pattern for Riffle Ranges: Composite built for each 4 target groups

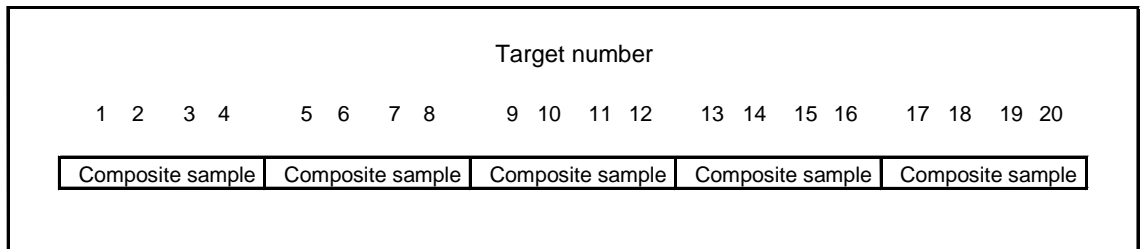
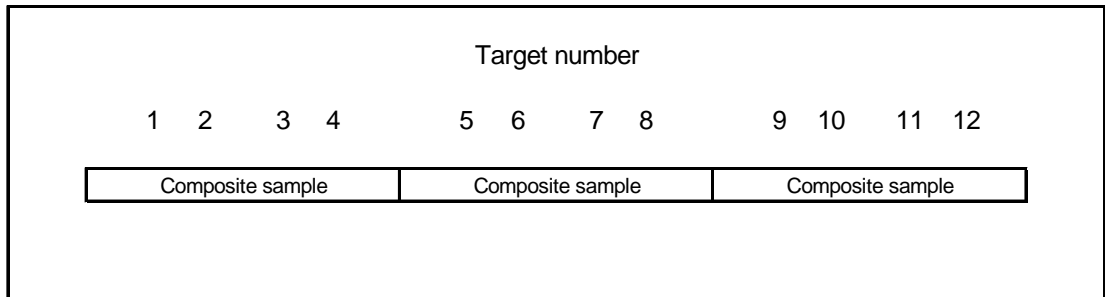


FIGURE 10

New Circular Soil Sampling Pattern Designed for Air-To-Ground Targets.
The Total Number of Samples is 26 Around a Target.

