WORKSHOP REPORT

SERDP and ESTCP Workshop on Research and Demonstration Needs for Management of Munitions Constituents

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ACRONYMS

AEC	U.S. Army Environmental Command
ASTM	American Society for Testing Materials
BIP	blow-in-place
BMP	best management practice
CS	consolidated shot
DAAN	diaminoanisole
DESHE	Developmental Environment, Safety and Occupational Health Evaluation
DNAN	2,4-dinitroanisole
DNT	dinitrotoluene
DoD	Department of Defense
EOD	explosive ordnance disposal
EPR	enhanced performance round
ER	Environmental Restoration
ERDC EL	U.S. Army Engineer Research and Development Center Environmental Laboratory
ESOH	environment, safety, and occupational health
ESTCP	Environmental Security Technology Certification Program
GAC	granular activated carbon
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine
IHE	Insensitive High Explosives
IM	insensitive munitions
IMX	insensitive munitions explosives
LAP	load/assemble/pack
MC	munitions constituents
MEC	munitions and explosives of concern
MR	munitions response
NC	nitrocellulose
NEW	net explosive weight
NQ	nitroguanidine
NTO	3-nitro-1,2,4-triazol-5-one
OB/OD	open burn/open detonation

OECD	Organization for Economic Co-operation and Development
PAX-21	Picatinny Arsenal Explosive-21
PM	project manager
QA/QC	quality assurance/quality control
QSAR	quantitative structure-activity relationship
RDECOM	U.S. Army Research, Development and Engineering Command
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
RO	reverse osmosis
SERDP	Strategic Environmental Research and Development Program
SOP	standard operating procedures
TNT	2,2,6-trinitrotoluene
TREECs	Training Range Environmental Evaluation and Characterization System
TTCP	The Technical Cooperation Program
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
UXO	unexploded ordnance
ZVI	zero-valent iron

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) are the Department of Defense's (DoD) environmental technology programs. SERDP and ESTCP address environmental matters of concern to DoD through funding for basic and applied research and development, as well as demonstration and validation of technologies that can enhance the capabilities of DoD to meet its environmental obligations. These programs fund projects in the areas of Environmental Restoration, Munitions Response, Resource Conservation and Climate Change, and Weapons Systems and Platforms. The Environmental Restoration Program Area funds research and demonstrations in the area of risk assessment, fate and transport of chemicals of military concern, mitigation of the impact of munitions constituents, as well as remediation of contaminated soils and waters. For additional information, refer to www.serdp-estcp.org.

To help define future needs, the Environmental Restoration Program Area held a 2-day workshop in Washington, DC in July, 2015. The objectives of the workshop were to (1) review the life cycle process for use of munitions constituents and identify data gaps and research needs that are appropriate to address under the Environmental Restoration program area; (2) apprise representatives from the Services of applicable research and demonstrations funded by SERDP and ESTCP; and (3) develop a prioritized list of research, demonstration, and technology transfer needs for management of munitions constituents that could be addressed by SERDP and ESTCP over the next five years.

2. METHOD

The SERDP and ESTCP Workshop on Research & Demonstration Needs for Management of Munitions Constituents was held on 28-29 July 2015, in Washington, D.C. Approximately 70 invited personnel representing DoD program managers, federal and state regulators, engineers, researchers, industry representatives, and consultants were in attendance. The agenda for the Workshop may be found in Appendix A and the Attendee list is provided in Appendix B. A steering committee composed of representatives from the Services provided critical input on the meeting's focus, specific structure, and participants.

The agenda was designed to identify the most pressing needs in a focused manner, while ensuring that all participants could express their views. The workshop opened with a series of introductory presentations describing the life cycle of munitions constituents, relevant lessons learned, as well as an overview of relevant research and demonstrations funded by SERDP and ESTCP.

Two breakout sessions, each with four working groups, facilitated discussions of each stage in the munitions constituents lifecycle: development phase, manufacturing phase, operation and use phase, and demilitarization phase. In the first breakout session, participants reviewed the associated management challenges, data gaps and research needs where research and development or field demonstrations related to the Environmental Restoration Program Area would improve the management of munitions constituents.

The second breakout session built on the first session by focusing on development of a prioritized list of research, demonstration, and technology transfer needs that could be addressed over the next five years. Research paths and demonstrations were prioritized as either critical or high priority, largely based on the sequence of events required to impact DoD decisions within 3 to 5 years of research & demonstration initiation (Table 1).

A poster session was held in the evening of the first day of the workshop. This poster session highlighted key SERDP and ESTCP funded efforts as well as additional case studies and other efforts supported by the Services.

The entire group participated in the final discussions and selection of the key issues and the research and demonstration needs. Several of the participants contributed to sections of this report describing specific issues and needs, and/or edited the draft versions.

Table 1. Definition of Research Need Prioritization

	Critical	High
Research	Research that potentially could have a significant impact in the short term.	Research that is of high priority but may not be able to be initiated until critical research needs are addressed or may be more clearly defined after critical research needs are addressed.
Demonstration	Field demonstrations or assessments that can improve on munitions constituents management.	Field demonstrations or assessments that are of high priority but may not be able to be implemented until critical demonstrations or assessments are completed.
Technology Transfer	Specific actions or documents that could be undertaken immediately to promote technology transfer of key concepts or technologies.	Actions or documents that should be undertaken to promote technology transfer of key concepts or technologies once specific research and/or demonstrations have been completed.

3. OVERARCHING ISSUES

Several overarching issues were discussed throughout the workshop and are summarized in the following sections. Research needs were not necessarily associated with all issues; however, these thoughts shaped some of the discussions regarding research needs during the workshop.

3.1 Following the ASTM Standard

The American Society for Testing Materials (ASTM) "Standard Guide for Assessing the Environmental and Human Health Impacts of New Energetic Compounds" was issued in May 2008 (ASTM E2552-08). This international guide provides a standard method to evaluate the potential environmental impacts of prospective candidate energetic substances in an iterative phased manner. This phased approach allows compound development simultaneously with environmental and health effects testing, thus preventing the full production and release of materials to the environment prior to understanding their fate and environmental effects. The methods and data requirements are deliberately balanced with: 1) the level of funding used in munitions compound development: 2) inexpensive testing done early in compound development; and 3) the more expensive tests done only when a compound is ready for engineering and manufacturing.

Discussions during several of the breakout groups indicated that following the ASTM approach would significantly reduce the uncertainty associated with the potential for negative environmental effects from MC releases, although there may be room to improve this standard. However, there is no requirement or policy directive to follow this or a similar standard. Although munitions developers follow most of the early compound testing recommended in the ASTM standard, the later-stage tests are not done, particularly the two-year cancer studies and Tier II Ecotoxicity studies. The only current requirement is to ensure safety during the development and fielding of insensitive munitions as identified in USC, Title 10, Chapter 141, Section 2389, December 2001.

3.2 Open Detonation

Open detonation is used throughout the life cycle of explosives development, training, and demilitarization. Open detonation areas have the highest concentrations of explosives residues compared to other types of ranges (Jenkins et al., 2006). This is largely the result of how these ranges are used. Open detonation areas tend to have low-lying centers, and higher edges (i.e., bowl shaped), for safety reasons. Open detonations, in addition to covering smaller areas for safety reasons, often use unconfined materials to create detonations (block or shape charges, typically C4). This unconfined material does not detonate as efficiently and tends to leave a greater mass of explosive on the ground surface (Hewitt et al., 2003; Taylor et al., 2004).

Alternatives to open detonation are needed and a summary of potential alternatives to open detonation needs to be produced. This summary should include method details, whether the method is commercial availability or in development as well as the cost benefit (e.g. recycling material or waste to energy).

3.3 Source Terms

The amount of energetic residue resulting from energetic material production, training, testing, and demilitarization is unknown. It is difficult to determine the potential for exposures or to develop management plans without better information on the nature and extent of the sources. Understanding the source term characteristics is of paramount importance; however, given that vast areas of land serve as testing and training ranges, it is unclear how precise this understanding must be for proper range management. It may well be cost prohibitive to fully characterize any testing and training range; therefore, other measures may have to be taken to understand the source term and its implications to range management. Some potential measures include improved methods for automated tracking and reporting of munitions use and disposal on active ranges that can be leveraged for improved uncertainty quantification of source terms at active ranges.

4. RESEARCH & DEMONSTRATION NEEDS

Several overlapping research needs were identified often in multiple breakout sessions. Therefore, research needs have been grouped into four broad categories:

- Treatment options
- Sampling and analytical techniques
- Fate and effects of munitions constituents
- Research and demonstration needs for munitions constituents lifecycle stages

The following sections provide more detail on the research needs identified during the workshop.

4.1 Treatment Options

Treatment options for different media and sources are discussed in the following sections. The current situation is summarized for each material to provide context on the drivers for the recommended needed research. Research needs were identified, and in some cases expanded descriptions are provided herein. Some of the needs are described in more detail in subsequent sections.

4.1.1 Wastewater from Manufacturing

4.1.1.1 Waste Composition and Regulatory and Safety Drivers. Munitions constituents (MC) manufacturing and load/assemble/pack (LAP) operations generate liquid waste streams from various plant activities. Manufacturing generates wastewater containing both organics (MC) and inorganics (nitrate). The waste stream volume is obviously lower and more easily handled during the initial MC development and test stage than during the acquisition stage, where flows as high as five million gallons a day may be generated. For LAP operations, the volumes also tend to be smaller, and the main constituents are MC, with traces of any processing agents. While efforts are made to keep solid MC out of the liquid waste stream using crystallization, settling, and filtration, the presence of micron-sized MC is still probable.

4.1.1.2 Current Treatment Options. The established treatment trains at specific manufacturing and LAP facilities vary, but some generalizations can be made. Manufacturing facilities tend to use sequential anaerobic/aerobic biological treatment to remove both the inorganic nitrate and the organic MC using traditional wastewater treatment plant processes, with discharge to surrounding surface water. While these processes have been reasonably effective for treating manufacturing wastewaters containing legacy MC (e.g., TNT, RDX, HMX, DNT, NC), a stricter regulatory environment and the need to produce a range of new MC, including insensitive high explosives (IHE) like NTO, DNAN, and NQ, is putting demands on existing systems.

For instance, while the legacy MC are considered to be not very soluble (e.g., 10’s to 100’s mg/L), newer IHE constituents like NTO has a solubility of 20,000 mg/L, leading to both high concentration wastewater and a much larger loss of the end product to the waste stream.

Additionally, while legacy MC are amenable to the current biological treatment approaches, not enough is known about the degradative pathways, or potentially more toxic end-products, of IHE to assure the existing wastewater treatment trains will be sufficient to meet release criteria.

LAP facilities tend to use diatomaceous earth filters combined with granular activated carbon (GAC), and run their processing water in closed loops through the plant (e.g., zero discharge), with spent GAC removal and disposal as a hazardous waste (ERDL/EL TR-13-20). It is likely that the more highly soluble IHE (like NTO and NQ) will sorb less to GAC than the legacy MC, thereby reducing the effectiveness of the existing LAP wastewater treatment process, and requiring new technologies to ensure effective IHE treatment (ERDL/EL TR-13-20).

4.1.1.3 New Developments and Research Opportunities. Several treatment options for MC wastewater and specifically IHE in LAP wastewater were compared in a 2013 effort by the U.S. Army Engineer Research and Development Center Environmental Laboratory (ERDC EL). A document titled "Evaluation of Treatment Technologies for Wastewater from Insensitive Munitions Production. Phase 1: Technology Down-Selection" (ERDC/EL TR-13-20) was produced as a result. The report presented a technical and cost evaluation comparing the current diatomaceous earth and GAC process with other alternatives (Table 2).

The report concluded that no single technology would meet all the criteria for robust and cost-efficient treatment, mostly due to existing data gaps, and seemed to advocate for a staged treatment train (Table 2). The work covered in the report also did not directly examine the issue of mixed waste streams (e.g., legacy MC and newer IHE), and as it was focused on LAP facility wastewater, did not deal with the treatment of inorganics like nitrate.

While this ERDC EL work provides a starting point for developing new or improved treatment technologies for liquid MC waste streams (while continuing to meet explosive safety considerations), the workshop participants identified several outstanding questions and areas where additional research and development are needed.

The co-manufacturing of both legacy MC (e.g., RDX) and newer IHE (e.g., NTO) is expected to continue for several decades. Additionally, new IHE are continually being developed. Therefore, technologies capable of handling mixed waste streams were deemed a critical need. Specific research needs included the following:

- Develop a better fundamental understanding of technologies and mechanisms for specific MC or MC mixtures (SERDP)
- Determine the impacts of IHE wastes on treatment of legacy MC wastewaters (SERDP/ESTCP)
- Develop treatment technologies which are able to satisfactorily treat both IHE and legacy MC (SERDP/ESTCP)
- Evaluate if modular or "pod" treatment trains can be used to treat the diverse waste stream compounds more effectively (SERDP/ESTCP)

Table 2. Potential Technologies for Integrated Treatment Train (ERDC/EL TR 13-20)

Primary Treatment Technology	Potential Technologies for Integrated Treatment Train
Biological	• Possible GAC adsorption for low concentrations of diaminoanisole (DAAN)
Bimetallic Catalysts	• Advanced oxidation process • Aerobic biodegradation • Gas sparging • Nitrogen removal
Zero Valent Iron	• Pretreatment to remove suspended solids • Biological treatment after ZVI reduces toxicity • Advanced oxidation process
Reverse Osmosis	• Must be coupled with destructive treatment
Fenton	• GAC adsorption • Advanced oxidation process
Sonochemistry with Fenton oxidation	• May not require additional treatment, but IHE have not yet been studied
UV peroxide/peroxone	• May not require additional treatment, but not all IHE have been studied
Alkaline Hydrolysis	• GAC adsorption to remove DNAN color • ZVI to remove NTO and NQ • Advanced oxidation process
Persulfate	• Sulfate removal process
Direct Electrochemical Destruction	• GAC adsorption for color removal

Additional needs that could lessen the burden on, or extend the useful life of existing treatment systems, and help achieve compliance with tightening regulatory constraints on releases were also identified:

- Develop methods for more efficient/complete recovery of products to decrease the concentration of waste streams (e.g., NQ by cooling) (SERDP).
- Design treatment trains to achieve zero discharge (e.g., closed loop water usage). (ESTCP).
- Identify improvements to existing technologies to help meet regulatory requirements (SERDP/ESTCP).

4.1.2 Solid Wastes from Manufacturing

4.1.2.1 Waste Composition and Regulatory and Safety Drivers. During both MC manufacture and LAP operations, solid MC wastes are generated. These wastes range from excess solid neat explosives and propellants (e.g., melt cast lifts, wash-down solids, etc.) to disposable plastic bags and other consumables. As these wastes are considered both explosive (or at a minimum, combustible) and hazardous/toxic, they must be disposed of in a safe manner.

4.1.2.2 Current Treatment Options. The established method for bulk MC solid wastes is open burn (OB), which is deemed the most effective and safe disposal option. MC contaminated materials are often treated using alkaline hydrolysis.

4.1.2.3 New Developments and Research Opportunities. Regulatory scrutiny of OB operations for MC disposal is increasing due to the uncontrolled nature of the process and resistance by local community stakeholders to large OB operations. OB operations may, therefore, need to be phased out in favor of more acceptable, yet currently unrecognized, alternatives. The fate of IHE in OB operations also needs to be assessed. Further, research and demonstrations are needed in the following areas:

- **Perform more complete characterization of OB emissions *(ESTCP Critical):*** The characterization should measure and model emission rates from OB operations with respect to both organics and inorganics (e.g., Pb, Cr), and particulates, and should include both legacy MC as well as newer IHE.
- **Develop alternatives or improvements to OB for aged, off-spec, and excess propellants and energetics *(SERDP/ESTCP Critical):*** The range of possibilities could include thermal, photochemical, biological, catalytic, etc., as long as the primary safety concerns in handling these solid wastes are considered. Both legacy MC and IHE need to be addressed.
- **Develop methods for resource recovery or energy recovery from decontamination and destruction technologies *(SERDP/ESTCP High):*** The wastes produced, by nature, contain a great deal of combined nitrogen and energy. Therefore, recovery of some of this nitrogen and energy during the waste processing would be very beneficial and could offset some of the cost associated with switching from relatively inexpensive OB methods to another more expensive technology. Examples include production of fertilizer or industrial feedstocks from MC wastes. These methods would be particularly valuable for off-spec products, and in place of OB/OD for disposal. Both legacy MC and IHE need to be addressed.
- **Adopt a Best Management Practices similar to the protocol developed by Canada or other countries to improve facility OB operations for range wastes *(ESTCP High).***
- **Review and optimize MC processing practices to minimize MC contaminated solid wastes or use materials that are more amenable to non-OB treatments *(ESTCP High).***

4.1.3 Contaminated Soils

4.1.3.1 Overview of the Issue and Current Treatment Options. The DoD needs to balance military preparedness with MC contamination of soils at testing and training ranges. This balance is made more difficult by residential developments that encroach upon existing installations and more stringent environmental regulations.

While exposure to MC in soil on DoD sites is mainly an issue of protecting site personnel and the indigenous flora and fauna, soil contamination also serves as a source for contamination of groundwater and surface water (via surface runoff). Therefore effective management of MC residues in soil is key to overall MC risk mitigation.

SERDP and ESTCP have previously funded a wide range of research focused on MC in soil, including, but not limited to, the following aspects:

- MC residue deposition from high order and low order detonations of mortars, bombs, and other munitions.
- Aging and transport of MC residues.
- Fate and transport of MC, including photodegradation, sorption, and biodegradation.
- Toxicity of legacy MC to flora and fauna.
- In situ and ex situ technologies to retain and/or degrade MC in soil (biotic/abiotic).

4.1.3.2 New Developments and Research Opportunities. Previous research has greatly expanded the fundamental understanding of how legacy MC behave in soil, and has resulted in treatment technologies, some of which are being applied at select ranges. However, ongoing testing and training with legacy MC continues to contaminate soil, and the development and fielding of IM has raised several new issues that need to be addressed. The workshop participants identified several research and development needs based on these issues:

- **Determine the fundamental reasons for the persistence of RDX in soil *(SERDP Critical):*** RDX is known to be recalcitrant to biodegradation in the environment and while bacteria have been isolated that can degrade RDX, it is a stable compound and is known to persist at contaminated sites for many years. Previous research has detected aerobic RDX-degrading bacteria (or genes associated with aerobic RDX degradation) in almost every soil tested from sites contaminated with MC from around the world (ER-1504). However, despite the presence of these species in contaminated surface soil, RDX residues are not degraded to the extent needed to prevent migration and contamination of groundwater or surface water (ER-1378, ER-1607, ER-1609). It is known that TNT is a potent inhibitor of the RDX degrading enzyme XplA, also the regulation of the expression of the XplA/B system appears to be regulated by nitrogen availability. Further studies are required to understand the regulation of XplA by RDX and factors affecting its mechanism of activity. An unusual feature of the microbial degradation of RDX is that XplA/B is the only enzyme system that has been demonstrated to be directly responsible for RDX metabolism and is limited to a relatively small group of bacteria. Additional selective enrichment combined with meta-omic studies from RDX contaminated sites may reveal new RDX degrading activities and shed further light on the reasons for RDX recalcitrance.

If plants native to military sites could be modified through molecular breeding approaches to immediately absorb and degrade RDX after dissolution of particles from the surface of the soil, this technology could represent a low-cost sustainable strategy to contain RDX at these sites. Plant roots readily absorb RDX and translocate it to the aerial organs, but despite high uptake rates, plants have inherently low endogenous abilities to degrade RDX (ER-1317, ER-1318, ER-1319, ER-1498, ER-1412, ER-1499). Since the microbial RDX degrading enzyme XplA is a cytochrome P450 and plants contain many hundreds of P450s in their genomes, identification of an RDX degrading plant P450 would potentially offer a low cost sustainable non-GM solution to re-vegetating and remediating contaminated sites.

- **Evaluate the applicability of current technologies for treating new IHE (especially NTO) and mixtures of legacy and IHE, as well as ionic energetic materials, aluminized formulations, binders/additives, plasticizers, and processing agents *(ESTCP Critical).***
- **Develop technologies to maximize sorption/biodegradation at the soil surface, and/or minimize transport of the more soluble IHE to the subsurface *(SERDP High):*** As stated above, some of the newer IHE like NTO dissolve quickly and are very soluble in water. These compounds pose an even greater risk to groundwater (and by extension, surface water) than most of the legacy MC. Surface treatments or amendments that can effectively retain and promote the degradation of these compounds are therefore needed now before these materials are more widely used on ranges.
- **Develop new or improved means to deliver treatment amendments to range soils *(SERDP/ESTCP High):*** Impact areas are inherently difficult to treat given the repeated detonations which can move amendments out of the area or destroy them. Some success has been seen at grenade ranges using hydrated lime (ESTCP project ER-200216), but these are already well managed training areas. New techniques will be needed to deliver amendments effectively to more remote ranges, with much larger areas.
- **Develop standardized sampling and analysis protocol for IHE in soil *(ESTCP High).*** Progress has been made in this area over the last decade. These developments are a foundation for standard protocols to measure the effectiveness of different treatment methods developed in the future.

4.1.4 Contaminated Groundwater

4.1.4.1 Overview of the Issue and Current Treatment Options. Military training at DoD facilities deposit MC in soil and in surface waters which, when dissolved, can contaminate groundwater. Because groundwater can move off base effective management of MC in groundwater is key protection of community drinking water resources.

SERDP and ESTCP have previously funded a wide range of research focused on MC in groundwater, including, but not limited to, the following aspects:

- Fate and transport of MC in groundwater, including sorption and biodegradation
- In situ and ex situ technologies to retain or degrade MC in groundwater (biotic/abiotic)

4.1.4.2 New Developments and Research Opportunities. As with MC in soil, the previous research has greatly expanded the fundamental understanding of how legacy MC behave in groundwater, and have resulted in several treatment technologies that are being applied at several ranges. However, the development and fielding of IM has raised several new issues that need to be addressed, including:

- Determine the fate and transport properties of IHE in groundwater, including sorption, biotransformation, and biodegradation (***SERDP***).
- Evaluate the applicability of current technologies for treatment of new IHE (esp. NTO) and mixtures of legacy and IHE, as well as ionic energetic materials, aluminized formulations, binders/additives, plasticizers, and processing agents (***SERDP/ESTCP***).
- Develop standardized sampling, preservation, and analysis protocol for IHE in groundwater (***SERDP/ESTCP***).

4.1.5 Contaminated Surface Runoff and Surface Water

4.1.5.1 Overview of the Issue and Current Treatment Options. As a result of range activities, surface soils have become contaminated with MC residues. MC residues generated can be small enough to be readily transported by storm water runoff over land and into drainage areas, eventually making their way into surface water receptors. Additionally, larger MC residues can undergo in-place weathering, leading to entrainment and transport of dissolved and particulate MC during precipitation events. Many areas where detonations occur have sparse vegetation, due to repeated soil disturbance and range management efforts to minimize fires and facilitate UXO clearance; this may lead to reduced chances that the transport of MC in storm water runoff will be mitigated by vegetation before reaching surface waters.

Some limited DoD funded efforts at selected ranges have indicated that MC in surface water is not a major issue. The issue of MC in storm water runoff and surface water has not been extensively studied during SERDP or ESTCP funded projects. However, some initial findings during SERDP project ER-1689 detected low, but consistently measureable concentrations of RDX, HMX, and perchlorate in surface runoff from a range at a DoD site in the northeast. Due to the limited data on the scope of the problem, no technology evaluations for treatment of MC contaminated surface runoff or surface water have been performed or reported.

4.1.5.2 New Developments and Research Opportunities. Due to the wide range of climates, and the different types of surface waters on DoD facilities, more efforts are needed to gain a basic understanding of this issue and to draw reasonable conclusions about the scope and mitigation potential of MC contaminated surface runoff and surface water.

- Determine the fate and transport properties of legacy MC and IHE in surface runoff and surface water, including sorption, biotransformation, and biodegradation (***SERDP***).
- Develop technologies to treat surface runoff contaminated with legacy MC, new IHE, and mixtures of legacy and IHE, as well as ionic energetic materials, aluminized formulations, binders/additives, plasticizers, and processing agents (***SERDP/ESTCP***).
- Develop standardized sampling, preservation, and analysis protocols for IHE in surface runoff and surface water (***SERDP/ESTCP***).

4.2 Sampling and Analytical Techniques for Munitions Constituents

Despite the current use of IM, environmental concerns associated with their disposal persist. During the entire manufacturing, testing, operation, and demilitarization process, there is potential for releases, management approaches, mitigation response technologies, and atmospheric emissions. Several soil/water/air sampling and analyses approaches are available to quantify that impact, however, standardized sensitive, rapid and reproducible sampling, preservation and analytical methods for IHE precursors, IHE and IHE daughter products in water, air, soil, and tissues are not available. Application of specific sampling and/or analytical approaches can impact life cycle costs, range management, and mission readiness.

There are no standard methodologies in place, so the community operates by interpreting common methodologies perceived to be Best Management Practices (BMP). Improvements are needed with respect to sampling and analytical techniques for MC through additional research and development (SERDP) funding.

Although current regulations require DoD to determine human and environmental impact resulting from exposure to these IHE, there is no standard methodology consistently used across the community that delivers sensitive, rapid, and reproducible sampling, preservation, and analytical performance for IHE precursors, IHE, and IHE daughter products in water, air, soil, and tissues. Field analysis methods are also needed (SERDP) for monitoring around range areas, and within manufacturing facilities. A robust standard methodology that validates accuracy, precision and reproducibility on existing methodologies is also needed (ESTCP). Ultimately, these results feed into toxicity models; therefore it is critical that the results represent a precise measure.

Specific needs for research and development (SERDP), and demonstration/validation (ESTCP) are discussed in the following sections.

4.2.1 Critical Research and Demonstration Needs

4.2.1.1 Standardized Analytical and Extraction Laboratory Methods for IHE and Metabolites *(SERDP/ESTCP Critical)*. An approved method (or methods) similar to EPA Method 8330B for nitroaromatics and nitramines is needed for IHE and their metabolites, including NQ, DNAN, NTO, and nitrophenols (including picric acid, explosive D, and dinitrophenol). It is critical that the method accurately and precisely captures the information that will eventually be used in toxicity models. Standardized methods for nitrophenols are also needed for sites with legacy munitions.

4.2.1.2 Standardized Sample Extraction and Analytical Methods and QA/QC for Munitions Compounds and Metabolites in Environmental Matrices *(SERDP/ESTCP Critical)*. Methods are needed for analyzing IHE and their metabolites (NQ, DNAN, NTO) in all media, including groundwater and surface water. Critically, none of the available research methods allow for quantification in soil. There is an urgent need to develop standard methods and calibration techniques, and to validate these methods using actual contaminated soils. Also needed are standardized extraction methods, including techniques for soils, sediments, plant and animal tissues, and biota).

An important part of such methods is the need for commercially available calibration standards for many of these compounds and their metabolites. Although it is recognized that this need may well be beyond the SERDP and ESTCP purview, several discussions during the meeting alluded to the difficulties associated with the availability of calibration standards, which are vital for a standardized analytical and extraction method.

4.2.2 High Priority Research and Demonstration Needs

4.2.2.1 Validated Standard Operating Procedures (SOP) for Incremental Sampling in Sediments (*ESTCP High*). A validated SOP is needed for incremental sampling of sediments. The SOP is envisioned as an ESTCP validation of costs and performance in a range of settings, including lakes, streams, and marshes. Workshop attendants emphasized that large numbers of incremental sampling demonstrations have occurred in soil, using methodologies like the Training Range Environmental Evaluation and Characterization System (TREECs™) or MultiIncrement Sampling. However, no standard validated method exists for sediments. Perhaps using the demonstration of incremental sampling in sediments that U.S. Army Environmental Command (AEC) is funding at Fort Jackson may serve as one such technology transfer opportunity.

4.3 Fate and Effects of Munitions Constituents

Munitions compounds may be released into the environment at several points during manufacture, training, and combat. These releases have resulted in significant costs to the DoD in the past, and continue to represent significant liabilities.

Better understanding of the fate and effects of MC, especially the IM currently in development, can minimize future costs for characterization, cleanup, and natural resource damages. Exposure to frangible Cu particles from bullet coatings is one recent example of the problems that can result from not evaluating fate and effects at the earliest possible stage of munition development. The ASTM standard (ASTM E225-08, 2014) provides a roadmap for such testing, and improving the cost-effectiveness and accuracy of these test methods should foster adoption of appropriate fate and effects assessments at each stage of the lifecycle of MC.

It is therefore important to have user-friendly tools to screen and evaluate the fate and effects of new MC, and to use those tools during the development process. Incorporating fate, transport, and toxicity predictions into new compound screening protocols would be particularly helpful. Finally, the development and use of improved fate and effects models as well as more accurate data inputs for those models can help managers better predict and minimize the environmental impacts of range operations.

4.3.1 Critical Fate and Transport Research Needs

4.3.1.1 Standardized Computational and Experimental Evaluation Methods for IHE Fate and Transport (*SERDP Critical*). The development process for new MC should include environmental evaluations early in the process to screen out potential unwanted environmental impacts. These evaluations should be standardized, to allow cost-efficient and rapid screening to prevent undesirable environmental impacts. The first step will likely rely on modeling to estimate the key chemical parameters and fate and transport after release. Accurate and user-friendly models are important, especially because there are limited resources for experimental studies to measure fate and transport parameters.

Several models and protocols are available, each with their strengths and weaknesses, as well as with different degrees of validation. A clear need is to evaluate the existing models and select the model(s) appropriate for use by MC developers. In particular, models providing an integrated assessment of environmental fate and transport for new compounds are needed. Further, new computation methods that are currently in development could provide a better framework for the needed environmental evaluations (e.g. SERDP Project ER-1734). The approach used for pesticide fate and transport evaluations for several decades can provide robust order of magnitude parameters. This approach may be adopted or modified for MC use.

4.3.1.2 Measurements of Fate- and Transport-Determining Properties of IHE (*SERDP Critical*). To better predict and measure the fate and transport, improved models and data on the key properties controlling these processes are needed. Key fate-determining properties include ionization constants (e.g., pK_a), and rate constants for hydrolysis, oxidation (including photooxidation), and biotic and abiotic reduction. For transport, these properties include water solubility, Henry’s law constant, and partitioning coefficients to octanol (K_{ow}) and native organic matter (K_d). These fate and transport constants are used in qualitative assessments of MC fate and in models for quantitative simulation of actual fate and transport field scenarios.

Experimental data for fate-determining properties of IHE are still scarce, and often of uncertain reliability. More and better-measured data are needed for the whole range of current and future MC. In particular, studies of the processes that are relatively difficult to characterize are needed. Although most existing studies of the new IHE have focused on the simpler processes (e.g., partitioning and hydrolysis), potentially important processes that are more difficult to evaluate are critical to understand. Such processes include biodegradation and photodegradation. In addition, abiotic degradation may affect some MC (like RDX), and plant uptake and degradation may be important for some of these compounds.

Biodegradation data are needed for aerobic and anaerobic conditions in both soil and groundwater, and possibly also in wastewater treatment processes. Both pure and mixed culture systems could be of interest, since there have been few studies of the biodegradation of specific IHE compounds Some IHE (like NTO but not DNAN) are unlike compounds with well-characterized biodegradation potential. In particular, identities and fate of degradation intermediates and byproducts needs to be understood.

Photodegradation has received little attention in recent years even though it is well established that some MC are quite labile to photodegradation. Direct photolysis will most likely give the most distinctive results, but indirect photolysis could also be important. Photodegradation will only occur in the upper photic zone, and many types of MC compounds released to the terrestrial environment will be subject to photodegradation.

Fate and transport studies need to be conducted with the actual munitions formulations used. The fate of MCs in typical mixtures, and the effects of the other formulation materials (e.g., binders) on MC fate need to be assessed. Since mixtures with other MC are likely, these effects should be considered as well. In addition, impacts on other contaminants of concern should be evaluated. One notable example is the potential for acidity associated with NTO to enhance metals mobilization. Finally, improved tools for fate and transport studies would be helpful, such as reactive tracers to simulate IHE behavior in the environment.

4.3.1.3 Improved Fate and Transport Models to Predict Exposure and Risk of MC in Field Scenarios (*SERDP High*). Although there are several existing models that can be used to predict these fate- determining properties, most are not entirely satisfactory for MC chemicals. New efforts should build on prior art, starting with systematic assessment of the actual performance of existing tools, and any overlap and gaps in their coverage. Models responsive to this need may be of several types: 1) quantum chemical models for chemical properties from first principles (requires no experimental data for calibration); 2) empirical and statistical correlation models (quantitative structure-activity relationships, QSARs); or 3) expert systems that encode decision trees.

Existing fate and transport models use “fate-determining” property data that is either measured or predicted. Their output is generally contaminant concentration (potential exposure) distributed over time and space. The various models should be systematically compared in terms to application range, output capability, precision, accuracy, usability, and transparency for IHE and related MC. In addition, while fate/transport models generally provide contaminant concentrations over time and space, they could be extended to endpoints more directly relevant to risk assessment through coupling to risk models and incorporation of toxicology data.

4.3.2 Critical MC Effects Research Needs

4.3.2.1 Surface Water/Runoff (*SERDP Critical*). The amounts of MC that leave ranges as runoff and reach surface waters are generally not known. Better methods to measure runoff losses would help understand the potential impacts as well as allow mitigation measures to be used more efficiently. Better methods to mitigate runoff losses are also needed to minimize off-site impacts or potential ecological damages on the range.

4.3.2.2 Long Term Toxicity of DNAN and NTO Formulations (*SERDP Critical*). Two-year chronic mammalian toxicity studies are critical for understanding the potential impacts of recent IM compounds.

4.3.2.3 Effects of IHE Compounds on Vegetation (Phytotoxicity and Uptake) (*SERDP Critical*). Ranges benefit from having vegetation (aquatic and terrestrial). Vegetation provides critical habitat, preserves soil and prevents runoff, and retains and degrades contaminants. Vegetation can prevent downward migration of contaminants and eventual groundwater pollution both through uptake and by reducing water infiltration. It is therefore important to know if IHE compounds affect vegetation, and if so, how and at what concentrations. It is also important to understand whether IHE compounds accumulate in the plants, or whether they are transformed or degraded. Translocation of MC compounds within plants (i.e., movement from roots, to stems & leaves) can also be important. Photodegradation can also occur within plants, in situations where photo-sensitive MC compounds move into the leaves. The presence of residual MC in leaf litter can also be a concern. Understanding the eventual fate of IHE compounds if consumed or degraded after plant death may also be important.

4.3.2.4 Effects of IHE Compounds on Fauna (Toxicity and Uptake) (*SERDP Critical*). Ranges also benefit from fauna present, both aquatic and terrestrial fauna, that serve vital environmental functions and also can be important receptors of concern. It is critical to understand if IHE compounds will affect the range fauna, and if so, how and at what concentrations. It is also critical to understand if fauna accumulate the compounds or transform them after uptake.

4.3.3 High Priority Fate and Effects Research and Demonstration Needs

4.3.3.1 Fate and Effects of Other Energetic Components (*SERDP High*). Recent work on new MC has focused on a very small number of the most major components of IM formulations. There are other energetic components, generally used in smaller quantities that may have significant environmental effects. These include ionic energetic materials and aluminized formulations.

4.3.3.2 Fate and Effects of Other Components of Munitions Formulations (*SERDP High*). In addition to the “minor” energetic components of some IM, there are other materials included in IM formulations that are not energetic but might have environmental consequences. Better characterization of fate and effects of these other components of munitions formulations could uncover significant concerns (e.g., nonbiodegradable surfactants/polymers, and lead compounds used as propellant burn-rate modifiers). To do this work will require complete information about compositions. Materials of potential concern include binders/additives, plasticizers, processing agents, and burn-rate modifiers.

4.3.3.3 Byproduct Identification and Characterization (*SERDP High*). All recent work on new MC has been focused on the primary/parent MC compounds. However, a large body of work on traditional MCs (most notably TNT and RDX) has shown that degradation involves complex pathways that lead to a variety of intermediates and products, some of which can be problematic. Some of these pathways are likely to apply to IHE and other new MC, so it is important to identify potential byproducts and determine the properties. A chemoinformatic approach (based on reactivity rules from experts or literature) can be used to determine the likely products once there is sufficient information accumulated for a particular group of compounds. Once identified, the key fate- and effects-determining properties should be measured (including toxicity), potentially followed by detailed fate and/or effects modeling.

4.3.3.4 Interaction Effects (*SERDP High*). Many environmental effects of contaminants are different in the presence of other contaminants. The best known examples are in toxicology, but interaction effects arise in transport (through changes in solubility or partitioning) and transformation (through competition for degraders, catalysis, etc.) These “interaction” effects can be very important but generally are left until after all the “pure” effects are well characterized. Studies explicitly designed to address interaction effects will be needed.

4.3.3.5 Techniques to Minimize Transport (*SERDP/ESTCP High*). A distinctive characteristic of some IHE is their relatively high water solubility (e.g., NTO). This increased solubility means that these compounds are more prone to leaching into ground or surface waters, with less retardation in soils and sediments. This characteristic is different than most conventional energetics (e.g., TNT), and could pose serious environmental concerns and eventual liabilities for DoD.

Therefore, it may be necessary to develop and test novel methods of minimizing solubilization and transport for use with these compounds. This issue could be addressed by modification of the IM material formulations, or by developing and testing methods to treat sites to minimize dissolution and transport. Treatment after contaminant release could be done, to minimize subsequent transport, or pretreatment of a site to contain releases might also be done. Possible treatment strategies could include amendments to retain NTO as it is released, or reactive amendments to degrade NTO as it is mobilized.

4.3.3.6 Improved Fate and Effects Measurement Methods (*SERDP/ESTCP High*). As noted above, new and better data are needed on the fate- and effects-determining properties of novel energetics. The need for measured values and predictive models was noted earlier, but in some cases, the ability to measure these properties is limited by the available measurement methods. Improved methods could improve toxicology evaluations, as existing toxicology assays tend to require significant quantities of test material. These methods are often expensive to perform, and interpretation of the results can be ambiguous or controversial. In addition to improving existing individual toxicity test methods, there is a need for work on optimizing the combination of methods to be used (to cover the range of essential endpoint).

With respect to fate- and transport-controlling properties, better measurement methods are not as critical, but there are examples where improved methods could be highly impactful. For example, fate and transport testing at the column- or pilot-scale generally will require more test material than is feasible. Therefore, some method development might be needed to develop methods for doing "micro-scale" testing of macro-scale processes.

4.4 Research and Demonstration Needs for MC Lifecycle Stages

Research needs are different for the different stages in the lifecycle of MC. Workshop participants considered these different stages and the current state of knowledge and technology to identify research and demonstration needs specific for each stage.

4.4.1 Development

Participants tasked with addressing issues associated with MC development emphasized an overall need for consensus on the assessment protocol that should be followed in evaluating new materials. At the same time, developers perceive a need for improved modeling and test standards, in order to both screen and validate the ESOH characteristics of MC. Existing models and tests, as currently specified in the available phased approaches, can be used to satisfy recommended data points, but will only be effective in evaluating risk if they provide an accurate approximation of how the MC will behave in the environment. In short, DoD needs better methodologies for understanding fate, transport, and toxicology of MC, with a particular focus on families of materials specific to energetic materials – high nitrogen materials, ionics, and organometallic compounds. The three needs identified by this group are discussed below.

4.4.1.1 Consensus Assessment Protocol (*ESTCP Critical*). At the time of the workshop, there were multiple phased approaches to gathering environment, safety, and occupational health (ESOH) data for new materials. These include: the ASTM E-2552-08 (primarily authored by the U.S. Army Public Health Command); an approach developed by the U.S. Army Research Development and Engineering Command (RDECOM); the Developmental Environment Safety and Occupational Health Evaluation (DESHE) approach; the Technical Cooperation Program (International) CP 4-42 "Assessing the Potential Environmental and Human Health Consequences of Energetic Materials: A Phased Approach" and a Draft (under development) Office of the Secretary of Defense Collection of Chemical, Physical, and Toxicological Data to Support DoD Systems Acquisition.

All of these protocols built upon the framework of the ASTM E-2552-08 using a very similar approach but were tied to different milestones in development, or were intended for slightly different audiences. While all have their merits, the PM community is most interested in a single, DoD approved methodology that can be used as guidance for energetic material development. This will require standardization/validation/refinement of ESOH testing protocols to be used by primary MC developers.

Workshop participants identified a need for the scientific community to review the existing ASTM/TTCP/DESHE guidelines to reconcile differences and come up with a consensus protocol that is optimal for primary MC developer use. This final protocol should satisfy data requirements for applicable domestic and international environmental regulation as well as occupational safety requirements. It was recommended that this could include one dedicated task for systematic validation and comparison of these methodologies. This recommended data set should also include a list of relevant DoD, industry, or academic partners that can gather each specific data point using appropriate Good Laboratory Practices and U.S. Environmental Protection Agency (USEPA) recognized methods.

The screening protocol is vital to support the development of new materials, processes and technologies under the Weapon Systems and Platforms program area; however, the environmental impacts of materials in the environment are often more thoroughly studied by the Environmental Restoration community. This is an excellent opportunity for the two program areas to work towards a joint solution to screening materials throughout development.

4.4.1.2 Improved Fate and Transport Experimental Data (*SERDP/ESTCP Critical*). One of the key pathways for MC migration in the environment is through unexploded energetic materials on training ranges. It is vital to understand generally how this material will either break down under different conditions or be transported around and potentially off-site. There are currently multiple variables associated with this exposure scenario, ranging from physical factors such as soil type, pH, and climate, to biological factors such as vegetation cover and microbial community composition. There does not appear to be a relatively simple answer for this kind of test and it is not feasible for a material in development to be subjected to this extensive level of testing. There are available ASTM and Organization for Economic Co-operation and Development (OECD) based standards for individual scenarios, but there is no current standard for degradation or transport across DoD relevant conditions for MC.

Discussions during the workshop suggested that the scientific community would benefit from a database containing the standard available set of test protocols to screen materials. This information could be presented to USEPA so as to establish a baseline amount of data for new compounds in the future. This will not completely replace site specific testing for specific conditions, but will provide a baseline comparison for evaluating different materials. This database should be developed for all MC, so that future materials can be evaluated against this standard. This could include the development of a limited data set of standard soils and/or conditions (sunlight, water, microbe)—representative of relevant DoD sites—to be used in material developer sponsored testing. If this set of soils becomes an established standard for this purpose, then it would help the developers address various regulatory requirements.

4.4.1.3 Improved Predictive Models (*SERDP/ESTCP Critical*). Multiple models have been developed to predict the chemical properties and fate of new chemical materials, including efforts through academia, industry, and the government. However, these models are developed and validated for high-use production chemicals that are often neutral compounds. DoD has used these existing tools to fit a modeling database to novel energetic compounds with varying degrees of success. Currently available QSAR models are best-suited to predictions for uncharged compounds, such as pharmaceutical products and pesticides, since these are the primary components of the training sets.

However, emerging energetic materials are poorly-predicted by these models. The DoD requires new computational models capable of predicting toxicological, fate and transport properties to a high degree of accuracy of newly developed energetic materials. Emerging energetics contain functional groups and moieties that are outside the training sets of current QSAR models, including high nitrogen (>50% nitrogen) neutral compounds, organo-metallic complexes and energetic salts. Additional quantum chemistry models are needed to predict behavior of the novel compounds through breakdown in the environment. Models are needed that are capable of predicting key properties that determine important human toxicology parameters, including:

- Mutagenicity
- Oral toxicity (both acute and chronic)
- Inhalation toxicity (both acute and chronic)
- Dermal corrosivity and sensitization potential
- Ocular irritation
- Developmental and reproductive toxicity
- Carcinogenicity

Additional models are needed for prediction of physical properties relevant for assessing environmental fate and transport, including the following parameters:

- Aqueous solubility
- pH sensitivity
- Octanol-water partition coefficients
- Vapor pressure/Henry's Law Constant
- Abiotic hydrolysis half-life for compounds in aqueous phase
- Acid / Base dissociation constants (or pK_a / pK_b)
- Biodegradability/bioaccumulation in relevant environmental receptors
- Toxicity towards green algae, *Daphnia*, and fish

Both of these areas of need are vital to the Environmental Restoration and Weapon Systems and Platforms program areas, as the Environmental Restoration area requires this data to support adequate site conceptual models that will guide restoration and remediation efforts into the future. At the same time, the Weapon Systems and Platforms community requires this data to screen novel materials in real time, as they are being developed in order to guide selection of more environmentally sustainable alternatives. It is recommended that any efforts in this field be closely coordinated between these two groups.

4.4.2 Manufacturing

4.4.2.1 Application of Environmental Economics to Equipment and Process Changes to Inform Cost-Benefit Analyses (*ESTCP High*). One of the highest priority needs for manufacturing is a new infrastructure to replace the existing manufacturing facilities. This conclusion was reached by the realization that the difficult environmental problems associated with the various processes involved in manufacturing are exacerbated by the outdated and deteriorating facilities. The existing facilities were built during World War II, over 70 years ago. Their design and construction was dictated by the need to produce the equipment needed for the war. Little attention was paid to potential environmental problems. As more environmental problems are uncovered and more environmentally protective regulations are issued, it is becoming more and more difficult to design cost-effective solutions. In particular, the advanced age of the equipment and facilities precludes the use of most modern green processes and advanced treatment technologies.

It is clear that a rethinking of the strategy to manufacture, assemble, and deliver the necessary war fighting equipment is the highest priority research need. The manufacture of MC is a specialized and difficult undertaking since the basic materials and final products are inherently hazardous. Outside of the existing military manufacturing sector, there is little applicable industrial experience that can serve directly as a guide. Although modern chemical and mechanical manufacturing green techniques have been, and are being, developed, they would need to be adapted to be safe for use with MC as well as effective. This will require research projects that include specialists from the MC manufacturing establishment as well as engineers experienced in designing more environmentally benign manufacturing and assembly facilities.

The reason that the facilities have not been replaced appears to be related to the availability of the large one-time cost of the replacement. As an example, an estimated cost of one billion dollars committed in one year was not possible, whereas the commitment of 100 million dollars for each of ten years was possible. Unfortunately, the latter expenditures do not result in permanent solutions but rather interim quick fixes. This is not an efficient use of the available resources.

The economic analysis that supports this choice also needs replacement. The cost-benefit analysis of new infrastructure have not to date examined the entire life cycle of the products including the costs associated with transportation, storage, and eventual disposal. Nor have environmental economics been employed which would include the value of reducing the environmental impact of the facility. The savings from using more closed-loop processes, less water and energy, less waste generation, and in general lessening the environmental impact of the manufacturing can be included in the analysis.

A rigorous cost-benefit analysis of the present situation compared to a new infrastructure might cast a different light on the economic cost-benefit comparison. It would also point to the areas that need initial attention, and may allow prioritization of the MC manufacturing and LAP processes that need further investigation.

4.4.3 Operations

4.4.3.1 Mass Loading and Characteristics of New Enhanced Performance Round (EPR)-Copper Round M855A1 (*SERDP/ESTCP Critical*). The Army adopted the 5.56mm M855 round to improve performance in the early 1980s. However M855 rounds are an environmental concern due to the lead (Pb) content in the rounds. Therefore, partly as a result of mounting environmental concerns, the Army adopted the M855A1 Enhanced Performance Round (EPR), which not only offers improved performance but it's also lead-free. Since then, estimates show that accuracy testing has improved to 95%, and removing this lead hazard from operations and the manufacturing environment has eliminated (nationwide/year) 2,000 metric tons of lead from the environment. However, little is known about the health hazards associated with the new lead-free improved propellant formulation in the (EPR)-Copper Round M855A1. Both impact to the environment and health hazards need to be assessed, specifically as it relates to copper (Cu), which replaced Pb in the EPR M855A1.

Research (SERDP) and demonstrations (ESTCP) are needed in two areas: 1) Cu mass loading onto the environment, and 2) characteristics and potential health impacts associated with the Cu mass as well as potential exposure pathways. These are described below:

- **Assess Cu mass loading of EPR M855A1 to the environment *(SERDP/ESTCP Critical):*** Testing shows that accuracy with the new EPR M855A1 is much higher, meaning that much more Cu mass is deposited and accumulated in the same area than would otherwise be. Even though the EPR M855A1 has been fielded for years, there are no studies performed addressing the environmental and human health hazard impacts resulting from the new Cu-based formulation. Of particular interest are studies focused to determine how much Cu mass the EPR M855A1 leaves on our small arms ranges (outdoor and indoor ranges and shoot houses) and what form that mass is in (i.e. particle size, degradation state, etc.) so that mitigation measures can be determined and implemented. Inhalation hazards are of particular interest as recently, metal fever was reported in personnel who were repeatedly exposed to Cu-based bullets in Norway.

  Research (SERDP) is needed specifically on the fate and transport mechanisms for the Cu associated with the EPR M855A1 formulation. There is a concern that Cu, if released into the environment, could dissolve and be carried in surface waters either in the form of Cu compounds, free Cu or Cu-bound particles suspended in the water. Even though Cu binds strongly to suspended particles and sediments, there is evidence to suggest that some water-soluble Cu compounds could enter groundwater. Further, research (SERDP) or strategies (ESTCP) are also needed to mitigate Cu's potential mobility as a result of operating practices. Practitioners need to know optimum methods and time frame for recovery of Cu in order to minimize mobility. Furthermore, users are interested in fortuitous recovering and or recycling techniques for the Cu if possible. In general, users would like to know if and under what conditions Cu migration is a concern, and if so, what mitigation methods are available.

- **Determine characteristics and potential health impacts associated with Cu mass *(SERDP Critical):*** The health impacts of Cu in EPR M855A are not known. Cu can be transported in the air. Exposure to high doses of Cu can be harmful and long-term exposure can irritate nose, mouth, and eyes, in addition to causing headaches, dizziness, nausea, vomiting, stomach cramps, and/or diarrhea. It is not known whether Cu is a carcinogen. USEPA does not classify Cu as a human carcinogen since no human or animal cancer studies have been conducted to date. Therefore, we do not know if there are any future liabilities associated with the Cu-laced EPR M855A1 munitions. Currently, neither the scientific community nor practitioners know if there is any health hazard primarily via inhalation, which may eventually result in potential liabilities. This concern is of special concern since metal fever has recently been reported in Norway in personnel dealing with a Cu-based bullet. Users are interested in both air concentrations and toxicity so that mitigation measures can be implemented if necessary.

  Research (SERDP) is needed specifically on the toxicological effects associated with the Cu in the EPR M855A1 formulation. Of particular concern are inhalation hazards. Since there is no toxicity-based study regarding Cu, studies need to be performed to identify and manage the health risk associated with EPR M855A1 operations. Such studies must target exposure pathways so that they can model environmentally relevant concentrations.

4.4.3.2 Dud Rates and Low Order Rates Under Training Conditions and Feedback to Manufacturer for Main Charge and Fuse (*SERDP/ESTCP Critical*). Dud and low order detonations contribute most of the contamination in the form of munitions and explosives of concern (MEC) range residues. The dud and low order rates are needed to estimate the explosive mass deposited at active ranges. What is currently known is limited and outdated. Two studies were done in the early 2000s (Daulphin et al., 2000, Daulphin et al., 2001) that looked at ammunition lot acceptance test results from years prior to the reports published dates. As newer munitions and fuses are available today, information is needed on their dud and low order rates. Additionally, testing of dud and low order rates must take into account live fire conditions rather than test conditions. Test conditions are very controlled and do not have the variability associated with training at active ranges (distance to target, direct and indirect fire, and variability with regard to soil type/density where munitions impact) may affect dud and low order rates).

Measuring the dud and low order rates for each munitions type in the current inventory of munitions in use (high caliber and medium caliber) under realistic training conditions in order to better estimate the MEC load on ranges would be of use. Of necessity, more accurate total detonation data on active ranges is needed to improve dud and low order rate estimates. The information on each munitions and each fuse will help the manufacturing community to improve the detonation properties of munitions and will help to improve fate and transport models for the source terms.

4.4.3.3 Develop and Test a Replacement for C4 for Donor Charge in BIP and Demolition (*SERDP/ESTCP High*). Current blow-in-place (BIP) demilitarization procedures generally require blocks of C4 manually attached to the unexploded ordnance (UXO). The energy from the C4 is used to initiate the detonation of UXO. BIP generally detonate most of the explosive in the UXO, thereby eliminating their explosive threat. However, two major environmental issues were identified at the workshop related to this practice.

1. Based on research conducted by CRREL, each individual block of C4 may leave around 20 mg of RDX residue (or unexploded energetic) at the detonation point (Walsh et al., 2011; Walsh, 2007; Hewitt et al., 2003). Even if the dispersion of mg quantity of RDX per block of C4 might appear small, when considering the amount of C4 blocks used per year/per at each installation, kg of RDX could be dispersed per year. Using RDX, the US EPA guideline for RDX in drinking water (2 ppb), this means that large volume of water bodies could potentially be impacted over the guideline. As RDX was identified as a surface soil, surface water or groundwater contaminant in ranges across North-America, and as C4 blocks represent one of the identified sources of RDX, there is a need to study potential alternatives to C4, or in other words, to find a non-RDX based plastic explosive. This practice introduces more MC to the environment in addition to any residue left behind from the detonated munitions. DoD needs either a more efficient BIP explosive formulation to reduce residual energetics or a more efficient BIP practice to reduce the probability of releasing explosives to the environment.
2. The traditional BIP procedure is not effective at detonating insensitive energetic materials, in particular for the family of IMX compositions. In some cases, as much C4 is needed to detonate the UXO as energetics contained in the round. The IM community is addressing this issue already to improve the detonation of non-ideal explosives and improve EOD technology.

4.4.3.4 More Efficient and Safe BIP Methods for IM (*SERDP/ESTCP High*). In general, dud rates on ranges are not known. Regardless of whether these IM provide a lower or higher dud rate than legacy munitions, one thing is certain; detonating expended munitions and UXO through BIP procedures will remain a needed operation. However, with the insensitivity of filler materials comes the difficulty of achieving high order detonations using standard BIP operating procedures.

In addition, EOD teams or range operators performing BIPs need the ability to clearly identity whether the subject munitions is conventional or an IM. Having the ability to clearly identify the munitions will decrease the likelihood of applying an inappropriate BIP procedure.

4.4.3.5 Methods to Quantify Explosive Mass Loads from Live Fire on Terrestrial Training Ranges for New Formulations (*SERDP/ESTCP High*). Current in-field command detonation techniques have been used successfully to simulate live-fire high order and low order detonations. The Cold Regions Research and Engineering Laboratory and the Picatinny command fire systems have been used in these previous studies but differ in their detonation process. While these techniques are very useful and valuable, there is still an important need for residue deposition data from live-fire detonations for comparison and validation of the results from the command detonation techniques.

Additionally, early results suggest that the new formulations (e.g. PAX-21, IMX-104) deposit more explosive mass than traditional formulations when an item is detonated low order. Results also show that high order detonations of new formulations are not as efficient and are depositing significantly more residues than the high order detonations of the traditional formulations. As all the current data are based on the limited command detonation data, live-fire and additional command detonation data are needed to confirm the higher mass depositions previously observed.

4.4.3.6 Fate of Post-Detonation MC as Affected by Geographic Location and Climate (*SERDP/ESTCP High*). Particles scattered by low order detonations are a common source of MC on the ranges. However, fate of the energetic materials in these residues is not well quantified. Particles can dissolve, break apart, and phototransform. The relative importance of these processes (and therefore amount and type of compounds entering soil and water bodies) depends on a variety of factors including composition of the formulation, particle size distribution, as well as environmental factors such as the amount of solar irradiance, the temperature, and the amount and intensity of rainfall. For conditions of US Northeast it has been shown that up to 60% of the total mass that is being released from post-detonation residues can photodegrade, with the remaining 40% being dissolved.

The type of phototransformation products strongly depends on the parent compound, with some of energetics forming volatile products (RDX), while others form highly colored, soluble compounds (TNT). Changes in surface area of the particles as they dissolve and/or crumble would affect dissolution and phototransformation rates, as well. For example, IM residues are more friable due to presence of highly soluble components like NTO and NQ. Natural fires or controlled burns can consume residues and change their physical properties, also affecting the fate of deposited munitions residues. Once traditional MC residues decrease into the micron size range, they are able to be transported into the soil, and their larger surface area leads to faster mass transfer of dissolved phase explosive compounds. Studies comparing cm-, mm-, and micron-sized IM residues have not been performed to date.

Once MC enter soil in solution, they are a subject to abiotic and biotic transformation and reactions with soils, as well as uptake by the plants. The extent of these processes is highly dependent on vegetation and soil type, which in turn are dependent on geographical location and climatic conditions of the region. As military installations are located across the United States, one needs to accurately predict the fate of munitions under all climatic conditions.

4.4.4 Demilitarization

4.4.4.1 Optimize BIP and Consolidated Shot (CS) Procedures for MC and IM to Limit Contamination and Human Exposure (*SERDP/ESTCP Critical*). Current BIP and CS procedures may result in widespread dispersion of MC. Characterizing the residual MC in soil resulting from different BIP and CS procedures is needed to develop best practices. The amount of metal fragments resulting from these procedures, as well as the size and distribution of residual energetic should be measured under a range of conditions. Methods to ensure complete detonation and thereby minimize environmental contamination should be developed. In particular, there is concern that recent IM will have a higher dud rate and more residual energetic than conventional munitions. Passive samplers and/or remote sensing techniques would allow for more accurate evaluations of the potential human and environmental exposures resulting from excess munitions destruction.

4.4.4.2 Alternatives to BIP for Underwater Munitions (*SERDP/ESTCP Critical*). Currently, the only feasible method of detonating or removing underwater munitions is using divers that have been trained in EOD techniques. Diving operations by their nature are considered hazardous without the additional risk of dealing with explosive hazards. The compounding risk factors often generate the need for dive teams and rely on BIP operations to detonate the munitions in the safest manner available.

However, increased concerns, not only from explosive safety but also the potential release of munitions constituents and environmental impacts for the existing MR sites and BIP operations continue to grow. It is critical that DoD pursue alternatives to divers and BIP protocols for underwater munitions. Alternatives such as use of remotely operated vehicles or encasement of munitions were discussed. Encasement could be problematic as stakeholders may interpret this procedure as a “no action” alternative. With further testing and demonstration, munitions filler could be extracted using high-pressure, water-jet systems that have been used in land based demilitarization. Until a better option is found, encasement would offer a significant increase in safety and reduce the potential for release of MC.

4.4.4.3 Alternatives to BIP for MC on Land (*ESTCP High*). The breakout group discussed land-deposited MC and focused on the increased water solubility of IHE. This higher solubility increases potential for offsite migration of MC. To minimize scattering IHE and legacy explosives, the group thought that alternatives to BIP operations are a high priority. There was some discussion promoting the development of robotic systems but no clear path forward was suggested.

4.4.4.4 Metals Recycling/Recovery (*ESTCP High*). Although the specific volumes and nature of the metals deposited on ranges are not known, recycling and recovery of these metals could be economically valuable to DoD. Recovery of these metals could prevent any environmental and human health risks, and costs, associated with leaving metals on site, or with disposing of the metals and metal-contaminated soil off-site. Cu bullets in particular represent a high-value waste material that could be recovered for sale or reuse.

Investigations are needed to determine the volumes and forms of metals present on ranges, and evaluate their potential value. The technical options available for recovery and recycling need to be identified, and the costs and performance of these options need to be identified. Range design modifications that could allow easier recovery of metals, such as the use of modular berms, also should also be developed and tested.

4.4.4.5 Alternative Methods for Reusing or Recycling Energetic Products (*SERDP/ESTCP High*). Producing energy from propellant-containing materials (e.g., off-spec, expired, discarded, or other materials contaminated with relatively high levels of propellant) would not only produce energy but remove propellants as potential sources of contamination. Pre-processing steps would be included for diluting materials containing high concentrations of propellant such that they could be safely handled (e.g., diluted and blended into the feedstock of waste-to-energy incinerators). Other energy recovery technologies would be valuable (e.g., generation of methane via biological treatment processes). Given the propensity for propellants to contain heavy metals or other toxic constituents (e.g., Pb), new technologies would need to include processes to prevent or minimize the release of metals or other toxic constituents to the environment.

4.4.4.6 Standard Guidance on Demilitarization Procedures (*ESTCP/Tech Transfer High*). A need exists for standard procedures for demilitarization of explosive filled rounds, as demilitarization of rounds represents a major potential source of munitions contamination. BIP procedures, for example, vary considerably and there are key differences in procedures between services. Standardized procedures will be even more important for IMs. However, even current information is often not reaching range managers, partly because of travel restrictions, but there may be potential security concerns in discussing the management of residual munitions. Standard procedures could reduce potential liabilities, but it needs to be accompanied by effective training and technology transfer to field personnel.

5. CONCLUSIONS

The workshop focused primarily on the insensitive munitions. The development of these munitions is continuing, and their use is increasing. Critical information on these new compounds is lacking and current models do not adequately predict their fate and transport. Too little is known regarding the potential amounts and characteristics of energetic materials likely to be released to the environment, for both new and current munitions constituents. Most concerning is the lack of key information on the health and environmental impacts of IHE compounds that are currently being developed and used.

New and current MC will continue to pose significant challenges to DoD. Explosive developers need standard guidance and sound methods to cost-effectively evaluate potential new compounds. Manufacturing of new munitions is occurring in aging facilities designed for other materials, and current demilitarization practices release MC to the environment. Munitions contamination is an ongoing management and remediation challenge at DoD's ranges, and research to improve risk assessment, characterization, disposal, and remediation of new and existing munitions compounds is an urgent need.

The overarching needs identified during the workshop are:

1. Assess the impacts of new munitions. Although there is an existing ASTM standard for assessing the environmental impacts of these compounds, development is outpacing the risk assessments. In particular, greater effort is needed to understand the human health effects and the environmental fate and transport of new munitions compounds.

2. Evaluate alternatives to open detonation. OD is used throughout the life cycle of explosives during development, training, and demilitarization. However, OD leaves explosives in the environment, and thus ongoing liabilities. Increased management of munitions throughout the life cycle of their development and use could reduce the potential for environmental impacts, and possibly reduce overall costs.

3. Improve characterization of source terms. The understanding of munitions sources is not sufficient for modeling or predicting the environmental impacts of range operations and new munitions. There is too much uncertainty regarding key parameters, including the mass of explosives deposited and available for dissolution, dud and low order rates for different conditions, and the distribution of residues.

The workshop examined the research and demonstration needs in four technical areas - treatment, sampling and analysis, fate and transport, and environmental effects. The most critical specific needs for improving treatment are: 1) technologies capable of handling mixed waste streams, as newer compounds are increasingly mixed with legacy munitions wastes; 2) more complete characterization of OB emissions, including organics, metals, and particulates, from both legacy MC and newer IHE; 3) alternatives or improvements to OB for aged, off-spec, and excess propellants and energetic; and 4) an understanding of the reasons for the baffling persistence of RDX in soil.

The key sampling and analytical needs are to develop standard techniques for MC, including:: 1) standard analytical and extraction laboratory methods for new MC, including IHE and their metabolites (NQ, DNAN, NTO), as well as nitrophenols (picric acid, explosive D, dinitrophenol); and 2) analytical methods and QA/QC for new MC and metabolites in environmental matrices (soil, groundwater and surface waters), particularly the IHE and their metabolites.

A better understanding of MC fate and transport is also needed. The critical needs are to: 1) develop standardized computational and experimental evaluation methods for IHE fate and transport; 2) measure the fate- and transport-determining properties of new MC; and 3) improve the current MC fate and transport models.

The environmental effects of the new MC, particularly the IHE compounds, are not sufficiently understood. The most critical needs are: 1) better methods to measure and mitigate runoff losses; 2) measurements of the effects of NTO and DNAN, including essential 2-year chronic mammalian toxicity studies; and 3) assessments of the environmental impacts of IHE compounds on both flora and fauna.

The workshop also addressed needs during the four phases of the MC life cycle – development, manufacturing, operations, and demilitarization. The critical development needs are: 1) fate and transport data on new MC, 2) computational models capable of accurately predicting toxicological, fate, and transport properties of newly developed energetic materials; and 3) an environmental assessment protocol that is designed for MC developer use while satisfying the data requirements for applicable environmental and safety regulations.

The highest priority need from the manufacturing discussion is a rigorous cost-benefit analysis of alternative strategies to manufacture, assemble, and deliver the necessary war fighting equipment. Applying environmental economics to the current situation, and to possible infrastructure improvements, could lead to significantly more efficient use of resources. Additionally, the development and evaluation of new waste treatment technologies, or treatment trains, needs to be pursued, especially in light of the new mixtures of legacy and IHE compounds that are expected to be used for several decades to come.

The critical operations needs are to: 1) evaluate the impacts of the Enhanced Performance Round (EPR)-Copper Round M855A1, including mass loading of Cu to the environment and the potential associated health impacts; and 2) measure dud and low order rates under training conditions.

Finally, the critical demilitarization needs are to: 1) optimize BIP and consolidated shot procedures for MC and IM to limit environmental contamination and minimize human exposure; and 2) to develop alternatives to blow-in-place for underwater munitions.

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APPENDIX A: AGENDA

TUESDAY, JULY 28, 2015			
0830	Welcome and Introduction Workshop Objectives and Structure	Andrea Leeson SERDP and ESTCP	
0845	Development of Energetic Formulations	Kimberly Spangler US Army ARDEC	
0915	Munitions Constituent Life Cycle: Manufacturing	Greg O'Connor PEO AMMO/PD Joint Services	
0945	Research and Demonstration Needs for Management of Munitions Constituents: Operations and Use	Jennifer Wilber Headquarters Marine Corps	
1015	**Break**		
1030	Munitions Constituent Life Cycle: Demilitarization	Ruanne Mikkelsen Sparq Environmental, Inc.	Thomas Bernitt EQC, Inc.
1100	PM CAS Lessons Learned Implementing Insensitive Munitions	James Chang Office of the Project Manager Combat Ammunition Systems	
1130	Summary of Munitions Constituents Research and Demonstrations under SERDP and ESTCP	Andrea Leeson SERDP and ESTCP	
1200	**Working Lunch**		
1230	Breakout Session I: Thorough discussion of management challenges and identification of research or demonstration needs, as well as technology transfer limitations. • Development Phase • Manufacturing Phase • Operation & Use Phase • Demilitarization Phase	Led by Session Chairs	
1600	Reception with Poster Session		
1730	**Adjourn**		

Wednesday, July 29, 2015		
0830	Reports from Breakout Session I	Breakout Session Chairs
1000	Open Discussion	
1015	**Morning Break**	
1030	Breakout Session II Discussions: Development and Prioritization Research & Demonstration Needs and Technology Transfer Opportunities	Breakout Groups
1200	**Lunch**	
1230	Breakout Session II Discussion (cont'd)	Breakout Groups
1430	**Afternoon Break**	
1515	Breakout Session II Reports	Breakout Session Chairs
1645	Closing Remarks	Andrea Leeson
1700	**Workshop Adjourn**	

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