

Executive Summary

WERC, a consortium of New Mexico universities and national laboratories was requested by the Massachusetts National Guard to perform an independent technical review of the performance of potential alternatives to remediate explosive residues at the Massachusetts Military Reservation (MMR) site. A technical advisory group consisting of explosives remediation experts was established and met in Albuquerque, New Mexico on May 10, 2001 to perform this evaluation. The review is based on the panel's current knowledge of alternative technologies and research being performed on the remediation of explosive and propellant residues. It does not necessarily cover all technologies being developed by private industry. Their conclusions are:

- Groundwater Remedial Action Objectives (RAOs) for explosive and propellant residues are being proposed at levels that are non-detectable by current analytical methods. This is an admirable goal and may be achievable, yet may also be stymied by being technically infeasible and/or overly conservative to protect human health and the environment.
- Because the MMR is a Superfund site, its nine regulatory evaluation criteria were initially suggested for use in evaluating the technologies. The panel however expressed the concern that insufficient information was available to use these criteria. Among the outstanding issues are: future land use, human and ecological risk assessments, practicality/acceptability of institutional controls, extent of unexploded ordnance (UXO), fate and transport modeling, volume of contaminated soils, extent of residual explosive chunks and size distribution, extent of perchlorate contamination, plume extent and movement, identification of applicable or relevant and appropriate requirements, accepted RAOs, and numerous other information gaps that the ongoing Feasibility Study will address in 2002. The technical evaluation therefore proceeded on the scientific and engineering judgment of the panel based on their experience and knowledge of current research.
- The technology review process included three steps. The first was to compile a list of explosive remediation technologies and their basic attributes. The survey produced 62 potential technologies. This group of basic technologies was culled to a smaller subset that was more appropriate to the conditions that exist at the MMR and consisted of twelve ex situ and ten in situ technologies. A list of alternative technologies was then developed that potentially could achieve remediation objectives and, as importantly, are known to likely work (see Table Ex-1). Their acceptability will, in large part, be determined based on information developed as part of the ongoing Feasibility Study.

Table Ex-1: Best Available Technologies Applicable at the MMR Site for Explosive Compounds.

Media	Technology
Surface Soils	Removal with Ex Situ Treatment by * Composting * Offsite Treatment and Disposal Zero-Valent Iron Bioreactor for Soil Slurry
Vadose Zone (note: all technologies assume removal of sources in surface soils)	Soil Flushing * Bio Treatment Chemical Treatment Phytoremediation Monitored Natural Attenuation
Groundwater	Hydraulic Containment with Ex Situ Treatment by * Granular Activated Carbon * Ultraviolet Oxidation Constructed Wetlands In Situ Treatment Methods: Bioremediation Chemical Oxidation Chemical Reduction Zero-Valent Iron Sodium Dithionite Monitored Natural Attenuation

* Refers to technologies most likely to be effective.

- The panel also identified a number of technologies that may be appropriate for the treatment of the propellant, perchlorate. These include anaerobic composting, anaerobic landfarming, in situ biodegradation, and phytoremediation for soils; and fluidized bed reactor/bioreactor, anion exchange, in situ bioremediation, and chemical reduction for groundwater.
- If required to make an immediate decision with the goal of protecting human health and the environment, the panel would recommend going with what is known to work. For the MMR site this would include:
 1. Concentrated areas (hot spots) of contaminated soils should be excavated and treated by aerobic composting for destruction of explosive compounds followed by anaerobic composting for destruction of perchlorate. The excavation and treatment process could remove 50 percent of the contaminants at 20 percent of the total remediation cost. This approach would likely involve residual explosives chunk screening to remove much of the source. At other sites, residual explosives as flakes, nuggets, or chunks represented up to 90 percent of the source problem. Lightly contaminated soils may also require removal and treatment by composting if overall source volume is significant. An

essential element of surface soil remediation at the MMR site is the location and retrieval of UXO and its appropriate treatment.

2. The contaminated groundwater should be hydraulically contained at plume boundaries. The pumped groundwater should then be treated by granular activated carbon for explosives removal followed by either anion exchange or chemical reduction using titanous ions (Ti^{3+}) to treat perchlorate if detected in the groundwater. These are both relatively simple approaches and would fit into a granular activated carbon treatment train.
3. Treated groundwater should be injected upgradient to enhance the flushing of contaminants from the vadose zone. However, natural flushing may be all that is required because of the unique recharge characteristics of the soil and the amount of annual precipitation at the MMR site. If this is the case, the treated water should be placed downgradient to recharge the aquifer or it should be discharged to surface waters.

1.0 Introduction and Purpose

In January 2001, WERC, A Consortium for Environmental Education and Technology Development, was requested by the Massachusetts National Guard to perform an independent technical review of the performance of alternatives to remediate explosive and propellant residues at the Massachusetts Military Reservation (MMR) site. WERC's consortium members include New Mexico State University, the University of New Mexico, the New Mexico Institute of Mining and Technology, Diné College, Los Alamos National Laboratory, and Sandia National Laboratories. A Technical Advisory Group (TAG) was established and met in Albuquerque, New Mexico on May 10, 2001 to perform this evaluation. Members of the TAG and their affiliation are:

Explosives remediation experts:

Todd Harris	BWXT Pantex
Michael Kelley	Sandia National Laboratories
John McCann	Los Alamos National Laboratory
Jim Phelan	Sandia National Laboratories
Corey Radtke	Idaho National Engineering and Environment Laboratory
Van Romero	New Mexico Institute of Mining and Technology

WERC facilitators and staff:

Gary Brown	Sandia National Laboratories
Jason Capron	WERC/New Mexico State University
Tim Carlson	Sensible Environmental Solutions
Abbas Ghassemi	WERC/New Mexico State University
Louise Maffitt	University of New Mexico
Roseann Thompson	WERC/New Mexico State University

Biographic sketches for the TAG are included in Appendix A.

The purpose of this technical review is to provide an independent identification of alternative technologies that would be reasonable options for remediating contaminated soil and groundwater at the MMR. It is not intended to replace the regulatory requirements outlined under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The review is based on the panel's current knowledge of alternative technologies and research being performed on the remediation of explosive and propellant residues. It does not necessarily cover all technologies being developed by private industry.

2.0 Background on the Massachusetts Military Reservation

2.1 Regulatory Background

The MMR is a CERCLA, commonly referred to as a Superfund, site and remediation of contamination is regulated under the guidelines and requirements of this law. Under CERCLA, the U.S. Environmental Protection Agency (EPA) Region I issued an Administrative Order (AO) to the National Guard Bureau and Massachusetts Army National Guard on January 7, 2000. This AO order specified a series of Rapid Response Actions and Remedial Actions be implemented to be protective of groundwater at the MMR Camp Edwards Training Site. The overall objective of this order is to evaluate potential remedial alternatives for Remedial Action at Areas of Concern in the Training Ranges and Impact Area at Camp Edwards to provide the basis for selection and implementation of appropriate Remedial Actions that are protective of groundwater.

In response to the AO, a Feasibility Study (FS) Work Plan (*Final Feasibility Study Work Plan, Massachusetts Military Reservation, Cape Cod, Massachusetts, AMEC Earth and Environmental, December 19, 2000*) was prepared by the MMR and submitted to EPA for approval in December 2000. The FS Work Plan outlines a series of activities that include: additional sampling to fill voids in existing characterization; performing fate and transport modeling to aid in risk-based decisions; developing remedial action objectives that are protective of human health and the environment; and identifying and evaluating alternatives that achieve the remedial action objectives. Under CERCLA, the analysis of alternatives is conducted through the use of nine specific evaluation criteria. These nine criteria are defined in the Code of Federal Regulations (40CFR, Section part 300, National Oil and Hazardous Substances Pollution Contingency Plan) and are as follows:

- Overall protection of human health and the environment;
- Compliance with applicable or relevant and appropriate requirements (ARARs);
- Long-term effectiveness and permanence;
- Reduction of toxicity, mobility, or volume through treatment;
- Short-term effectiveness;
- Implementability;
- Cost;
- State acceptance; and
- Community acceptance.

The following background information on the MMR site is derived from the recent FS Work Plan and is intended only as a general description of historic and existing conditions at the site.

2.2 Site Description

The MMR is a 21,000-acre facility located on Cape Cod in the towns of Bourne, Falmouth, Mashpee, and Sandwich in Barnstable County, Massachusetts (see Figure 1). The Massachusetts Army National Guard conducts training operations at the MMR on approximately 14,000 acres of land identified as the Training Ranges and Impact Area. The Training Ranges and Impact Area lie directly over the Sagamore Lens, a major groundwater recharge area and the most productive part of the Cape Cod Aquifer. Groundwater flows radially in all directions from the apex of the Sagamore Lens located in the southeast corner of the Impact Area.

Military use of portions of the MMR began as early as 1911; however, the majority of activity occurred after 1935 and was most intense during World War II and during demobilization after the war. During the period of 1955 to 1970, the U.S. Air Force maintained intensive aircraft operations along the flightline areas in the southeastern portion of the Cantonment Area. Ongoing operations at the MMR include Army National Guard and Reserve training, Coast Guard air station activities, and Air Force missile and space vehicle tracking.

2.3 Climate

The climate at the MMR is classified as humid continental. Proximity to the Atlantic Ocean has a moderating effect on temperatures, producing warmer winters and cooler summers than nearby inland areas. February is usually the coolest month of the year, with daily temperatures ranging from an average minimum of 23 °F to an average maximum of 38 °F. The warmest month is July, with average daily temperatures ranging from 63 to 78 °F.

Precipitation is fairly evenly distributed throughout the year, with the least rainfall typically occurring during June. Average annual rainfall is 47.8 inches. Average monthly precipitation is 4 inches with a variation of 2 to 4.8 inches. Prevailing winds are from the northwest from November to March, and from the southwest from April to October. Wind speeds vary from an average of 9 miles/hour during the summer and early autumn to an average of 12 miles/hour from late autumn through early spring.

2.4 Geography

The MMR site is located on two distinct types of terrain. The Cantonment Area lies on a gently southward-sloping outwash plain with elevations ranging from 100 to 140 feet above mean sea level. The area to the north and west of the Cantonment Area is dotted with irregular hills and lies in the southern extent of Wisconsin Age terminal moraines. Elevations in this area range from 100 to 250 feet in elevation. Kettle holes and expressions are found over the entire site with some containing water.

2.5 Geology

The geology of western Cape Cod is comprised of glacial sediments deposited during the retreat of the Wisconsin stage of glaciation. Three extensive sedimentary units dominate the regional geology: the Buzzards Bay Moraine, the Sandwich Moraine, and the Mashpee Pitted Plain. The Buzzards Bay Moraine and the Sandwich Moraine lie along the western and northern edges of western Cape Cod, respectively. The Mashpee Pitted Plain, which consists of fine- to coarse-grained sands forming a broad outwash plain, lies between the two moraines. Underlying the Mashpee Pitted Plain are fine-grained, glaciolacustrine sediments and basal till at the base of the unconsolidated sediments. The Buzzards Bay Moraine and Sandwich Moraine form hummocky ridges composed of ablation till, which is unsorted material ranging from clay to boulder size. The total thickness of unconsolidated sediments overlying bedrock varies from approximately 175 feet near the Cape Cod Canal in the northwest to approximately 325 feet at the thickest portion of the Buzzards Bay Moraine. The portion of overburden composed of Mashpee Pitted Plain outwash sediments varies in thickness from approximately 225 feet near the moraines in the north to about 80 feet near the shore of Nantucket Sound. Glaciolacustrine sediments and till underlying the Mashpee Pitted Plain generally increase in thickness as the proportion of Mashpee Pitted Plain sediments decrease. Bedrock lies approximately 300 feet below the ground surface.

2.6 Hydrogeology

The hydrogeology discussion is confined to the Mashpee Pitted Plain, because the hydrologic characteristics of the other two moraines are not well defined. A single groundwater flow system underlies western Cape Cod, and includes the MMR. The aquifer system is unconfined and recharged by infiltration from precipitation. Surface water runoff at the MMR is virtually nonexistent, because of the high permeability of the sands and gravels underlying the area. The high point of the water table, or apex of the Sagamore Lens, occurs as a groundwater mound beneath the northern portion of the MMR. Groundwater flow generally radiates outward from this mound. The aquifer is bounded by the ocean on three sides, with groundwater discharging into Nantucket Sound on the south, Buzzards Bay on the west, and Cape Cod Bay on the north. The Bass River in Yarmouth forms the eastern lateral aquifer boundary.

Surface water is present on the MMR in a few of the drainage swales and as ponds in kettle holes on the Mashpee Pitted Plain. The kettle hole ponds are depressions of the land surface below the water table. On a regional scale, these kettle hole ponds influence groundwater flow in a manner similar to large aquifer heterogeneity. The larger or deeper the pond, the greater the effect on slope and direction of the regional water table near the pond. While horizontal groundwater flow is dominant in the aquifer system, vertical flow driven by piezometric head differences is important in areas near ponds.

The Mashpee Pitted Plain consists of coarse-grained sand and gravel outwash sediments underlain by finer grained sediments. The hydraulic conductivity of the outwash sediments is up to 380 feet/day, while the fine-grained sediment hydraulic conductivity is only 10 to 40

feet/day. Thus, the bulk of regional groundwater flow is transmitted through the upper outwash unit, with horizontal flow velocities ranging from 1 to 3.4 feet/day. The hydraulic gradient across the MMR ranges from 0.0014 to 0.0018 feet/foot.

2.7 Groundwater Use

The primary drinking water supply for the MMR comes from a groundwater supply well located on the base. The adjacent towns of Bourne, Falmouth, Mashpee, and Sandwich also derive their drinking water from wells, although Falmouth also utilizes a surface water reservoir. The water supply wells at the MMR and the surrounding towns range between 40 to 412 feet deep, with the majority of wells extending to depths of 50 to 100 feet below ground surface. In areas where public water supply lines are not available, residents use private wells for domestic water supplies.

The following information summarizes the Cape Cod regional water supply situation:

- The Cape Cod Aquifer is a single continuous aquifer which serves as the sole source of drinking water for approximately 150,000 permanent residents and 425,000 peak seasonal residents of Cape Cod.
- There is no existing alternative drinking water source, or combination of sources, that provides 50 percent or more of the drinking water to the designated areas, nor is there any reasonably available alternative future source capable of supplying Cape Cod's drinking water demand.
- As a result of highly permeable soil characteristics, the Cape Cod Aquifer is susceptible to contamination through its recharge zone.
- The MMR Training Range and Impact Area lie directly over the Sagamore Lens, the most productive portion of the aquifer, and represent major groundwater recharge areas.
- The Sagamore Lens has been identified by the Cape Cod Commission as the portion of the Cape Cod Aquifer most capable of supplying sufficient water to satisfy future demand.

Future land use considerations at the MMR assume that the top priority is protection of the sole source aquifer as a drinking water resource (i.e., watershed protection). Military training activities that are compliant (as yet undefined) with this objective will also be allowed.

2.8 Ecological Setting

Approximately 80 percent of the MMR's 21,000 acres are underdeveloped lands that provide a natural habitat for wildlife. The remaining 20 percent of the MMR site has been developed to support various military needs. Forested areas on the MMR occur mainly in the Training

Ranges and Impact Area, and are classified as pine-oak climax forests. The Cantonment and flightline areas consist of open mowed grasslands.

2.9 Characterization of Areas of Concern

Based on existing data and evaluations conducted, the following Areas of Concern (AOCs) were identified in the AO when issued in January 2000.

- Demolition Area 1
- Central Impact Area
- Southeast Corner of Training Ranges

The AOCs are delineated on the map of the MMR in Figure 2.

2.9.1 Demolition Area 1 – Demolition Area 1 (Demo1) is located north of Forestdale Road and south of the Impact Area, near the current H range at the MMR. Demo 1 includes a natural one acre kettle hole depression that is approximately 45 feet below the surrounding grade. An access road surrounds the depression and delineates a 7.4-acre area. Demolition activities were concentrated within the depression based on historic information.

The depth to groundwater from the bottom of the kettle hole depression is approximately 40 feet. Drilling logs indicate that clay and sand are present in the top 7 to 10 feet below ground surface changing to predominantly sand below 10 feet. Groundwater flows from east to west with a 0.001 feet/foot hydraulic gradient. Groundwater flow velocity is estimated at 1 foot/day. A vertical hydraulic gradient is also present due to localized recharge from precipitation. Chemical characteristics of the groundwater indicate an aerobic environment, at near neutral pH with low ionic strength.

From the mid 1970s to late 1980s, the Demo 1 Site was used for heavy demolition. Ordnance use during this period included C-4 (Royal Demolition Explosive (RDX) with plasticizer), 2,4,6-trinitrotoluene (TNT), and other explosive charges under 40 pounds. Historical activities conducted at Demo 1 include disposal, demolition training, detonation, and other Explosive Ordnance Disposal activities.

Six explosive compounds have been detected in surface soil samples. These include: RDX, His Majesty's Explosive (HMX); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 2-amino-4,6-dinitrotoluene (2A-DNT); and 4-amino-2,6-dinitrotoluene (2A-DNT). A summary of the three most frequently detected compounds in surface samples is presented in Table 1.

Table 1: Explosive Compound Concentrations in Demo 1 Surface Samples.

Compound	Explosive Residual Samples			Random Grid Samples		
	Frequency of Detection	Concentration (mg/kg)		Frequency of Detection	Concentration (mg/kg)	
		Average	Maximum		Average	Maximum
RDX	28 of 30	539	14,000	9 of 84	1.2	39
HMX	26 of 30	56	1,300	4 of 84	2.3	7.2
2A-DNT	11 of 30	210	550	1 of 84	170	170

mg/kg – milligrams per kilogram

RDX, HMX, nitroglycerin, and several TNT breakdown products were detected in soil boring samples. The highest RDX concentration of 9,300 µg/kg was detected at 3 to 4 feet below ground surface. The highest HMX concentration of 800 µg/kg was observed in the same boring at the same depth.

Six explosives were detected in groundwater sampled at the Demo 1 Site. These included: RDX, HMX, 4A-DNT, 2A-DNT, TNT, and 2,4-DNT. Based on current sampling data and groundwater modeling, it is believed that the explosives and propellant contamination from Demo 1 has migrated at least 3,600 feet down gradient. A summary of the explosive compounds detected in the groundwater samples is presented in Table 2.

Perchlorate, a rocket and missile propellant, is also a Contaminants of Concern (COC) in groundwater at the Demo 1 site. Region I EPA recently informed the site that, in lieu of a promulgated standard, the groundwater remediation goal should assume concentrations of perchlorate greater than or equal to 1.5 µg/l will require remediation.

Table 2: Explosive Compound Concentrations in Demo 1 Groundwater Samples.

Compound	Maximum Concentration (Φg/l)	EPA Lifetime Health Advisory (Φg/l)
RDX	370	2
HMX	93	400
TNT	16	2
2A-DNT	4.6	NA
4A-DNT	7.8	NA
2,4-DNT	0.52	NA
Perchlorate	NA	NA

NA – not available; Φg/l – micrograms per liter

2.9.2 Central Impact Area – The Central Impact Area, covering 2,000 acres, contains artillery and mortar targets used for practice firing activities. Numerous firing ranges, artillery and mortar positions, and training areas surround the Central Impact Area.

Within the area the groundwater table is typically between 60 and 70 feet below ground surface, and is found in very coarse sand and gravel units. The lithology consists of a heterogeneous mixture of cobbles to silt with some stratified sand and gravel zones.

For over 50 years, the Central Impact Area received ordnance discharged from small arms, guns, hand grenades, artillery, mortar, rockets, and ordnance disposal through demolition. The U.S. Army operated the area until 1974 after which it was turned over to the Army National Guard.

Explosive compounds were detected in the soil within the southeastern portion of the Central Impact Area at the Mortar Target Site. The explosive compounds detected were RDX, HMX, 4A-DNT, 2A-DNT, TNT, and 2-nitrotoluene (NT). The most frequently detected explosive compound was RDX at 5.1 percent (17 of 332) of the samples. The concentrations of RDX were typically less than 800 µg/kg with a maximum of 38,000 µg/kg. The soil sampling results indicate a sporadic and heterogeneous detection of explosives. The compounds detected are consistent with the known use of RDX as the principal explosive in artillery and mortars.

Three explosives were detected in groundwater sampled at the Central Impact Area, including RDX, HMX, and 4A-DNT. A summary of the explosive compounds detected in the groundwater samples is presented in Table 3.

Table 3: Explosive Compound Concentrations in Central Impact Area Groundwater Samples.

Compound	Maximum Concentration (Φg/l)	EPA Lifetime Health Advisory (Φg/l)
RDX	29	2
HMX	93	400
4A-DNT	7.8	NA

2.9.3 Southeast Corner of Ranges – The Southeast Corner of the Ranges is the least characterized of the Areas of Concern at the MMR. The ranges designated as J-1, J-2, J-3, and L comprise this area along with the J-3 wetland and adjacent private property located north of Snake Pond. This largely vegetated area is close to the apex of the Sagamore Lens with groundwater found in the very coarse sand and gravel units of the Mashpee Pitted Plain sediments.

For over 50 years, the Training Ranges received ordnance discharged from small arms, guns, hand grenades, artillery, mortar, and ordnance demolition. Explosive and unexploded

ordnance (UXO) containing high explosives were disposed at the Southeast Corner of the Ranges via detonation, burial, and burning.

Contaminants detected in soil within the J Ranges include RDX at 24,000 µg/kg, HMX at 9,300 µg/kg, and 2,4-DNT at 200 µg/kg. RDX, HMX, and 4A-DNT explosive compounds were detected in monitoring wells on the Southeast Corner of the Ranges at 55 to 85 feet below ground surface. The highest concentration of RDX at 5.4 µg/l and HMX at 17 µg/l was observed at 70 to 75 feet below ground surface. A summary of the explosive compounds detected in the groundwater samples is presented in Table 4.

Table 4: Explosive Compound Concentrations in Southeast Corner of the Ranges Groundwater Samples.

Compound	Maximum Concentration (Φg/l)	EPA Lifetime Health Advisory (Φg/l)
RDX	5.4	2
HMX	17	400
4A-DNT	0.52	NA

2.10 Unexploded Ordnance

Historical records and visual evidence have revealed that during the 60-year period of operations at the MMR, training exercises made use of a variety of weaponry including small caliber rifles and machine guns, grenades, rockets, mortars, mines, and artillery shells. Occasional misfires of live rounds resulting in detonation failure have resulted in both damaged and intact unexploded ordnance (UXO), some containing high explosives. The average dud rate and low order detonation rates for this wide range of ammunition sizes is 3.45 percent and 0.28 percent, respectively (*Final Feasibility Study Work Plan*, December 19, 2000). Historical evidence suggests that a common disposal method for these materials was to dig a trench and bury ammunition rather than to destroy them by burning or detonation. Apparently it was also common to discard unneeded ammunition into an on-site pond or lake for disposal.

Subsurface geophysical investigations were conducted in approximately 12 acres of the Demo 1 Area during the spring of 2000 to identify the potential for UXO. The investigation detected over 800 anomalies of which 25 were selected for excavation. Materials retrieved included debris such as razor wire, railroad rails, and metallic mesh; practice ordnance such as 3.5-inch rockets, 75, 155, and 175 mm projectiles (the 175 mm projectile contained high explosives); spent 20 and 30 mm rounds; smoke flares; and one 20 mm round with full ballistic tip.

The condition of UXO observed in surface and near surface soils at the MMR range from recently fired rounds that exhibit little or no evidence of environmental degradation, to heavily corroded ordnance and others that have been damaged to the extent that explosives have been exposed.

Figure 1: Location Map of the Massachusetts Military Reservation



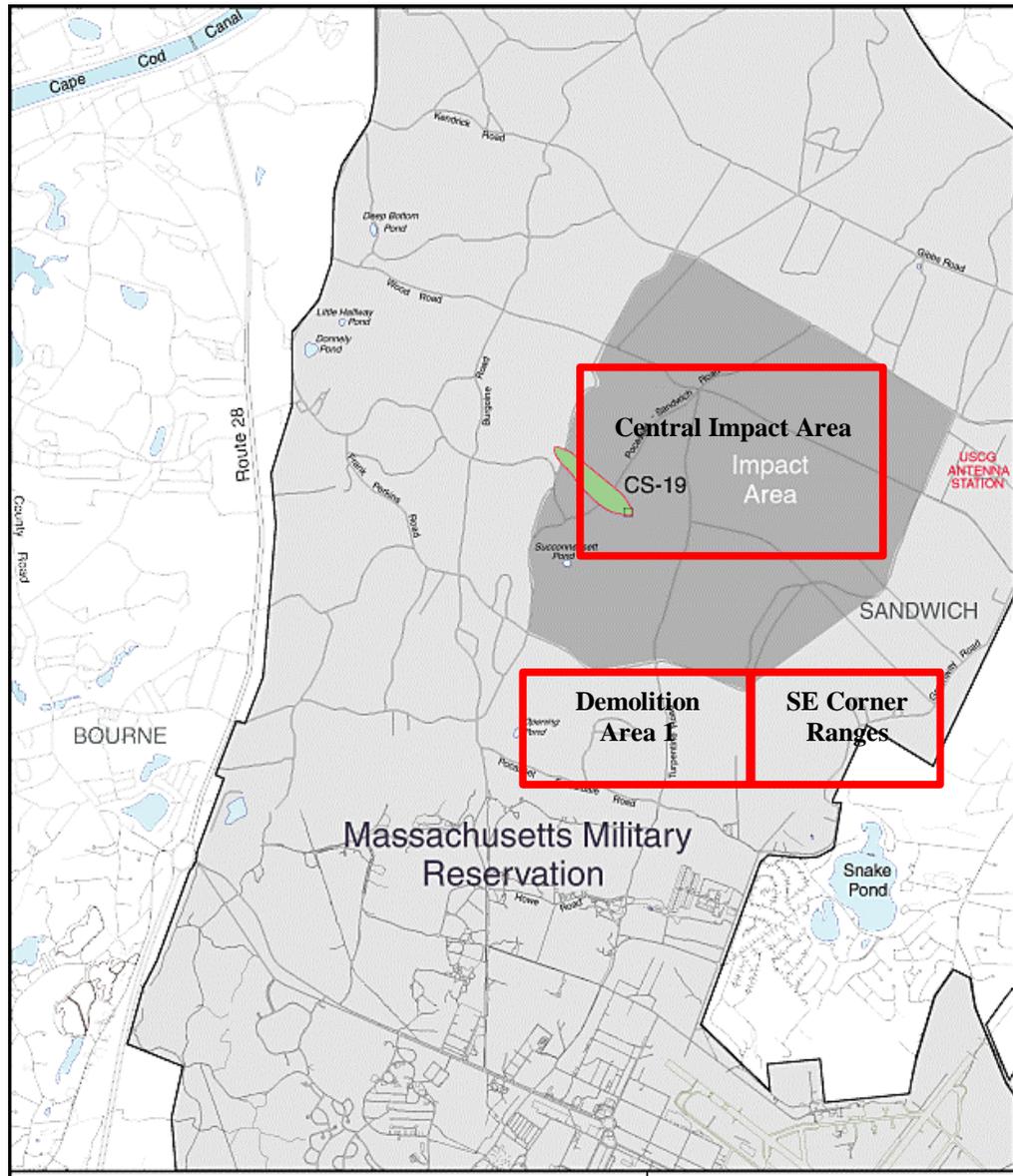


Figure 2: Massachusetts Military Reservation Areas of Concern

3.0 Technical Advisory Group Process

3.1 Technology Review Process

The technology review process included three steps. The first was to compile a list of explosive remediation technologies and their basic attributes. This entailed a survey of the literature, the Internet, and academic and industrial professionals and was conducted by WERC to identify potential technologies for the remediation of explosives contaminated media. The survey produced 62 potential technologies that are presented with comment in Appendix B. This work was completed in February 2001.

In April 2001, the basic technologies group was culled to a smaller subset that was more appropriate to the conditions that exist at the MMR. The technology subset is presented in Table 5. The criteria used in technology selection included technology effectiveness, implementability, and cost. The technology effectiveness criterion focused on the extent of contaminant concentration reduction, toxicity reduction, and sole source aquifer protection that could be produced in a timely manner. The implementability criterion focused on the technical feasibility and availability of the technologies, and the administrative feasibility of implementation. The final criterion, cost, included construction, maintenance, and operating costs in the short and long term.

Table 5: Selected Technologies that may be Appropriate at the MMR for Explosive Compounds

Technology			
<i>Ex Situ</i>		<i>In Situ</i>	
groundwater	soil	groundwater	soil
bioreactor	biopile	natural attenuation	natural attenuation
biofiltration	composting	bioenhancement	bioenhancement
constructed wetland	chemical extraction	redox manipulation	phytoremediation
adsorption	thermal desorption	electrokinetics	chemical flushing
UV oxidation	incineration	reactive treatment wall	redox manipulation
precipitation	chemical reaction	impermeable barrier	chemical reaction

The final stage of technology review was performed at the May 10, 2001 meeting in Albuquerque, New Mexico. The purpose of the meeting was to familiarize the TAG members with the specifics of the MMR site, review the matrix of identified potential technologies, reduce the number of technologies to be considered for the site, and to provide a professional opinion on appropriate technologies for remediation of the MMR site. More discussion on the outcome of the meeting is found in Section 3.3.

3.2 Remedial Action Objectives

A strong conceptual understanding of the desired remediation objectives is a basic component of developing acceptable alternatives. Within the FS Work Plan and through correspondence with the site personnel, the Remedial Action Objectives (RAOs) have preliminarily been identified. RAOs are site-specific, quantitative goals defining the extent of cleanup required to achieve response objectives; i.e., protection of human health and the environment. The RAOs for soil, groundwater, and UXO are generic for all COCs at this time. As additional site characterization becomes available, site specific contaminants of concern identified, fate and transport modeling completed, ARARs identified, and risk assessment work completed, it will be possible to articulate the actual RAOs to be used for remediation of the MMR. These activities will occur through year 2002.

The preliminary RAO for soil and UXO is the prevention of COC migration resulting in groundwater contamination in excess of background levels (to the extent technically feasible), EPA maximum contaminate levels, Health Advisories, drinking water standards, and an unacceptable excess lifetime cancer risk or Hazard Index for non-carcinogenic chemicals. The RAOs for soil cleanup levels, based on existing information, are presented in Table 6.

Table 6: Proposed Soil Cleanup Levels

Target Analyte	Soil Cleanup Standard (mg/kg)
EDB	0.005
PCP	5.0
2,4-DNT	0.7
Lead	300
Barium	1,000
Cadmium	30
Copper	1,000
2A-DNT	1.24
4A-DNT	0.33
2,6-DNT	0.06
HMX	0.25
Di-n-butyl phthalate	1,042
N-nitrosodiphenylamine	99
Dieldrin	0.246
RDX	0.12
TNT	0.25
Nitroglycerine	2.5

The preliminary RAO for groundwater is the prevention of ingestion of water containing COCs in excess of background levels (to the extent technically feasible), EPA maximum contaminate levels, Health Advisories, drinking water standards, and an unacceptable excess lifetime cancer

risk or Hazard Index for non-carcinogenic chemicals. For explosive compounds and perchlorate this is considered to be the analytical detection limits.

Groundwater RAOs for explosive residues and perchlorate are being proposed at levels that are non-detectable by current analytical methods. This is an admirable goal and may be achievable, yet may also be stymied by being technically infeasible and/or overly conservative to protect human health and the environment. The work elements identified in the FS Work Plan, which will be performed through the end of year 2002, are essential to help make decisions on the RAOs for groundwater.

3.3 May 10, 2001 TAG Meeting

The purpose of the TAG meeting was to familiarize the members with the MMR site, provide site characterization information, present the matrix of identified potential and applicable technologies, and reduce the number of technologies to be considered for the site. The meeting provided the explosives remediation experts an opportunity to independently identify reasonable options for remediating explosives contaminated soil and groundwater at the MMR.

Because the MMR is a CERCLA site, the nine evaluation criteria identified in Section 2.1 were initially suggested for use in evaluating the technologies. The panel however expressed the concern that insufficient information was available to use these criteria. Among the outstanding issues were: future land use, human and ecological risk assessments, practicality/acceptability of institutional controls, extent of UXOs, fate and transport modeling, volume of contaminated soils, extent of residual explosive chunks and size distribution, plume extent and movement, ARARs, accepted RAOs, and numerous other information gaps that the ongoing FS will address.

The evaluation therefore proceeded on the scientific and engineering judgment of the panel based on their experience and knowledge of current research. A list of alternative technologies was then developed that could potentially achieve remediation objectives at the MMR. The selected technology list is presented in Table 7. The technology list is grouped by media of concern and the alternatives are presented in order of success potential. Technologies were excluded from the list because of: site soil and groundwater chemical conditions, low maturity, high-volume secondary waste streams, cost, and/or site physical constraints. Proprietary technologies may be appropriate but their use has been limited and insufficient site-specific information and treatability studies precluded their consideration. While technically feasible, some technologies, such as thermal desorption, simply do not have track records with treating high explosives and; thus, add a level of risk that would need considerable field-scale testing to alleviate.

Table 7: List of Best Available Technologies Applicable to the MMR Site for Explosive Compounds.

Media	Technology
Surface Soils	Removal with Ex Situ Treatment by * Composting * Offsite Treatment and Disposal Zero-Valent Iron Bioreactor for Soil Slurry
Vadose Zone (note: all technologies assume removal of sources in surface soils)	Soil Flushing * Bio Treatment Chemical Treatment Phytoremediation Monitored Natural Attenuation
Groundwater	Hydraulic Containment with Ex Situ Treatment by * Granular Activated Carbon (GAC) * Ultraviolet Oxidation Constructed Wetlands In Situ Treatment Methods: Bioremediation Chemical Oxidation Chemical Reduction Zero-Valent Iron Sodium Dithionite Monitored Natural Attenuation

* highest remediation potential

If required to make an immediate decision with the goal of protecting human health and the environment, the panel would recommend going with what is known to work. For the MMR site this includes:

- Highly contaminated soils (hot spots) should be excavated and treated by composting. The excavation and treatment process could remove 50 percent of the explosives contamination at 20 percent of the total remediation cost. Lightly contaminated soils may also require removal and treatment by composting if overall source volume is significant. Because residual explosives as flakes, nuggets, or chunks represented up to 90 percent of the source problem at other sites, the excavation process may require a screening step to remove much of the source. An essential element of surface soil remediation at the MMR site is the identification, retrieval, and treatment of UXOs.
- The contaminated groundwater should be hydraulically contained at plume boundaries by extraction and coupled with ex situ treatment of pumped water using granular activated carbon.
- Treated groundwater should be injected upgradient to promote mobilization of vadose zone contaminants and enhance source removal at the groundwater extraction wells. However,

the unique recharge characteristics of the soil and the large amount of annual precipitation at the MMR site may be sufficient to mobilize contaminants without injection of the treated water. If this is the case, the treated water should be injected downgradient to recharge the aquifer or alternatively be discharged to surface waters.

- The panel also identified a number of technologies that may be appropriate for the treatment of the propellant, perchlorate. These include anaerobic composting, anaerobic landfarming, in situ biodegradation, and phytoremediation for soils; and fluidized bed reactor/bioreactor, anion exchange, in situ bioremediation, and chemical reduction for groundwater. The recommended approach for perchlorate contamination based on existing information and integrated into the explosives remediation recommendation is:
 1. Following surface soil excavation with treatment by aerobic composting for explosives destruction, the logical second phase is anaerobic composting for perchlorate destruction.
 2. If perchlorates exist in the groundwater, the second phase of treatment after ex situ treatment of pumped water by granular activated carbon for explosives reduction should be either anion exchange or chemical reduction using titanous ions (Ti^{3+}).
 3. The other components of the recommended system for explosives remediation, namely hot spot soil removal and treatment, hydraulic containment, and flushing of the vadose zone apply to the remedy for perchlorate.

4.0 Surface Soil Remediation Technologies for Explosive Compounds

4.1 Surface Soils Considerations

This section describes the broad categories of remedial measures, called general response actions, that could be used to achieve the cleanup levels identified for the MMR explosives remediation in surface soils. A particular general response action might be accomplished by any of several technology types. In turn, a single technology type might encompass several more specific methodologies called process options. For example, treatment would be a general response action, chemical treatment would be a technology type, and solvent extraction and oxidation would be two examples of process options.

The following general response actions, considered alone or in combination, could potentially achieve surface soils cleanup goals:

- No Action;
- Institutional Controls;
- Containment;
- Removal;
- Immobilization; or
- Treatment.

After reviewing the numerous options available, the TAG determined that the only reasonable and responsive first-stage option for the surface soils is removal. Removal technologies involve moving the waste or contaminated material from its location at the site to another location either onsite or offsite for storage, treatment, and/or disposal. Although removal by itself can disrupt the exposure pathway(s), it has little or no effect on the toxicity or volume of the contaminated material. In fact, removal might temporarily increase exposure by increasing the mobility of the contaminants (e.g., production and dispersion of contaminated dust during excavation).

Excavation of contaminated soil serves two purposes. First, it removes the source of contamination impacting the vadose zone and subsequently the groundwater. Second, it minimizes the exposure to individuals using the site in the future. However, removal alone does not reduce the toxicity, mobility, or volume of the contaminants in the soil and is therefore not an appropriate stand-alone technology. It is an option to be used in conjunction with ex situ treatment and disposal alternatives. The best available technology options selected as applicable for treatment of the MMR surface soils include: composting, off-site treatment and/or disposal, ex situ zero-valent iron, and ex situ bioslurry reactor. Composting was deemed the best alternative.

4.2 Composting Treatment

Composting is a biological treatment process by which organic materials or contaminants are decomposed by microorganisms. The decomposition process utilizes the carbon and nitrogen found in the organics to metabolically synthesize biomass while producing simpler organic and inorganic molecules and heat as byproducts. Composting results in higher degradation rates than those observed in the natural soil environment because of greater microbial diversity, higher temperatures, and greater aeration. Composting is accomplished by mixing contaminated soil with nutrients and high-organic bulking agents (typically manure or waste agricultural products), and actively controlling temperature, aeration, and water content. The three most common types of composting technology include static pile, windrow, and mechanically agitated in-vessel.

Composting was selected as the most appropriate method for treatment of the surface soils because it is relatively simple, well documented, has a high degree of acceptance, and is cost effective. Additionally, composting is a well-developed technology for explosives contaminated wastes.

Temperature, moisture content, oxygen content, pH, and concentrations of the organic substrates and inorganic nutrients affect the efficiency of the composting process. Control of the self-generated heat is especially critical, since the desired microbial activity can be seriously inhibited by temperature extremes. The three types of composting systems differ in their technical complexity and the degree to which they control temperature, moisture content, and aeration as discussed below.

- **Static Pile.** The soil and amendment mixture is composted in a pile without mixing of any type. Amendments are bulking agents, such as wood chips, hay animal bedding, or corn stalks; organic food sources such as potato processing wastes; and the inorganic nutrients, nitrogen and phosphorus, found in manure. The pile is typically aerated using blowers to introduce air into the bottom of the pile helping to maintain oxygen levels and disperse heat. The principal problems encountered with static piles are temperature and moisture gradients, and pockets of anaerobic activity that produce uneven and spotty contaminant decomposition.
- **Windrows.** The soil and amendment mixture is formed into elongated piles, known as windrows, and turned periodically using a mechanical composter. Turning helps aerate the mixture and distribute heat and moisture. A problem encountered with windrow composting is heat loss during turning, which temporarily slows the composting process.
- **Mechanically Agitated In-Vessel.** The soil and amendment mixture is placed in a reactor vessel and agitated periodically. Air and water are introduced to control temperature and moisture content. A relatively even distribution of heat, moisture, and microbial activity can be achieved, but at a higher cost than static pile or windrow systems.

Composting is relatively easy to implement from both a technical and administrative standpoint. The necessary amendments are readily available locally and can be trucked in with conventional hauling equipment. Control of the critical parameters (temperature, moisture, and aeration) would be the most difficult aspect of implementation requiring careful evaluation during the remedial design. The US Army Corps of Engineers is developing a guidance document on composting. EPA has also developed an engineering bulletin on composting.

Previous cleanups and studies of composting at Umatilla and Hawthorne Army Depots have demonstrated the effectiveness of composting for remediating explosives contaminated soils. Significant degradation of TNT and RDX was observed when composting parameters were optimized. Identification of appropriate amendments and optimization of composting parameters is a site-specific exercise. The treated soils meeting compliance criteria could be used as backfill on the MMR site without use restrictions.

At Umatilla, approximately 11,000 cubic yards (yd³) of TNT contaminated soils (averaging 1,200 parts per million (ppm) after screening to 1 inch) were treated by composting. After 15 days, the proposed remediation goal of 30 ppm was achieved with a turnkey cost of \$300 – 350/yd³. Five commercial vendors capable of performing full-scale work were identified.

Evaluation of four different composting amendments was conducted at Hawthorne Army Depot. The evaluated amendments contained various proportions of soil, hay, potato, cow manure, and wood chips. The initial combined TNT and RDX concentration in 40,500 yd³ of blended soil was approximately 5,700 ppm. After composting treatment, the combined explosives concentration was reduced to 300 ppm with TNT reduced to 233 ppm and RDX reduced to 67 ppm. The full-scale turnkey cost of composting was \$167/yd³.

4.3 Offsite Treatment and Disposal

Offsite treatment and disposal at a licensed hazardous or solid waste landfill is another appropriate option to be considered. There are, however, several issues that may be difficult to overcome: (1) EPA, state environmental agencies, and the Army have usually expressed a preference for onsite remediation, reflecting EPA's policy to pursue response actions that involve treatment versus land disposal; (2) offsite disposal increases the short-term risks of an accident and subsequent public exposure associated with the transportation of the contaminated soil; (3) no known offsite landfill willing to accept explosives-contaminated soil, with or without treatment; and (4) Army regulations require the decontamination of debris or equipment before it is released to the public sector for unrestricted use. Resolution of these issues would be required prior to the implementation of this option.

4.4 Ex Situ Zero-Valent Iron Treatment

Oxidation/reduction or redox reactions chemically convert organic contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another. One reactant is

oxidized or loses electrons, and one is reduced or gains electrons. In explosives contaminant treatment, the redox reaction involves the reduction of the explosive compound and the oxidation of a reducing compound.

Although a variety of reducing media can be used to treat explosive contaminants, the most commonly used media are zero-valent metals, particularly iron. As the zero-valent metal in the reaction is oxidized, the resulting electron activity can reduce the explosive compounds to potentially nontoxic products. Zero-valent iron (ZVI) has been demonstrated in laboratory applications; however, more work is needed to assess the reaction products and evaluate methods to recover the iron from the soils. Laboratory studies indicate that hydrogen peroxide addition following ZVI treatment results in the oxidation of TNT, TNT reduction products, RDX, and RDX reduction products. With time, TNT products were found to strongly sorb to soil particles and were not susceptible to further oxidation. RDX and RDX products were not strongly sorbed and thus were more readily susceptible to oxidation. ZVI treated TNT was found to be more susceptible to biodegradation than untreated TNT in liquid media inoculated with a microbial consortium obtained from TNT contaminated soil. However, even with pretreatment with ZVI, the rate of biodegradation was slow.

The data suggests that this type of system may be technically feasible, depending on the application, but the cost effectiveness of the system relative to other technologies needs to be closely assessed and compared before being suggested for full-scale implementation.

4.5 Ex Situ Bioslurry Reactors

Ex situ bioslurry treatment involves creating an aqueous slurry composed of soil or sludge, water, and various additives. The slurry is mixed in a bioreactor to keep solids in suspension and the microorganisms in contact with the contaminants. After the treatment goal has been reached, the slurry is dewatered by clarifier, vacuum filter, centrifuge, or other method. Much of the work on this technology has been done by the Department of Defense and the Department of Energy.

A slurry reactor demonstration was recently performed at Joliet Army Ammunition Plant. A semi-batch process using molasses as the co-substrate, aerobic/anoxic cycling, and a 6 to 8 startup period achieved 99.6 percent TNT reduction. At the Iowa Army Ammunition Plant, a 10,000 yd³ demonstration was performed to develop cost and performance guidelines. The process used a 40 percent slurry in an open lagoon method. Batch treatment times were about 6 to 8 weeks to reach remediation goals of 196 ppm for TNT and 53 ppm for RDX. The free release criteria of 47 ppm for TNT and 2 ppm for RDX were achieved in 11 weeks.

The primary problems encountered with ex situ bioslurry treatment are non-viability at low temperatures and waste stream treatment requirements. The waste water generated in the dewatering process requires treatment because of high biochemical oxygen demand and very high suspended-solids content.

System cost estimates for treating explosives contaminated soils ranged from \$307 to \$408/yd³ for these demonstration projects.

Bioslurry systems appear feasible for excavated materials, but there does not seem to be a clear advantage over composting. With composting, waste volumes increase while with slurry reactors the waste water volume increases.

5.0 Vadose Zone Soil Remediation Technologies for Explosive Compounds

5.1 Vadose Zone Considerations

The vadose zone soil at the MMR serves two functions for this discussion. First, it serves as a contamination transport conduit to the underlying groundwater from the surface, and second, it serves as a reservoir for contamination. The vadose zone should therefore be considered as both a static reservoir and a transition medium between source and receptor. Each of these functions should be independently considered in the overall cleanup objectives. The objectives of the cleanup are presumably to prevent 1) further surface soil contamination transport, and 2) vadose zone contaminant mobilization into the groundwater.

Surface soil cleanup impacts vadose zone remediation choices. Small particles of explosives are likely to be found in the MMR soils from low-order detonations, breaching, and duds. These particles will persist in soil and continue to leach small amounts of explosives into the surrounding water. Therefore, rainwater recharge without source removal will be an ineffective baseline process. The “no treatment” option is actually a decision to allow rainwater recharge to continue the transport of surface contamination into the groundwater. The groundwater contamination at the MMR provides evidence of this natural process and will continue unless surface soil cleanup, especially hotspots, occurs. Until this is accomplished, source material in these surface soils will continue to smear through the vadose zone and contaminate the groundwater. The result may be unacceptable concentrations of explosives in the groundwater persisting for tens of years after groundwater remediation. Therefore, the certainty of surface soil decontamination should in part drive the decision to actively remediate the contaminated vadose zone.

Before any treatment of vadose zone contamination is implemented, groundwater hydraulic containment must first be achieved at the MMR. Groundwater hydraulic containment alone will mitigate the transport of explosive compounds to downgradient receptors. Complete hydraulic containment of the contaminated aquifer gives added flexibility to vadose zone remediation options. With the groundwater contamination contained, vadose zone remediation can include aggressive treatments using bulk water additions. Hydraulic containment and subsequent treatment options for extracted groundwater are presented in Section 6.0.

The following basic assumptions were used in the evaluation of options for the vadose zone:

- The vadose zone is defined as the unsaturated soil from surface to groundwater after surface soil decontamination and/or removal;
- The vadose zone is the unsaturated zone between 40 and 100 feet below the surface;
- Extensive groundwater recharge from rain with radial groundwater flow from the contaminated site is the norm;

5.2 In Situ Soil Flushing

In situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids must be recovered from the underlying aquifer and, when needed, they are processed to remove contaminants and then are returned to the injection points.

At the MMR, in situ soil flushing should either use the natural rainwater to continue to flush vadose zone contamination or use reinjected treated groundwater from the groundwater containment system. It is not recommended to use surfactants or other extraction fluids because they are seen as unnecessary and costly for the MMR's situation.

A water flush process to remediate a 350-acre plume was deployed at the Umatilla Army Depot and is currently under evaluation. At Umatilla, source term remediation efforts first removed lagoon sediments plus approximately 20 feet of subsoil, and then set up a recirculating or soil flushing cell using the lagoon areas for a re-infiltration gallery. The soils at Umatilla, like those at the MMR, have a high hydraulic conductivity gravel/sand mix. About 300 gallons per minute is flushed through the soils over a 1-acre area. Soil flushing at the site has been effective in removing the more soluble RDX, but significant levels of TNT remain in the soil. The pump-and-treat operation is expected to continue for 20 years to achieve effective remediation of the vadose zone source term. Because the MMR has primarily RDX contamination, in situ soil flushing may be a feasible treatment option. However, in situ soil flushing also presents some added risks.

The primary concerns associated with the application of soil flushing at the MMR site include soil flushing control, probability of increased contaminant transport into the groundwater, the ability to reduce all contaminants of concern, and cost effectiveness of technology implementation. Another concern is that any vadose zone remediation process using bulk water additions may channel and leave behind relatively untreated areas. The injection of treated water to help flush RDX from the soil in situ is potentially feasible from a technical standpoint, but control of the injected water and compliance verification are issues requiring additional study prior to technology deployment.

Like rainwater recharge, in situ soil flushing transports vadose zone explosives contamination to the groundwater, and therefore requires near-perfect hydraulic containment. In situ soil flushing is most logically applied after surface soil removal or treatment, to prevent flushing the relatively immobile surface soil contamination into the groundwater. To establish subsurface connectivity, it is recommended that groundwater tracer testing be performed before implementing an in situ soil flushing system.

5.3 Bioremediation

The technology to effectively remediate explosives in situ in the vadose zone is likely in the near future, but technologies are currently too immature to apply broad scale at this time. In work performed in batch studies at Department of Energy's Pantex site, anaerobiosis in vadose zone soil resulted in stimulation of RDX degradation. This work also showed that biological degradation of explosives does not require complete anaerobiosis. Adding carbon sources enhanced this degradation, but phosphorus additions had no effect. These studies were carried out in batch reactors with small soil aliquots, and therefore must be interpreted carefully.

The first field pilot-scale demonstration of a technology for in situ remediation of vadose zone soils contaminated with explosives was also performed at the Pantex site. The explosive compounds of concern at the demonstration site were RDX and 1,3,5-TNB, with concentrations ranging from 5 to 35 ppm, above the risk reduction clean-up criteria of 2.6 and 0.51 ppm, respectively. The shallow (<10-meter depth) soils at the pilot test site could not be excavated due to the presence of buried utilities. A five-spot well pattern, with injection at the central well and extraction at the four outer wells (each 4.6 meters from the injection well), was used to flood the target vadose zone soils with nitrogen gas with the intent of stimulating the explosive degraders. The system was monitored periodically for gas composition as well as explosive concentrations and microbial activity in retrievable soil samples. After 295 days of treatment, the target explosive concentrations dropped by 40 percent from the initial conditions. Operation of the site continues. Department of Energy's Idaho National Engineering and Environmental Laboratory and Pantex are currently developing a system to augment the in situ reaction degradation, using nontoxic gases to induce anaerobiosis and subsequent degradation of the explosives. This work will be available in September 2002.

It is recommended that MMR estimate, at the conceptual level, the feasibility of inducing partial anaerobiosis in the vadose zone at key locations at the site. It is even possible that surface soil treatment will be of minimal importance if the reaction rates for explosives remediation are quick enough in the vadose zone to prevent contamination of the underlying groundwater.

Inducing partial anaerobiosis may require adding a surface covering to inhibit atmospheric oxygen diffusion into the soil. Therefore, anaerobic in situ vadose zone bioremediation will be a particularly strong option at the MMR site if capping is implemented to prevent rainfall recharge in the contaminated zones.

5.4 Chemical Oxidation/Reduction

Chemical oxidation/reduction reactions may be a feasible future option for remediation of vadose zone soil at the MMR, however, these remediation technologies are currently only in the research and development phases. Potential oxidants for in situ chemical oxidation of explosives include potassium permanganate, Fenton's reagent, ozone, hydrogen peroxide, hypochlorite, chlorine, and chlorine dioxide. Typical reducing agents employed include ascorbic acid, calcium polysulfide, ferrous sulfate, hydrogen sulfide, hydroxylamine, sodium

dithionite, sodium metabisulfite, sodium sulfide, ferrous iron, and zero-valent iron. The reducing agent is chosen according to its ability to reduce the redox potential of the pore water or groundwater without adverse reaction with site geochemistry. Based on the current state-of-technology and the MMR site restrictions, it is recommended to not implement studies of chemical oxidation/reduction at the MMR until the technologies mature past research and development phases for unsaturated soils.

5.5 Phytoremediation

Phytoremediation uses vegetation and associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants. It is generally used as an in situ technology, but can also be used ex situ. The technology exploits the natural hydraulic and metabolic processes of plants, and thus is passive and solar driven. The technology can be used in combination with mechanical treatment methods or as a stand-alone treatment method.

Several types of phytoremediation removal processes are applicable to vadose zone explosives contaminated soils. Phytoaccumulation or phytoextraction is the process in which specific species of plants are used to absorb unusually large amounts of soluble organic compounds from the soil and are subsequently harvested from the growing area. The biomass is composted or incinerated and the ash is sent to a landfill. Phyto- and Rhizosphere degradation is the process where plant or rhizome enzymes completely mineralize or partially breakdown organic contaminant compounds. Another removal process is phytovolatilization in which plants remove contaminants from the subsurface and evaporate or volatilize the contaminants from the leaf surface of the plant once it has traveled through the plant's system. Finally, organic pumping uses plants to control the migration of contaminants in the groundwater by exploiting their natural hydraulic properties. Using trees for water control is estimated to cost approximately one half the cost of traditional pump-and-treat systems.

Cellular enzymes have been found to be responsible for chemical reactions eliminating explosive compounds from natural systems. Nitro reductase has been shown to reduce nitro groups to amino groups on the structures of RDX and TNT. Laccase has been shown to participate in ring cleavage reactions. Experiments with certain plant species have shown significant reductions in the concentrations of aqueous phase constituents. TNT reaction rates are apparently faster than RDX by about a factor of ten. For soil or sediments containing explosives, the mass transfer from the solid to aqueous phase will likely be the rate-limiting step. The treatment depth of this technique is limited to the root zone and varies seasonally. The use of poplar trees or native plants could treat the soil from 2-15 feet deep. The end product of the reactions is often plant biomass. If the plants bioaccumulate toxic byproducts or metals, the biomass would need to be harvested to avoid ecotoxicity problems. High concentrations of explosive compounds have been shown to be toxic to plants.

There are several factors limiting the applicability and effectiveness of the phytoremediation process which include:

- Adaptability of specific plant species, which are known to successfully remediate organic contamination, to site-specific environments;
- Climatic or seasonal conditions may interfere or inhibit plant growth, slow remediation efforts, or increase the length of the treatment period;
- Requirement for large surface area for remediation;
- Low contaminant concentration remediation only due to plant toxicity effects; and
- Remediation is limited by contamination depth, although there are currently studies underway that are determining the potential for fast growing, deep-rooted trees.

More research is needed to determine the fate of various compounds in the plant metabolic cycle to ensure that plant droppings and products manufactured by plants do not contribute toxic or harmful chemicals into the food chain or increase risk exposure to the general public.

5.6 Monitored Natural Attenuation

Monitored natural attenuation is also known as intrinsic remediation, bioattenuation, intrinsic bioremediation, natural recovery, and natural assimilation. This process is not, in a strict sense, a technology. Rather, it is based on allowing natural mechanisms such as dilution, dispersion, volatilization, adsorption, and chemical reactions with soil materials to reduce contaminant concentrations. Monitoring of the progress of remediation is an essential element of this approach. Implementation of this process requires significant evaluation of site data and extensive modeling in order to show that natural processes will indeed reduce the presence of contaminants to acceptable levels. For regulatory purposes, this option is not the same as “no action,” and it has only been selected as an option where contaminants are not migrating and where it has been determined that active remedial processes would not significantly decrease remediation time.

Inspection of highly contaminated soils at army ammunition plants over decades has shown that bald spots in vegetative cover have gradually reduced in size. Plants, microorganisms, contaminant migration, and photodegradation reactions are probably responsible for reclaiming these contaminated areas. The highly contaminated areas observed as bald spots of vegetation often contained an average of 5,000 ppm with 100s of ppm on the fringe where grasses were growing, and 10s of ppm in the trees (that used to be part of the bald spot). At the Joliet Army Ammunition Plant, Crane Naval Weapon Station, funding for some natural attenuation research is ongoing to evaluate kinetic reactions. This work is being sponsored by the Strategic Environmental Research & Development Program, which has also developed a protocol for natural attenuation studies.

Natural attenuation is probably occurring at these army ammunition plants but verification of that may be difficult to quantify. Natural attenuation should not be discounted and should

continue to be considered, especially in combination with active efforts to remove source terms or large contaminant concentration areas. If natural attenuation is pursued, characterization is very important and a conceptual model should be developed to describe the processes involved.

6.0 Groundwater Remediation Technologies for Explosive Compounds

6.1 Groundwater Considerations

Groundwater remediation technologies for the MMR aquifer were screened to identify technologies that may be applicable for remediation of explosives contaminated groundwater. The technologies discussed below pertain to remediation of the explosives contaminated saturated zone beneath the MMR. Because treatment of the surface soils and the vadose zone source areas is critical to the prevention of further groundwater contamination, it is assumed that source area and vadose zone remediation will play an integral role in any groundwater remediation program conducted at the MMR.

Many of the required parameters that are collected for surface and vadose zone soils are also important for groundwater. However, there are other parameters specific to groundwater that should be collected; these include:

- Contamination identification and quantification;
- Soil and groundwater geochemistry characterization;
- Groundwater pH;
- Total organic carbon;
- Biological oxygen demand;
- Chemical oxygen demand;
- Reduction/oxidation potential (E_h);
- Suspended solid content;
- Major anions and cations;
- Iron concentrations;
- Hydraulic characteristics (permeability, hydraulic gradient, effective porosity);
- Groundwater velocity;
- Safe aquifer yield; and
- Recharge, discharge, and other boundary conditions.

This section of the report addresses the applicability of conventional and innovative technologies for groundwater remediation at the MMR. As with any innovative technology, laboratory- and field-scale tests are recommended to determine the technology's ability to remediate groundwater given site- and contaminant-specific conditions.

The first step of any remediation project consists of defining the RAOs to be completed at the site. This involves gathering enough background site information and field data to assess regulatory requirements, institutional constraints, and technical feasibility. The first determination is whether active cleanup or groundwater containment will be the most appropriate remedial action. If active cleanup is chosen, the final acceptable level of cleanup must be determined.

An extremely important component in the remediation of explosives contaminated groundwater is the determination of the exit strategy, also referred to as the termination criteria. The exit strategy is based on the cleanup objectives (RAOs) defined in the initial stage of the remedial process. The termination criteria may also be dependent on the site-specific conditions revealed during the characterization phase of the remediation.

Due to the general lack of site-specific background data (i.e., presence of UXO, future land use of the site, etc.) and clear definition of the RAOs for the MMR groundwater, the first action recommended by the TAG is the use of hydraulic containment of contaminated groundwater through groundwater extraction or injection with ex situ treatment to remove contaminants. It is important to hydraulically isolate the contaminated groundwater to prevent off-site migration of contaminant plumes and to decrease the risk to human health and the environment. Containment technology is based on physical removal of the contaminants by extracting numerous pore volumes of groundwater. Treated groundwater can either be returned to the aquifer by re-injection to further aid in contaminant flushing and control of groundwater flow patterns, or the treated water can be placed elsewhere. If the treated water is not returned to the aquifer, then groundwater extraction will serve to slowly de-water the aquifer. The de-watering process is expected to take an extremely long period of time and may never be accomplished without extreme withdrawal values due to the high recharge flux to the subsurface at the MMR.

Following the hydraulic isolation of the contaminated groundwater, innovative strategies may be investigated for implementation within the hydraulically isolated zone (e.g., placement of an in situ permeable reactive barrier within the containment zone). Following the initial recommendation of groundwater containment and remediation by an engineered pump-and-treat system, alternate in situ and ex situ technologies are identified for further evaluation. The benefits, limitations, and data requirements are outlined for each of the proposed alternate technologies to remediate groundwater at the MMR.

6.2 Hydraulic Containment

Groundwater containment prevents further migration of groundwater contamination by the use of physical barriers, hydraulic barriers, or reactive barriers.

A physical barrier involves the placement of an impermeable structure in the aquifer to prevent movement of the groundwater (e.g., sheet piles and slurry walls). A hydraulic barrier involves controlling the groundwater flow by groundwater extraction or injection. A reactive barrier involves the creation of a reactive zone in an area of passive groundwater flow, such that contaminants are treated as the groundwater passes through the area.

For the MMR, the TAG advocates groundwater containment through hydraulic barriers as a first step in the remedial process. Due to the extensive saturated thickness and the radial flow pattern of the groundwater at the MMR, there are significant limitations for successful application of either physical or reactive barriers to achieve full groundwater containment.

Hydraulic barriers are implemented through the injection or extraction of water from either vertical or horizontal wells. Groundwater extraction objectives include both the removal of dissolved contaminants and containment of contaminated groundwater to prevent further migration. Containment measures are often performed to prevent, or significantly reduce, the migration of contaminants in soils or groundwater. Hydraulic barriers may be engineered to compensate for the extensive thickness and radial flow pattern of the groundwater at the MMR.

Principal hydraulic containment engineering design requires definition of aquifer hydraulic (e.g., permeability, gradient, velocity) and contaminant (e.g., spatial concentration, sorption, intrinsic degradation) properties. Optimization of well locations and extraction/injection pumping rates can be performed with emerging simulation modeling methods. One must recognize that hydraulic containment is only a partial solution with long-term operation and maintenance commitments. For very large aquifer contamination problems, hydraulic containment may be economically taxing.

The main advantage of groundwater containment is that it can prevent additional migration of contaminant plumes and allow for contaminant reduction at sites where the source zone is undetermined, inaccessible, or where long-term remedial actions are being developed. Unlike ex situ treatment technologies, containment does not require excavation of contaminated soils, which leads to increased costs from engineering design of equipment, permitting, and material handling. However, groundwater pumping systems and monitoring wells require periodic inspections and maintenance. Groundwater monitoring wells used to verify plume containment also require periodic sampling and monitoring. Groundwater pumping for hydraulic containment is a commercially available technology that can be easily implemented with conventional pumps in both horizontal and vertical wells. System installation costs are low to moderate, depending upon the geology of the site and existing infrastructure. It is expected that well installation costs are low at the MMR due to the site's sandy soil conditions.

Several disadvantages may limit the effectiveness of hydraulic containment. The main disadvantage of containment methods is that potentially long periods of time may be necessary to achieve remediation goals. Additionally, containment systems may fail to contain the contaminant as predicted due to uncharacterized preferential pathways, allowing the plume to migrate beyond its current boundaries. Groundwater pumping is not applicable to contaminants with high residual saturation, contaminants with high sorption coefficients, or homogeneous aquifers with low permeabilities. Permitting, as well as operation and maintenance of the above-ground treatment system may be high. Additional cost may be realized due to pre-treatment factors (i.e., filtering sediments) or the disposal of secondary wastes.

6.3 Granular Activated Carbon (GAC)

The TAG recommends the use of granular activated carbon (GAC) for the removal of explosive contaminants from the contaminated groundwater stream. Actual treatment may include the design of a train of processes such as pre-filtering, phase separation, air stripping, and carbon systems for polishing.

Liquid phase carbon adsorption is a technology with a long history of use in treating municipal, industrial, and hazardous wastewater streams. The concepts, theory, and engineering aspects of the technology are well developed. It is a proven technology with well-documented performance data. Activated carbon is a relatively nonspecific adsorbent and has been proven to be a simple and effective method for removing explosives from waste streams and is an established technology for remediating explosives contaminated groundwater.

During the liquid phase carbon adsorption process groundwater is pumped through one or more containers packed with GAC. As the contaminated water passes through the carbon, the dissolved organic contaminants are adsorbed and removed from the waste stream. When the concentration of contaminants in the effluent exceeds a certain, pre-determined level, the carbon can be regenerated in place; removed and regenerated at an off-site facility; or removed and disposed. Carbon used for explosives contaminated groundwater usually cannot be regenerated and should be removed and properly disposed.

Two common reactor configurations are used for carbon adsorption systems: the fixed-bed and the moving-bed. The fixed-bed configuration is the most widely used for adsorption from the liquid phase. Pretreatment for removal of suspended solids from the groundwater is an important design consideration because high levels of suspended solids may accumulate and clog the column, reducing performance.

The duration of active adsorption to the activated carbon is a limiting factor. However, if low concentrations are run through the system, the duration is extended. The frequency required for operation and maintenance activities is dependent on contaminant type, concentration, and volume; regulatory cleanup requirements; and the presence of metals and their concentrations.

Liquid phase carbon adsorption is effective for removing contaminants at low concentrations (less than 10 mg/l) from water at high flow rates and for removing higher concentrations of contaminants from water at lower flow rates. GAC systems are particularly effective for polishing water discharges from other remedial technologies to reduce concentrations to or below regulatory compliance levels. Carbon adsorption systems can be deployed rapidly and contaminant removal efficiencies are high.

The major design variables for liquid phase carbon applications are the empty bed contact time (EBCT), usage rate, and system configuration. Particle size of the activated carbon and hydraulic loading (flow rate) are often chosen to minimize system fouling and to reduce or eliminate the need to backwash or clean the carbon of particulate matter. System configuration and EBCT have an impact on carbon usage rate. When the bed life is longer than 6 months and the treatment objectives are stringent, a combination of single beds operating in parallel is preferred. For a single adsorber, the EBCT is normally chosen to be large enough to minimize carbon usage rate. When less stringent objectives are required, blending of effluents from partially saturated adsorbers can be used to reduce the carbon replacement rate. When stringent treatment objectives are required and bed life is short, multiple beds in series may be used to decrease carbon usage rate.

Several disadvantages or concerns exist for the use of GAC systems. Multiple contaminants may impact, degrade, and shorten the performance life of the system. Contaminated water with high suspended solids may cause fouling of the carbon, thereby requiring pretreatment. Logistic and economic disadvantages arise from the need to transport and decontaminate spent carbon. In addition, the type, pore size, and quality of the GAC, as well as the operating temperature, will impact the performance of the system. Disposal costs are associated with the spent carbon material and regeneration of the carbon may not be possible with adsorption of explosives contamination.

6.4 Other Ex Situ Groundwater Treatment Alternatives

Technologies for the ex situ treatment of groundwater, other than GAC, have been demonstrated for the remediation of explosives contaminated groundwater. These other technologies may not have extensive performance data to support decisions on use.

6.4.1 Ultraviolet Oxidation – Ultraviolet (UV) radiation combined with ozone (O₃) or hydrogen peroxide (H₂O₂) is commonly used to destroy explosives contaminated water as it flows through a treatment tank. UV oxidation is a mature groundwater treatment technology that has been in use for full-scale groundwater treatment applications for more than 10 years.

UV oxidation is a destruction process that oxidizes organic and explosive constituents in wastewater by the addition of strong oxidizers and irradiation with UV light. Oxidation of target contaminants is caused by direct reaction with the oxidizers, UV photolysis, and through the synergistic action of UV light in combination with ozone and/or hydrogen peroxide. If complete mineralization is achieved, the final products of oxidation are carbon dioxide, water, and salts. The main advantage of UV oxidation is that it is a destruction process, as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase. UV oxidation processes can be configured in batch or continuous flow modes, depending on the flow rate and contaminant concentration under consideration. If ozone is used as the oxidizer, an ozone destruction unit is used to treat collected off gasses from the treatment tank and downstream units where ozone gas may collect or escape

In general, UV oxidation is performed with low-pressure lamps operating at 65 watts of electricity for ozone systems and lamps operating at 15 to 60 kilowatts for hydrogen peroxide systems. Nearly every organic contaminant that reacts with the hydroxyl radical can potentially be treated with UV oxidation including TNT, RDX, and HMX. Design and operational parameters include contact or retention time, influent water turbidity, metals and contaminant concentrations, existence of free radical scavengers, oxidizer influent dosages, pH, temperature, UV lamp intensity, and performance characteristics of catalysts.

Advantages to using UV oxidation include the lack of contaminant accumulation for subsequent disposal as the contaminants are completely mineralized to harmless end products. Costs are generally low for this technology, but may be influenced by desired flow rates, degree of contaminant destruction required, types and concentrations of contaminants, and pre-

or post-treatment requirements. UV oxidation systems may be designed to handle up to 1 million gallons of water per day, depending upon groundwater and contaminant characteristics.

Several disadvantages or limitations to UV oxidation are highlighted in the literature. The turbidity of the groundwater may decrease the effectiveness of the UV light treatment due to light transmission issues, thus requiring pre-treatment. The technology requires the use, handling, and storage of strong oxidizers. Heavy metal ions or oil and grease may foul quartz sleeves used in the process. Relatively high energy requirements may pose the bulk of the cost when compared to other technologies.

6.4.2 Constructed Wetlands – Although the technology of constructed wetlands incorporates principal components of wetland ecosystems, including organic soils, microbial fauna, algae, and vascular plants, it is theorized that microbial activity is responsible for most of the remediation. Water contaminated with explosives residue or other contaminants flows through and beneath the gravel surface of a gravel-based wetland, or through a lagoon wetland. Initial results indicate the gravel-bed configuration is preferable to the lagoon configuration.

The lagoon wetland uses submergent plants for remediation. The gravel-based wetland, using emergent plants, is a coupled anaerobic-aerobic system. The anaerobic cell uses plants in concert with natural microbes to degrade the contaminant. The aerobic cell further improves water quality through continued exposure to the plants and the movement of water between cell compartments.

Wetland treatment is a long-term technology that is intended to operate continuously for years. The wetlands remediation technology must be adjusted to account for the differences in geology, terrain, trace metal composition, and climate.

The U.S. Army Environmental Center is demonstrating two wetland system designs at the Milan Army Ammunition Plant – a subsurface flow gravel-bed wetland and a surface flow lagoon wetland. Overall, the gravel-based wetland system showed superior performance in degrading all explosives and their byproducts compared to limited degradation by the lagoon system. Gravel-bed wetlands have proven to be more successful than lagoon wetlands in degrading TNT, RDX, HMX, and other explosive residues in groundwater. Low maintenance and operating costs, aesthetics, efficiency, and overall water quality improvement make gravel-bed wetlands an excellent alternative technology for groundwater cleanup. The gravel-bed system has an efficiency rate of more than 95 percent for explosives residue reduction.

Limitations for the use of wetlands include unknowns regarding long-term effectiveness. Wetland aging may pose a problem that may contribute to a decrease in contaminant removal rates over time. The cost for building an artificial wetland varies considerably based on site-specific conditions. High installation costs may be associated with wetlands, but operation and maintenance costs are usually reduced compared to other technologies. In addition, current usage of the site, or lack of surface area for the implementation of wetlands may prevent their installation.

6.5 In Situ Water Treatment Alternatives

In situ groundwater treatment is a general response action that involves techniques to treat contamination in place in the aquifer, without extracting groundwater to recover the contaminants. For some contaminants, in situ treatment can involve special extraction techniques that do not require groundwater pumping, but usually in situ treatment involves addition of amendments that promote either a chemical or biological process to immobilize or destroy the contaminants. In situ treatment technologies are commonly applicable to a specific set of contaminant types. Several different in situ technologies may be required to treat a mixture of contaminants.

6.5.1 Bioremediation – Enhanced biological treatment, or bioremediation, is a developing technology that uses microorganisms to degrade contaminants into less hazardous compounds. Either indigenous or inoculated (introduced) microorganisms are used to degrade the contaminants found in soils and groundwater. Nutrients, oxygen, or other amendments may be used to enhance biological degradation in aquifers.

Bioremediation is most effective for dilute solutions of explosives and propellants. TNT in the crystalline form is difficult to treat biologically. TNT degrades under aerobic or anaerobic conditions into monoamine-, diamino-, hydroxylamine-DNT, and tetranitro-azoxynitrotoluenes. RDX and HMX require anaerobic conditions and degrade into carbon dioxide and water. Researchers have not identified any specific organisms that are particularly effective for degrading explosive compounds; an indigenous consortium of organisms usually affects the degradation.

The main advantage to enhanced bioremediation technology is the fact that it is an in situ process that does not require contaminant removal or above-ground treatment. Assuming enhanced bioremediation can accomplish remedial action objectives in an acceptable time frame, it may achieve significant savings compared to methods involving pump-and-treat. In addition, both soil and groundwater can be treated simultaneously, providing additional costs savings. In situ processes generally require longer periods of time, and there is often less certainty about the uniformity of the treatment because of inherent variability in soil and aquifer characteristics, and from difficulty in the monitoring process. Remedial time frames are often described in years, depending mainly on the degradation rates of specific contaminants, site characteristics, and climate.

Important contaminant characteristics that need to be identified in an enhanced bioremediation feasibility investigation are their potential to leach (i.e., water solubility and soil sorption coefficient); their chemical reactivity (i.e., tendency toward non-biological reactions, such as hydrolysis, oxidation, and polymerization); and most importantly, their biodegradability.

Aquifer characteristics that need to be determined include the depth and areal extent of contamination; the concentration of the contaminants; soil type and properties (i.e., organic content, texture, pH, permeability, and nutrient level); the competition for oxygen (i.e., the redox potential); the presence or absence of substances that are toxic to microorganisms;

concentration of other electron acceptors, nutrients; and the ability of microorganisms in the soil to degrade contaminants.

Limitations that may affect the implementation of bioremediation include the fact that cleanup goals may not be attainable if the soil matrix prohibits contaminant-microorganism contact. Available data suggest that the transport of mobile intermediates may be increased due to the circulation of solutions in the subsurface and may require treatment of underlying, uncontaminated groundwater. Further, biodegradation of explosive contaminants typically involves metabolism with an added nutrient source, which may be difficult to deliver uniformly to the subsurface. An additional concern is that regulators may not accept the addition of amendments or introduced microorganisms to the subsurface. Clogging of injection wells can occur if the nutrient addition strategy is too aggressive. Of particular interest at the MMR is the existence of preferential flow paths. These preferential flow paths may decrease the contact between nutrient-laden injection fluids and contaminants in the subsurface. The degradation rate has also been observed to decline with declining temperatures. Finally, the effectiveness of this in situ treatment process may be difficult to verify both during and after treatment without a rigorous and complete monitoring plan.

Principal issues that must be addressed in the use of enhanced bioremediation include the following: 1) determining the optimum microbial environment to achieve groundwater treatment (i.e., aerobic, anaerobic, or co-metabolic environment), 2) determining the type and quantity of amendments required to achieve the appropriate conditions in the aquifer, 3) characterizing the biodegradation kinetics sufficiently so that the process can be managed in situ to ensure complete biological treatment, and 4) documenting that the biodegradation does not result in any harmful, persistent transformation products.

Treatability or feasibility tests should be performed to determine whether enhanced bioremediation is viable in a given situation, and to define the remediation time frame and optimal parameters. Field testing can be performed to determine the radius of influence and well spacing and to obtain preliminary cost estimates.

6.5.2 Chemical Oxidation – Chemical oxidation involves the subsurface addition of an oxidizing compound to destroy contaminants in place. To be used in an environmental setting oxidants have to be effective in oxidizing the target contaminants and must leave no hazardous by-products. There are several oxidants that are currently used for in situ treatment, including (in decreasing order of oxidant strength): hydroxyl radical (OH), ozone, and permanganate ion (MnO_4^-).

Hydroxyl radicals are the most powerful in situ oxidant and can be generated as a reaction product of “Fenton’s reagent.” Fenton’s reagent involves the subsurface reaction of ferrous iron and hydrogen peroxide to produce hydroxyl radicals. Ozone gas is also a powerful oxidizer. It can be generated on-site using high voltage electrical equipment and can be injected into the subsurface where it dissolves in the water and oxidizes the contaminants. Permanganate ion is introduced as a liquid solution of either potassium permanganate (KMnO_4) or sodium permanganate (NaMnO_4). Permanganate is a less aggressive oxidant than

ozone or hydroxyl radicals, but is much more long-lived, which offers the possible advantage of less dense injection well spacing for subsurface delivery.

The primary issues involved in managing the application of any in situ oxidant are the following:

- Determination that a particular oxidant will react with and completely oxidize the contaminants of concern, leaving no harmful by-products;
- Determination of oxidant mass required to ensure complete treatment and to overcome competing oxidant consumption, such as by natural organic matter in the subsurface; and
- Provision of adequate subsurface transport of oxidant, so that all target contaminated areas are treated.

The reaction pathway and final reaction products of contaminant oxidation are specific to the oxidant used. For example, for explosives oxidation, the reaction pathways and products have been partly characterized for Fenton's oxidation, but not for other oxidants. Researchers have characterized the RDX reaction pathway for Fenton's oxidation and found that RDX formed nitrate, ammonia, formic acid, and carbon dioxide.

The kinetics of reactions between an oxidant and contaminants are obviously an important design factor. Faster treatment translates to more aggressive treatment, but can also mean more difficulty in attaining oxidant delivery at greater distances from the injection well. The primary considerations in selecting an appropriate oxidant among Fenton's reagent, ozone, and permanganate relate to a trade-off between oxidant strength and oxidant stability. For some contaminants that are difficult to treat, stronger oxidants are required to oxidize the contaminants. However, stronger oxidants are inherently less stable and consumed faster. Therefore, control over subsurface oxidant delivery and transport to contaminated areas is generally more difficult with stronger oxidants.

In applications of Fenton's reagent, the ferrous iron solution and hydrogen peroxide must both be delivered to the subsurface contaminants at the same time, since hydroxyl radicals persist for only a few seconds. This presents a large practical challenge for field application in the subsurface and generally requires well spacing on the order of several tens of feet, or less. This can be problematic for sites such as the MMR where current training activities may not allow the development of extensive well infrastructure and costly well field development.

Ozone gas is a powerful oxidizer that may be generated on-site from oxygen using high voltage electrical equipment. Ozone treatment is well suited for the vadose zone, where gas permeability is established. Ozone sparging into the saturated zone requires installation of permanent sparge injection points on fairly close spacing. At the MMR, this may prove to be uneconomical for groundwater treatment.

In contrast to Fenton's reagent and ozone, aqueous solutions of permanganate are highly stable and persistent over periods up to several months in the subsurface. For contaminants where permanganate is sufficiently strong to provide complete oxidation, the stability of permanganate offers an advantage. Because permanganate is highly persistent; it can be applied to the subsurface at wider injection point spacing and allowed to diffuse into and flow across impacted zones.

6.5.3 Chemical Reduction – In situ chemical reduction involves the injection of solutions containing reducing agents into the subsurface or aquifer material to either immobilize or chemically destroy a contaminant.

Reductive dechlorination and/or denitrification are technologies that can be utilized when treating water contaminated by hydrocarbon nitrate compounds such as TNT or RDX. TNT and RDX are compounds that are highly oxidized in which the nitrate groups are the oxidizers. Highly oxidized compounds typically resist oxidative destruction, whether by chemical or biological means. Instead of utilizing oxidative chemical reactions to destroy these types of chemicals, reductive chemical reactions can effectively be utilized.

Typical reducing agents employed include ascorbic acid, calcium polysulfide, ferrous sulfate, hydrogen sulfide, hydroxylamine, sodium dithionite, sodium metabisulfite, sodium sulfide, ferrous iron, and zero valent iron. The reducing agent is chosen according to its ability to reduce the redox potential of the pore water or groundwater while minimizing adverse reactions within a site's geochemistry.

Chemical reduction has the potential to be a very rapid and effective process for the cleanup of groundwater impacted by reducible organics. The in situ method eliminates long-term operation, maintenance, and sludge disposal; is applicable to sites with other commingled inorganic and organic contaminants; and requires minimal operating facilities during treatment. There are several ways to approach the addition of reducing agents into the subsurface. Three possible approaches include the following: 1) direct injection into the contaminant plume using vertical or horizontal wells, 2) injection ahead of the contaminant plume to form a geochemical barrier by reacting with the solid phases, and 3) use of a permeable reactive barrier containing the reducing agent.

The soil or the permeable reactive barrier must be created to assure that reducing conditions are maintained during treatment. The only way reductive chemical reactions can occur is if the chemical contaminant and the reducing agent come into direct contact in the relative absence of oxygen. At the MMR site, the oxygenated groundwater presents an obstacle to the implementation of chemical reduction treatment technologies.

6.5.4 Zero-Valent Iron – Zero-valent iron (ZVI) can be used in a permeable reactive barrier (PRB) wall configuration for the reduction of TNT and RDX contained in groundwater. Typically, a ZVI barrier is created by excavation in an area isolated by an impermeable sheet

pile barrier (below the groundwater table), refilling with a mixture of granular iron, or other iron bearing minerals, and sand, and removing the sheet pile to leave a permeable, iron-bearing zone in situ. Contaminated groundwater then flows through the treatment zone which results in a plume of treated water containing just explosives degradation products and dissolved iron.

As the iron in the wall is oxidized or corroded, the iron metal yields ferrous iron and hydrogen, both of which are possible reducing agents relative to the explosive contaminants. The iron in the barrier is dissolved by the process, but the metal disappears so slowly that the permeable barrier can be expected to remain effective for many years or even decades.

PRB performance and post-closure monitoring tests are being conducted by the U.S. Air Force, U.S. Navy, and in Department of Energy demonstration plots and are being designed for actual contaminated sites. Several full-scale and demonstration scale PRBs have been installed for remediation of groundwater contaminated with chlorinated aliphatic hydrocarbons. These sites include Lowry Air Force Base and Moffet Field Naval Air Station.

Factors that may limit the implementation of PRB ZVI systems include the following:

- Degradation rate for TNT and RDX;
- Expected design life of the ZVI barrier wall and replacement requirements;
- Depth to groundwater and saturated thickness;
- Precipitation of metal salts may reduce barrier permeability resulting in groundwater flow bypass around the barrier;
- Aquitard required to define the bottom of the system and to “key” the barrier within the reach of trench placement equipment; and
- Volume and cost of the iron treatment media.

6.5.5 In Situ Redox Manipulation Using Sodium Dithionite – In Situ Redox Manipulation (ISRM) uses an aqueous reductant, sodium dithionite, in combination with a potassium carbonate pH buffer to reduce naturally occurring iron in aquifer sediments to Fe(II) phases. The sodium dithionite treatment dissolves and reduces amorphous Fe(III) and a portion of the crystalline Fe(III) oxides to produce adsorbed Fe(II), Fe(II)-carbonate, and iron sulfides. Sediment reduction typically occurs within hours and contact times of 1 to 2 days are typically sufficient for near complete reduction. Experience with ISRM has shown the time needed to reduce 80 percent of Fe(III) was about 25 hours.

ISRM is used in a PRB-type configuration similar to the ZVI system described above. Once the iron in the sediments is reduced, contaminated groundwater flows through and reacts with the iron reduced zone and is partially or fully destroyed. It is estimated that a reducible iron content of 0.1 percent in the sediments will result in a barrier capable of treating 180 pore volumes, which may be years to decades at field scales.

Laboratory-scale studies have shown that dithionite-reduced sediments could be used to remediate TNT and RDX. Preliminary laboratory studies have shown that dithionite-reduced smectite clays can reduce TNT and RDX within 10's of hours. Because the environment created by reducing sediments with dithionite differs from ZVI walls, reaction pathways can differ.

Factors that may influence the applicability of this technology include those outlined above for the use of a ZVI barrier wall.

6.6 Monitored Natural Attenuation

Monitored Natural Attenuation involves documentation of natural mechanisms that serve to attenuate the concentration of contaminants in groundwater over time. It is frequently considered to be a supplement or a final polish step to active remediation measures. Natural attenuation mechanisms can include dispersion, dilution, sorption, and natural biological or chemical destruction or immobilization. Natural attenuation occurs for inorganic compounds such as chromium, and for organic compounds such as chlorinated solvents and explosive compounds. The determination of relevant attenuation mechanisms is specific to each individual contaminant of concern (TNT and RDX separately) and is dependent on site conditions.

Natural attenuation of explosive compounds is less well documented than for chlorinated solvents and metals. Natural attenuation appears to be promising to help reduce explosive concentrations in groundwater at some sites.

The conditions necessary for anaerobic breakdown of RDX and related compounds have not been totally elucidated, but a redox potential (E_h) between -11 and -300 millivolts appears to promote degradation. For this condition to occur, oxygen and nitrate must be removed from the system, and available iron (III) must be reduced to iron (II) to reach this potential.

Sulfate is another compound common in groundwater that can act as the electron acceptor in microbial metabolism. Sulfate reduction generally is associated with a E_h in the -11 to -300 millivolts range. Sulfate may not interfere appreciably with the breakdown of RDX, and there is some evidence that it may actually promote such breakdown of RDX and related compounds.

Explosive compound attenuation mechanisms primarily include biological degradation, because explosive compounds are not subject to the immobilization mechanisms involved in metals attenuation and are not strongly sorbed to soils. The possible explosives biodegradation mechanisms are fundamentally similar to the enhanced biodegradation processes described above. However, as these conditions are not favorable at the MMR, it is questionable if natural attenuation by biodegradation and chemical reduction will occur at this site.

7.0 Remediation Technologies for Perchlorate

7.1 Overview

Perchlorate (ClO_4^-) is an anion that originates as a contaminant in groundwater and surface waters from the dissolution of ammonium, potassium, magnesium, or sodium salts. Because adsorption in the environment is not significant and chemical reduction of the central chlorine atom occurs extremely slowly, perchlorate is exceedingly mobile in aqueous systems and persists for many decades under typical ground and surface water conditions. Sources for the contamination include chemical fertilizer and various other chemical and industrial uses. One major source of contamination is the ammonium perchlorate used as the oxidizer component and primary ingredient in solid propellant for rockets and missiles.

Perchlorate contamination became evident at various manufacturing sites and in drinking water supplies within several months following the development of a low-level ion chromatography detection method in 1997. The typical method detection limits in water for the ion chromatography method (EPA 314.0-1 test method) are 5 to 15 $\mu\text{g}/\text{l}$. For soil samples, a modified EPA 314.0-1 is used and provides typical detection limits of 10 to 15 $\mu\text{g}/\text{l}$.

There is currently no National Primary Drinking Water Regulation for perchlorate. However, the EPA established a Provisional Reference Dose for perchlorate in drinking water at 4 to 18 $\mu\text{g}/\text{l}$, based on adult exposure. Until further research information required for a regulatory determination is gathered, perchlorate is on the Safe Drinking Water Act's Contaminant Candidate List. Additionally, the Unregulated Contaminant Monitoring Rule (Federal Register, Volume 64, Number 180, September 17, 1999, pages 50556-50620) states that perchlorate is an unregulated contaminant that requires monitoring.

Using the EPA Provisional Reference Dose as a guideline, several states have established action levels for perchlorate contamination in drinking water. Provisional action levels for drinking water are set at 22 $\mu\text{g}/\text{l}$ in Texas, 18 $\mu\text{g}/\text{l}$ in California, and 14 $\mu\text{g}/\text{l}$ in Arizona. The action level for the MMR was set at 1.5 $\mu\text{g}/\text{l}$, which is well below the method detection limit, and may be technically unachievable.

Perchlorate treatment technologies are classified into categories of destruction or removal technologies. Destructive processes include biological reduction, chemical reduction, and electrochemical reduction. Physical removal processes include anion exchange, membrane filtration including reverse osmosis and nanofiltration, and electrodialysis. All physical removal processes require subsequent disposal of removed perchlorate.

The optimum treatment technology for a given perchlorate occurrence may depend on several factors including perchlorate concentration; the presence and concentration of co-contaminants; and water quality parameters, such as pH, alkalinity, natural organic matter, and total dissolved solids. Additionally, geochemical parameters, such as nitrate, sulfate, chloride, dissolved oxygen concentration, and redox potential may also influence optimum technology selection. The presence of indigenous perchlorate-reducing microbes, and substances

inhibitory to perchlorate-reducing microbial activity will also influence treatment technology effectiveness. For in situ treatment of perchlorate contamination, variables related to the site hydrogeological setting, such as depth to and distribution of contaminants, soil permeability, and groundwater flow velocity are also important factors in technology optimization.

7.2 Soil Remediation Technologies for Perchlorate

7.2.1 Anaerobic Composting – Anaerobic composting is a biological treatment process by which organic materials or contaminants are decomposed by microorganisms at very low oxygen levels. The decomposition process utilizes the carbon and nitrogen found in the organics to metabolically synthesize biomass while producing simpler organic and inorganic molecules and heat as byproducts. Composting results in higher degradation rates than those observed in the natural soil environment because of greater microbial diversity, and higher temperature. Composting is accomplished by mixing contaminated soil with nutrients and high organic content bulking agents, and actively controlling temperature and water content. The most common type of anaerobic composting technology involves the use of static piles.

In the static pile composting process, soil and amendment mixtures are composted in a pile without mixing of any type. Amendments are bulking agents, such as wood chips, hay, animal bedding, or corn stalks; organic food source, such as, potato processing waste; and the inorganic nutrients, nitrogen and phosphorus, found in manure. The principal problems encountered with static piles are temperature and moisture gradients, which produce uneven and spotty contaminant decomposition.

Factors that may limit the applicability and effectiveness of the process include: (1) substantial space requirement, (2) excavation of contaminated soils requirement, (3) odorous compound production and release, and (3) soil volume increase due to amendment additions.

Anaerobic composting was selected for a pilot demonstration at the Aerojet Superfund Site, California of soils from the former perchlorate burn area. Bench-scale studies showed degradation half-lives on the order of 2 to 4 days and perchlorate concentration reduction from 22 to 28 mg/kg to <3 mg/kg after 20 days of treatment. The field-scale composting demonstration consisted of a static pile with a 7 foot base with a 5 foot maximum height. Perchlorate concentrations were reduced from approximately 23 mg/kg to near 0.1 mg/kg in seven days with an estimated degradation half-life of one to two days.

7.2.2 Anaerobic Land Farming – Anaerobic land farming is a bioremediation treatment process that is performed in the upper soil zone or in biotreatment cells using the methods of rice farming. Contaminated soils, sediments, or sludges are incorporated into the soil surface, brought to anaerobic conditions by stimulated aerobic microbial activity under a water layer, and allowed to stagnate for a period of time.

Factors that may limit the applicability and effectiveness of the process include: (1) large space requirements, (2) conditions advantageous for anaerobic biological degradation of

contaminants are largely uncontrolled, which increases the length of time to complete remediation, and (3) the potential of large amounts of particulate matter released by operations.

Anaerobic land farming treatment was demonstrated at the McGregor Naval Weapons Industrial Reserve Plant in Texas. Approximately 1,500 yd³ of surface soil with a maximum perchlorate concentration of 1,800 mg/kg and a mean concentration of 500 mg/kg was treated. Because perchlorate serves as an electron acceptor in the absence of oxygen in microbial reactions, anaerobic treatment of contaminated soil was proposed as the most feasible treatment option.

Before constructing the anaerobic landfarming unit, bench-scale studies were performed to obtain design information including: (1) identification of optimal carbon and nitrogen nutrient additives, (2) microbial inoculation requirement, and (3) biodegradation rate estimate. Fructose and citric acid were evaluated in the bench-scale study as carbon sources, and microbial activity was assessed for both indigenous and previously acclimated inoculum microorganisms. Rapid perchlorate degradation was observed in a few days with an estimated first order biodegradation rate of 0.13 day⁻¹.

Following the successful bench-scale study, perchlorate contaminated site soil was transported to an onsite engineered treatment cell and mixed with citric acid (carbon source), nitrogen and phosphorus fertilizer (micronutrients), and soda ash (buffer) in designed quantities and ratios based on the bench-scale study. Additionally, the soil was saturated as it was placed in the treatment cell. Additional water was added maintain at least 2 inches of water above the soil to foster and sustain anaerobic conditions. Finally, the cell was covered with a 6-mil high-density polyethylene liner.

After six months, soil was sampled at six random locations and analyzed for perchlorate. All six of the sample concentrations were below the detection limit of 4 µg/l.

7.2.3 In Situ Biodegradation – In situ biodegradation refers to the degradation of organic contaminants in soil and/or groundwater by indigenous or transplanted/acclimated microorganisms, primarily bacteria and fungi. Organic contaminants are converted into carbon dioxide, water, and microbial cell mass under aerobic conditions. Under anaerobic conditions, methane, small quantities of carbon dioxide and hydrogen, and occasionally intermediate species, which may be less, equally, or more hazardous than the metabolized compound, are produced.

Perchlorate under aerobic conditions is not biodegradable, but perchlorate is utilized by perchlorate reducing bacteria as an alternate electron acceptor in an anaerobic environment. To promote microbial reduction of perchlorate, metabolic enhancers that stimulate metabolic activity are required. Such enhancers include carbon sources such as molasses, and micronutrients such as nitrogen and phosphorus. The molasses carbon source not only promotes perchlorate reducing bacteria activity, but also stimulates aerobic microbial activity rapidly depleting oxygen in the vadose and saturated zones creating the reducing conditions necessary for perchlorate reduction.

In bench scale tests, soil from the Longhorn Army Ammunition Plant in Texas contaminated with approximately 350 mg/kg of perchlorate was treated to non-detectable levels in less than 9 days. Batch tests and column studies have been completed and field tests are in progress at this site. The proprietary nutrient mix and delivery system are easily adaptable and optimized for soils with different concentrations of perchlorate and hydraulic conductivities. The low cost innovative in situ soil treatment system avoids the traditional expensive and intrusive method of dig-and-treat.

7.2.4 Phytoremediation – Phytoremediation refers to the use of plants to remove pollutants from soil and groundwater, or to assist in the degradation of contaminants to a less toxic form. Some plants are able to extract and concentrate particular elements from the environment, thereby offering a permanent means of remediation. The plant tissue, which is rich in accumulated contaminants, can be harvested and safely processed. Remediation also occurs when bacteria on the roots of the plant degrade pollutant species, or when the roots draw contaminated ground moisture closer to the surface, exposing contaminant species to microbes in a higher oxygen-containing environment.

Green plants (aquatic and terrestrial) were screened at the request of the United States Air Force and species capable of degrading perchlorate to chloride were identified. Subsequent investigations focused on long-term studies and possible factors that may influence phytoremediation of perchlorate-contaminated soils and water. Bench scale studies show that selected woody, edible, and aquatic plants, microbial mats and algae can be used to detoxify water, sediment and soil contaminated by perchlorate. The initial slow uptake and phytodegradation of perchlorate by plants exposed to perchlorate changes to very rapid removal by rhizodegradation after several days depending on the plant physiology and environmental conditions. Initial or prolonged exposure of rooted green plants to perchlorate-dosed media biostimulates the rapid growth of perchlorate-degrading microorganisms in the rhizosphere.

Although rhizodegradation accounts for the removal of most of the perchlorate in solution by plants with roots, uptake of perchlorate into the plants may become significant in environments with high nitrate concentrations (a competing terminal electron acceptor). The results of these studies demonstrate that rhizotransformation predominates if nitrate is replaced by ammonium/urea as the nitrogen source and the trees have a higher fraction root mass.

Exudates secreted by the plant roots supply nutrients that sustain the growth of rich and diverse consortia of the perchlorate-degrading microorganisms. Rhizodegradation is a very rapid process that minimizes the uptake of perchlorate into the tree leaves and branches. Any perchlorate taken up into the green plants is not simply accumulated, but slowly transformed.

Possible perchlorate phytoremediation schemes may include: (1) an intensively cultivated plantation of trees with phreatophytic characteristics at field sites with shallow groundwater, (2) irrigation of planted trees with perchlorate-contaminated groundwater pumped from deep aquifers, and (3) use of constructed anaerobic treatment wetlands.

The costs of phytoremediation of perchlorate are similar to those of phytoremediation systems currently used to treat organic contaminants and nutrients in soils and groundwater.

7.3 Groundwater Remediation Technologies for Perchlorate

7.3.1 Fluidized Bed Reactor/Bioreactor – The Fluidized Bed Reactor (FBR) is a reactor column that fosters the growth of microorganisms on a hydraulically-fluidized bed of media, usually sand or activated carbon. The fluidized media selected provides an extremely large surface area on which a film of microorganisms can grow thus producing a large inventory of biomass in a small reactor volume. The result is a system capable of high degradative performance for target contaminants in a relatively small and economical reactor volume. The FBR can be controlled to operate under aerobic, anaerobic or anoxic conditions depending upon the nature of the target compounds. The choice of media for the FBR bed is dependent upon the specifics of the treatment required. Sand is often selected for higher mass flow rates of contaminants where the yield of biomass is expected to be relatively high. Carbon is often selected for greatest assurance of producing low-concentration ($\mu\text{g/l}$) effluent.

The biological destruction of perchlorate by a biological fluidized bed is an anoxic reaction; the work is done by a consortium of organisms that would prefer to utilize oxygen, but in the absence of oxygen are able to use nitrate and perchlorate to degrade organic material. These are robust organisms and the fluid bed reactors provide a very stable physical environment in which very high concentrations of these organisms can be kept in contact with the water being treated. When nitrate is present, it in fact must be removed first before the organisms will utilize the perchlorate.

An advantage of the biological FBR process is the complete destruction of the perchlorate molecule. The products of the biochemical reaction are chloride ions and oxygen. Perchlorate is not transferred from one medium to another for subsequent treatment and/or disposal. The only waste byproduct generated from the biodegradation of perchlorate and nitrate is a small volume of excess biosolids. These solids are removed from the system on a continuous basis. They are non-hazardous and can be disposed in a number of cost-effective manners.

Envirogen-US Filter/Envirex performed a laboratory pilot-scale FBR treatability study using nitrate, chlorate and perchlorate contaminated water samples to demonstrate the performance of the first stage in a two-stage FBR system to remove nitrate, chlorate and perchlorate. The target effluent perchlorate concentration from the first-stage FBR was less than 5 mg/l with an inlet perchlorate concentration of 370 mg/l.

Two pilot FBR systems were operated in parallel at two different loading rates, corresponding to 2.1 hour and 3.1 hour hydraulic retention times. The two reactors were fed from a common feed tank. During the study, samples of the FBR feed and effluents were collected on a routine basis and analyzed for perchlorate, chlorate, nitrate and other organic and inorganic parameters following EPA methodologies.

The reactors were in operation for a total of thirty-four days. Both the high loaded FBR (2.1 hr hydraulic retention time) and the moderate loaded FBR (3.1 hr hydraulic retention time) achieved greater than 99.9 percent perchlorate reduction after biomass buildup and acclimation. In both reactors, the chlorate and nitrate were completely removed before the perchlorate. The treatability work demonstrated that FBR systems utilizing sand media are an effective method for treating high total dissolved solids water with perchlorate. A total of 388 reactor volumes were processed by FBR #1 while FBR #2 processed 270 reactor volumes.

7.3.2 Anion Exchange – Anion exchange is a reversible process in which anions are released from an insoluble, permanent material in exchange for other anions in a surrounding solution which in the case of the MMR are perchlorate ions. The direction of the exchange depends upon the affinities of the ion exchanger for the ions present, and the concentrations of the ions in the solution. Essentially, the process relies on the fact that water solutions must be electronically neutral, and therefore by inserting a negative ion, another negative ion can be removed from the water.

The resin-bed base anions, typically chloride or hydroxide anions, are eventually exhausted, and replaced by contaminant anions. When this occurs, the bed must be regenerated by flushing with a concentrated solution of the base anion recharging the resin-bed and flushing built-up contaminant.

Los Alamos National Laboratory conducted pilot tests of ion exchange treatment to remove perchlorate from Radioactive Liquid Waste Treatment Facility's effluent. Influent perchlorate concentrations to the treatment facility ranged from several 100 to several 1,000 µg/l. Based upon suggestions from US Filter, a Type I, strong base anion exchange resin was selected for removal of perchlorate from the facility's effluent.

In batch pilot tests, the concentration of perchlorate in the feed to the resin volumes varied dramatically, from 100 to 1,600 µg/l, due to fluctuating perchlorate concentrations in the influent to the treatment facility. The perchlorate concentrations in the effluent from the two columns were generally at the detection limit of 4 µg/l for both the chloride and hydroxide resins.

7.3.3 In Situ Bioremediation – In situ biodegradation refers to the degradation of organic contaminants in soil and/or groundwater by indigenous or transplanted/acclimated microorganisms, primarily bacteria and fungi. Organic contaminants are converted into carbon dioxide, water, and microbial cell mass under aerobic conditions. Under anaerobic conditions, methane, small quantities of carbon dioxide and hydrogen, and occasionally intermediate species, which may be less, equally, or more hazardous than the metabolized compound, are produced.

Perchlorate under aerobic conditions is not biodegradable, but perchlorate is utilized by perchlorate reducing bacteria as an alternate electron acceptor in an anaerobic environment. To promote microbial reduction of perchlorate, metabolic enhancers that stimulate metabolic

activity are required. Such enhancers include carbon sources such as molasses, and micronutrients such as nitrogen and phosphorus. The molasses carbon source not only promotes perchlorate reducing bacteria activity, but also stimulates aerobic microbial activity rapidly depleting oxygen in the vadose and saturated zones creating the reducing conditions necessary for perchlorate reduction.

Strategic Environmental Research and Development Program sponsored laboratory and field demonstrations have shown the applicability of bioremediation approaches for the remediation of perchlorate source areas in soil and groundwater. Groundwater studies have consistently demonstrated the biodegradation of perchlorate from concentrations up to 500,000 $\mu\text{g/l}$ to concentrations that comply with a provisional action level of 18 $\mu\text{g/l}$. The process is rapid with perchlorate degradation half-lives ranging from 1 to 5 days, robust, and is accomplished using a variety of different electron donors including alcohols, volatile fatty acids, and sugars.

7.3.4 Chemical Reduction – It has been known for a long time that titanous ions (Ti^{3+}) reduce perchlorate ions in acidic aqueous solutions, but that reaction is quite slow, generally having a half-time of many hours or a few days. Laboratory research carried out in the Chemistry Department of Georgetown University has identified reaction media in which reduction of perchlorate to chloride by Ti(III) takes place quite rapidly with half-lives of minutes. The group has also synthesized several new organic ligands that efficiently catalyze reduction of perchlorates by titanous ions in ordinary acid aqueous media, and have developed methods to bind the catalytic ligands to semi-solid supports providing an appropriate reaction environment for rapid destruction of perchlorates by titanous species. These heterogeneous catalytic media can be used in flow or batch methods efficiently and rapidly reducing perchlorates to chlorides. The ultimate products of the Ti(III) -perchlorate reaction are titanium dioxide and chloride salts, non-toxic and environmentally benign products. The reactant Ti(III) is inexpensive and readily available.

Researchers in the Department of Chemistry at the University of California have utilized another complex, oxorhenium(V) oxazoline, to catalyze the reduction of perchlorate to chloride with organic sulfides. Methods to bind the catalyst complex to supports for immobilization are also being developed.

7.3.5 Reverse Osmosis/Nanofiltration – Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane that impedes the passage of the solute, but allows solvent flow. If pressure is exerted above the natural osmotic pressure on the solution side, the flow reverses creating a condition known as reverse osmosis. Reverse osmosis and nanofiltration are established water treatment technologies used for the removal of contaminants such as salts, disinfection by-product precursors, nitrates, and selected pesticides. While it is anticipated that these processes may be effective for the removal of perchlorate, there is little to no peer-reviewed data that demonstrates their applicability to perchlorate contamination at concentrations of 1000 $\mu\text{g/l}$ and lower. Additionally, there is no information on the impact of background water quality matrices on the removal of perchlorate using reverse osmosis and nanofiltration.

Potential issues with membrane separation processes for perchlorate removal include the production of up to 20 percent perchlorate concentrate, the potential for losses of excessive quantities of water with the disposal of the concentrate, and the potential presence of co-contaminants in the concentrate such as explosives requiring disposal considerations. There may also be considerable regulatory concern in disposing of the waste and concerns with worker safety.

7.4 Recommended Perchlorate Remediation

Remediation of perchlorate at the MMR must consider the presence of explosive compounds and how these primary contaminants are treated. For the explosive contaminants in the surface soil, the recommended path is excavation with treatment by aerobic composting. A logical second phase to this process is anaerobic composting for perchlorate destruction. The composting amendments are already in place and anaerobic composting could proceed by eliminating air flow to the piles and letting the indigenous anaerobic bacteria take over once the explosive compounds have been reduced to target concentrations.

If perchlorates exist in the groundwater, the second phase of treatment after ex situ treatment of pumped water by granular activated carbon for explosives reduction should be either anion exchange or chemical reduction using titanous ions (Ti^{3+}). These are both relatively simple approaches and would fit into a GAC treatment train.

The other components of the recommended system for explosives remediation, namely hot spot soil removal and treatment, hydraulic containment, and flushing of the vadose zone apply to the remedy for perchlorate.

Appendix A
Biographic Sketches of
Peer Panel Members and WERC Staff

Appendix A

Biographic Sketches of Peer Panel Members and WERC Staff

Explosives Remediation Experts:

KELLEY, Michael – Mr. Kelley received his BS in Geology from Bloomsburg University of Pennsylvania and his MS in Hydrogeology from Oregon State University in Corvallis, OR. His research focused on a laboratory and modeling investigation into the quantification of mass transport parameters using the single-well push-pull test method. He has been employed with Sandia National Laboratories in Albuquerque, NM since receiving his degree in 1999. During this employment, Mr. Kelley has performed numerical modeling for numerous projects including the Waste Isolation Pilot Plant (WIPP), the Yucca Mountain Project (YMP), the Innovative Treatment and Remediation Demonstration (ITRD) Program, and the Saturated Flow Laboratory. He has served in various technical and compliance audit roles for YMP Analysis and Process Model Reports. He is a participating member on the In-Situ Micro-Chemical Sensor Development Team as part of a Laboratory Directed Research and Development (LDRD) funded project at Sandia National Laboratories. He currently acts in a project management role, as part of the ITRD Program, for the Y-12 Bioremediation project, the PORTS Bioremediation and Phytoremediation Request for Proposal Team, the Sandia National Laboratories Tech Area V TCE project, and the Hanford 100-N Remedial Options Evaluation project. He has participated in the Subsurface Contaminants Focus Area (SCFA) Needs Review Meetings at several sites across the Department of Energy (DOE) Complex.

MCCANN, John - Mr. McCann joined Los Alamos National Laboratory in 1989 and currently serves as Team Leader for Firing Sites and Deputy Focus Area Leader within the RCRA Corrective Actions Focus Area of the ER Project. In this capacity he is responsible for integrated planning, resource prioritization, risk assessment and accelerated cleanup planning and accomplishment for RAFA PRSs. From 1993 to 1997 Mr. McCann led the Human Health Risk Assessment Technical Team for the LANL ER Project Decision Support Council. Mr. McCann assisted in applying decision software tools to reprioritize sites across LANL, and has routinely applied risk-based decision approaches to assess current and future potential human health risk from DOE hazardous waste sites. Mr. McCann received his BS in Environmental Health from Colorado State University in 1979. An MBA from the Anderson Graduate School of Management at the University of New Mexico is pending, August 2001.

PHELAN, Jim – Mr. Phelan is a principal member of the technical staff at Sandia National Laboratories with 17 years of experience in environmental contamination assessments, restoration methods, innovative technology development and evaluations, project management and research. He has worked on operational environmental restoration programs including program management, completed field tests of passive vapor extraction and thermal enhanced vapor extraction technology, provided technical management support for technology development involving metals and radionuclide contamination, executed innovative technology remediation demonstration projects for organics in groundwater and explosives in soil, surface water and groundwater, and performed research on explosive chemical signature release, soil

transport and detection strategies related to sensing buried landmines and unexploded ordnance.

RADTKE, Corey - Mr. Radtke is currently a Principal Scientist at the Idaho National Engineering and Environmental Laboratory investigating in situ degradation of explosives in the vadose zone at the Pantex site in northern Texas. He has worked with aerobic picric acid bioremediation, as well as composting for the degradation of chunk explosives in soil (U.S. patent # 6,051,420). Mr. Radtke has additionally worked with subsurface processes as well as with above-ground processing in packed bed, fluidized bed, and bubble reactors for explosives degradation. As co-owner of a small environmental firm, he previously conducted treatability studies and developed analysis, treatment, and disposal protocols for a wide range of hazardous materials, including pesticides, explosives, PCBs, PCPs, propellants, and petroleum hydrocarbons. He designed and implemented successful biotreatment systems for three sites contaminated with heavy petroleum residues and participated in the characterization and remediation of a number of diverse RCRA sites. Mr. Radtke received a BS degree in Biology from Boise State University in 1989 and an MS in Toxicology from Utah State University in 1994.

ROMERO, Van - Dr. Romero received his BS and MS from the New Mexico Institute of Mining and Technology (New Mexico Tech) in Physics and PhD in Particle Physics from the State University of New York at Albany. He has more than 20 years of industrial and academic research. Dr. Romero is a Professor of Physics and is Vice President of Research and Economic development at New Mexico Tech. As the Vice President he serves as chief official of the Research and Economic Development Division responsible for the encouragement, leadership, and support of research at the Institute and for the administrative and policy making activities of the division. He acts as the advocate for research within the Institute, an external advocate and representative for New Mexico Tech's research activities, serves as mentor to new faculty, and identifies research opportunities at the institute. He serves as the director of the Geophysical Research Center, director of the National Domestic Preparedness Consortium, board member for the WERC, and Chancellor of Education at the Nuclear Nonproliferation Security Institute. Prior to becoming the Vice President, Dr. Romero was the Director of the Energetic Materials Research & Testing Center (EMRTC) at New Mexico Tech. As the Director he managed a multi-disciplinary team of scientists, engineers, and staff involved in RDT&E programs in energetic materials. EMRTC provides a working laboratory for conducting research in support of both government and commercial programs in the areas of ordnance, explosives, propellants and other energetic materials. Facilities include over 30 separate test sites, gun ranges, and research labs located within a 40 square-mile field laboratory.

WERC facilitators and staff:

BROWN, Gary, Dr. Brown is a senior member of the technical staff at Sandia National Laboratories, Albuquerque, NM, and has over twenty years experience in environmental research. He holds a PhD in Environmental Science and Engineering, and a BS in Chemistry and Biology. His professional experience also includes environmental research positions with

Lawrence Livermore and Los Alamos National Laboratories. Over the years, Dr. Brown has designed and developed innovative instrumentation and experimental methods for the advancement of environmental research, and has authored numerous publications in these areas. In recent years, he has worked with the EPA in the evaluation of site characterization and monitoring technologies, and with the DOE, EPA, and various state environmental agencies in the evaluation of innovative waste treatment and site remediation technologies. Dr. Brown is currently researching novel remediation methods for soil and groundwater organic and metals contamination and is developing an in situ microbial activity sensor.

Capron, Jason – Mr. Capron received his BS in Civil Engineering from New Mexico State University in May 2000, graduating with honors, and is currently pursuing a MS in Environmental Engineering there. He passed the Fundamentals of Engineering Exam in April 2000 and is focusing on the areas of water management and hazardous site remediation. Mr. Capron has been employed as a graduate assistant at WERC for the past 6 months. Prior to this, he developed the curriculum for and taught a summer course in engineering principles to middle and high school students as part of the Prefreshman Engineering Program and worked as a tutor for New Mexico State University's Math Learning Center where he twice received "Employee of the Semester" awards. Mr. Capron has extensive computer experience and knowledge and is known for his strong visualization and analytical skills.

MAFFITT, Louise - A Program Manager for the University of New Mexico's New Mexico Engineering Research Institute, Ms. Maffitt has over twenty years of experience as a producer, program manager and information management specialist for public, industry and government entities. She has been a producer and writer for public and cultural affairs programming for PBS; a producer, designer and author of communications and training for national industry; and a producer, designer, program manager and proposal developer for national environmental distance-learning programs.

A consultant to Sandia National Laboratories environmental programs for the past six years, Ms. Maffitt has served as program office manager, communications coordinator, facilitator, and technical training/outreach/website author/designer for environmental decision support and innovative technology programs. Working with scientists, public policy experts, federal agency staff, public stakeholders and environmental consultants, Ms. Maffitt has worked to facilitate open dialogue and help build consensus; to clearly communicate the objectives, methods and results of environmental decision support initiatives; and to coordinate the efforts and resources of multi-disciplinary collaborative teams.

CARLSON, Timothy - Mr. Carlson received a BS in Civil Engineering and an MS in Environmental Engineering at Arizona State University and is a registered Professional Engineer in Colorado. He has more than twenty-five years of experience in the environmental cleanup arena working in the private sector with various states, EPA regions, and federal agencies (DOE, DoD, Corps of Engineers, and the National Park Service). He is currently President of Sensible Environmental Solutions, a small non-profit environmental research corporation. Mr. Carlson's projects have included the planning, design, construction management, and operation assistance for numerous waste treatment systems under the

regulatory authority of the Clean Water Act and CERCLA. As a Principal Scientist for RUST Geotech Inc. at the Grand Junction Projects Office, work on DOE projects has included numerous CERCLA actions that have lead to Records of Decisions; DOE Headquarters support on the identification of needs for the Environmental Restoration Program and the relationship of technology efforts to meeting those needs; and the development and coordination of a comprehensive implementation program for several innovative treatment technologies. He is principally known for his abilities to gain acceptance by the public and regulatory agencies of difficult and controversial projects from planning and design through construction. These projects oftentimes involved innovative approaches that required the acceptance by a public with diverse priorities and agendas. Several of these projects received not only local acclaim, but also regional and national recognition for environmental engineering excellence. Another aspect of Mr. Carlson's capabilities has been the organization and performance of high-level peer reviews of environmental technologies. These included an overall assessment of existing technologies for DOE's radioactive and mixed-waste problems, molten salt oxidation for the treatment of organic wastes, a proprietary Russian technology for the separation of cesium and strontium from high-level wastes, engineering barriers for DOE's Waste Isolation Pilot Plant, and performance of Sandia's mixed-waste landfill. Mr. Carlson has participated on two peer panels that evaluated the technology options for treating mixed waste at Los Alamos National Laboratory and at the Savannah River Site.

GHASSEMI, Abbas - Dr. Ghassemi received his BS from the University of Oklahoma and his MS and PhD in Chemical Engineering from New Mexico State University in Las Cruces, NM. He has more than 20 years of industrial, academic, chemical, and environmental hands-on engineering experience. Dr. Ghassemi is an Associate Professor Chemical Engineering and is the Executive Director of WERC. Over the past 10 years, Dr. Ghassemi has been responsible for managing the following WERC programs: Industrial Affiliates, Summer Environmental Academy, International Environmental Design Contest, outreach, technology transfer and demonstration, new business development and new technology development programs. Prior to joining NMSU, Dr. Ghassemi compiled extensive experience in technical and marketing management, process control, process operation and optimization by more than ten years of employment at Fisher Controls International and Monsanto Company. He has extensive experience in the environmental field including pollution prevention, waste management, environmental remediation, and technology identification. He has served as technical expert in several environmental litigation cases as well as technical peer review panels and international training projects in the environmental health and risk assessment fields. He is the author of more than 75 papers and publications in the fields of process control, thermodynamics, environmental engineering and education. He is also co-editor and contributor to several textbooks in the area of environmental technology and management.

THOMPSON, Roseann – Ms. Thompson received a BA from Mount Holyoke College, an MS in Geology and a MPA from New Mexico State University in Las Cruces, NM. She has 13 years of private, government and academic experience in the environmental and public administration fields and is currently Project Manager at WERC. Her responsibilities include

preparing and updating research reports and documents, editing technical documents, interacting with researchers and consulting with state and private agencies, planning and tracking of current technology projects and identification of critical financial and schedule issues for effective project management.

Ms. Thompson has experience in analyzing geologic, hydrological, and chemical data to assess groundwater pollution; coordinating data collection activities; critically reviewing hydrogeologic and geologic reports to determine compliance with state and federal water quality laws; assisting the public on technical matters pertaining to state regulations and policies; supplying contractor oversight during field investigations; and evaluating costs and tracking budgets for environmental investigations and remediation systems. Responsibilities have included computer modeling; preparation of proposals and reports; coordination of field exploration and sampling programs; and interpretation of data for water supply, contamination, and geophysical projects.

Appendix B

**Initial Technology Identification
for the Remediation
of RDX in Groundwater and Soil**

March 1, 2001

**Prepared by: Jason Capron
Graduate Assistant I for WERC**

Appendix B

Initial Technology Identification for the Remediation of RDX in Groundwater and Soil

Introduction

This project was undertaken by WERC for the National Guard Bureau, Army Environmental Programs Division to serve as a third-party evaluation of remedial technologies. The purpose of this report is to identify remediation solutions for explosives-contaminated soils at the Massachusetts Military Reserve (MMR). The report contains a listing and description of all technologies for remedial activities identified thus far, as well as available information on limitations in implementation and operation for each technology. When available, standard cost estimates were also provided with the intent of use for comparative purposes only. Actual costs will be based on site-specific conditions.

Background

Royal Demolition Explosive (RDX), also known as cyclonite, hexogen, and 1,3,5-trinitro-1,3,5-triazine is a synthetic chemical used in explosives. RDX is slow to dissolve in water and evaporates slowly from water. It can be broken down within a few hours in water and the atmosphere, but will break down more slowly in soil. It does not cling strongly to soil.

RDX does not build up in people and the effects of long-term, low-level exposure are unknown, but large ingested quantities can lead to seizures. The United States Environmental Protection Agency has identified RDX as a possible human carcinogen and has a recommended maximum guideline of 2 parts per billion in drinking water. Additionally, the National Institute for Occupational Safety and Health and the American Conference of Governmental Industrial Hygienists recommend an exposure limit of 1.5 milligrams per cubic meter of air for a 10-hour workday, 40-hour workweek. The National Institute for Occupational Safety and Health also recommends a short-term exposure limit of 3 milligrams per cubic meter of air for no more than 15 minutes.

Enhanced Bioremediation

Enhanced bioremediation encompasses several specific treatment options. It is synonymous with biostimulation, bioaugmentation, and enhanced biodegradation. This process is based on the stimulation of indigenous or inoculated microorganisms through the addition of nutrients and possibly oxygen. The process may be either aerobic or anaerobic, and is done predominantly in situ. Care must be taken if an anaerobic process is used, as intermediate or final products of anaerobic degradation may be more hazardous than the original contaminants. Typically, uncontaminated water is mixed with nutrients and possibly saturated with dissolved

oxygen injected into the soil, either by an infiltration gallery, spray irrigation, or injection wells, depending on the depth of contamination. Bioremediation processes will be slowed by low temperatures and the process is viewed as a long-term one, possibly taking several years to achieve treatment goals. However, bioremediation has been shown to be successful in remediating both contaminated soils and groundwater without the need for excavation, generally making this option more cost effective than other processes, with a typical range of \$20 to \$80 per cubic yard of soil. When present in sufficient concentrations, inorganic salts, highly chlorinated organics, heavy metals, and long-chain hydrocarbons are likely to be toxic to most microorganisms and will severely hamper or prevent the use of bioremediation processes.

Oxygen Enhancement with Air Sparging

This specific bioremediation technology for contaminated groundwater involves injecting air at high flow rates below the water table to increase groundwater oxygen concentration, thereby enhancing the rate of biological degradation. Air sparging will also increase mixing in the saturated zone, which increases the contact between soil and groundwater. The process in effect creates an underground air-stripper, which will remove contaminants by volatilization. Small-diameter air injection wells are relatively cheap and easy to install, making this a fairly flexible process. It is often used in conjunction with bioventing at shallower depths and soil vapor extraction. Air sparging has a medium- to long-term duration, potentially taking up to a few years.

Hydrogen Peroxide Enhancement

This process involves adding a dilute solution of hydrogen peroxide to the contaminated groundwater to increase the oxygen concentration and thus increase the rate of aerobic biodegradation.

Nitrate Enhancement

In this process, solubilized nitrate is circulated throughout the contaminated groundwater to provide an alternative electron acceptor for anaerobic biological activity, increasing the rate of that biological activity. This technology is still at the pilot stage.

Bioventing

Bioventing is a specific process within the enhanced bioremediation category in which relatively low air flow rates are used to stimulate microbial activity, allowing the remediation of aerobically degradable compounds in soil. The oxygen is supplied to the soil via direct air injection. The process is often used in conjunction with soil vapor extraction. Its performance will be limited by a groundwater table that is relatively near to the surface, low soil permeability, and the same low temperatures that affect all biological processes. As with most bioremediation processes, this option is generally a long-term one, typically taking anywhere

from several months to several years to achieve treatment goals, depending on conditions. At this point, it is viewed as often being inadequate for the remediation of explosives. Typical costs for this process are in the range of \$10 to \$50 per cubic yard of material treated.

Bioslurping

Also known as dual-phase extraction (DPE), multi-phase extraction, and vacuum-enhanced extraction, bioslurping is a combination of bioventing and vacuum-enhanced free-product recovery. This process is designed to focus on hydrocarbon-contaminated soils where recovery of the hydrocarbons is desired.

Biopiles

Also referred to as heap pile bioremediation, bioheaps, biomounds, and static-pile composting, this ex situ technology involves mixing soil with organic amendments like those used in composting and placing it in above-ground enclosures. This process follows the same principles as composting, but the pile remains static and is aerated with blowers or vacuum pumps. This is a short-term technology, lasting anywhere from a few weeks to several months. The main drawbacks of this technology are that it does require the excavation of contaminated soils and that the nature of its static treatment may result in less uniform results throughout the treated soil than a process that involves periodic mixing. However, biopiles are simple to operate and maintain, requiring little personnel. Costs are typically \$100 to \$200 per cubic yard of soil, including a prepared bed and liner, with the nature of the contaminant, the need for off-gas capture and treatment, and the need for any pre- or post-treatment as the primary determinants. Biopiles have been previously used for RDX clean up at military sites (Army Demo, Louisiana Army Ammunition Plant).

Composting

Similar to biopiles, this technology involves excavating soil, mixing it with bulking agents and organic amendments to ensure optimum porosity and thermophilic, microbial activity. Typically, indigenous microorganisms are used, although inoculation may also be necessary, depending on the nature of the contaminant. Oxygenation, moisture, and temperature are then carefully maintained. Two basic designs are available in composting: 1) mechanically-agitated in-vessel composting, where a reactor mixes and aerates the compost, and; 2) windrow composting, where the compost is placed in long piles and periodically mixed using mobile equipment. The last of these is typically considered to be the most cost-effective, but it may also produce the most off-gassing. Pilot and full-scale studies have both shown composting as a viable option in reducing the concentration of explosives, with windrow composting achieving 99.8 percent RDX removal. This technology has been used for remediation activities at other explosive-contaminated military sites (Army Demo, Umatilla Depot). The primary limitations on the use of composting are the space it requires, the need for excavation, and a volumetric increase in material because of the addition of amendments. Windrow

composting used to treat explosives is estimated to cost approximately \$190 per cubic yard for soil volumes of approximately 20,000 cubic yards and mechanically agitated in-vessel composting is estimated to cost \$290 for the same conditions.

Landfarming

Landfarming is similar to composting, except that it can also be used as an ex situ bioremediation process to treat sludge. In this process, contaminated material is placed in lined beds and then periodically turned over or tilled to aerate the waste. As with composting, soil conditions are usually specifically controlled to optimize moisture content, aeration, pH, and nutrients. Typically, contaminated material is treated in lifts that are about 18 inches thick. Once the treatment goal for the lift is achieved, it is either partially or fully removed and the next lift placed there. Like composting, landfarming requires a large amount of space and, because it is a biological process, its performance is subject to temperature and the presence of toxic or inhibitory substances. It is a medium- to long-term technology and costs will typically be less than \$75 per cubic yard of soil.

Fungal Biodegradation

Fungal biodegradation uses specially cultivated fungi, such as white rot fungus, to degrade organic pollutants. It has been tested in bioreactors, assisting the composting process, and in situ. White rot fungus has also been shown to be effective in degrading and mineralizing the conventional explosives, although high concentrations of TNT may inhibit the process. One major drawback of fungal biodegradation is that it may not reduce concentrations sufficiently to meet target levels, and so it is best used in conjunction with other processes. White rot fungus has a specific set of optimal environmental conditions that should be duplicated if it is to be used. Costs for using white rot fungus are estimated at \$75 per cubic yard of soil.

Slurry Phase Biological Treatment

Also known as slurry biodegradation, this ex situ process involves creating an aqueous slurry composed of soil or sludge, water, and various additives. The slurry is mixed in a bioreactor to keep solids in suspension and the microorganisms in contact with the contaminants. As with any biological process, microorganisms may be added if the native population is not suitable. After the treatment goal has been reached, the slurry is dewatered by clarifier, vacuum filter, centrifuge, or other method. This technique has been successfully used to remediate soils, sludges, and sediments contaminated by explosives, with an aerobic bioslurry showing a 99 percent removal efficiency and a high degree of mineralization. This technology is considered to be short- to medium-term and costs are typically \$100 to \$150 per cubic yard, or \$125 to \$160 per cubic yard when off-gas treatment must be used.

Co-metabolic Processes

This technology stimulates the co-metabolic breakdown of contaminants by injecting a dilute solution of primary substrate into a contaminated groundwater zone. However, this technology is still largely in its infancy.

Bioreactors

In this ex situ process, contaminated groundwater is put into contact with microorganisms in attached or suspended growth biological reactors. Suspended systems include aeration basins while attached systems include rotating biological contactors and trickling filters. In a trickling filter, water is added to the top of a bed of highly permeable media and organic constituents are degraded by microorganisms attached to this media. Nutrients may be added to bioreactors to stimulate microbial activity. Bioreactors are a long-term technology, potentially taking up to several years and are used to treat any biodegradable organic material. Their effectiveness is greatly reduced with low temperatures, and costs are dependent on a variety of factors, including the nature of the contaminants and flow rates.

Aeration

The principle behind aeration is increasing the area of contact between water and air. This technology is well developed within the wastewater treatment industry and the goal can be achieved in several ways, such as bubbling air into water or converting the water into small droplets within an oxygen rich environment. This serves to transfer volatile organic compounds from wastewater to the air, which can then be treated with greater ease using off-gas treatment. Costs for this process are largely dependent on the volumes that must be treated.

Solidification/Stabilization

The principal behind in situ solidification is to physically bind contaminants within a fixed mass and trap them in the media they existed in without removing them. Similarly, stabilization aims to use chemical reactions between a stabilizing agent and contaminants to reduce their mobility. This makes the use of these processes highly dependent on the physical nature of the soil present. Another closely related process is vitrification, in which an electric current is used to create extremely high temperatures that will melt and fuse soils, trapping inorganics and destroying many organics by pyrolysis (discussed later). Solidification/stabilization processes are typically short- to medium-term, with vitrification tending to be shorter. The primary target of solidification and stabilization is inorganics, limiting their use on organic chemicals, but because of the use of heat, vitrification does have the potential to also destroy organics. All of these processes may require dewatering to achieve optimum performance. Costs vary widely depending on the specific option selected and the depth of application.

Solidification and stabilization can also be done ex situ. Just as with in situ, contaminants are either enclosed within a mass or their mobility is reduced. However, the ex situ process typically requires that the materials resulting from the stabilization or solidification process be disposed of under regulatory oversight. Ex situ solidification and stabilization options include bitumenization, emulsified asphalt encasement, modified sulfur cement and pozzolan/Portland cement encasement, encasement within a polyethylene extrusion, sludge stabilization, stabilization with soluble phosphates, and vitrification. As with the in situ process, the primary target of ex situ solidification and stabilization is inorganics with most organics not being immobilized by the processes, although, again, vitrification will destroy most organic contaminants. These technologies are among the most mature options available, and average costs are under \$100 per ton, including excavation.

Chemical Extraction

This ex situ process involves placing contaminated soil and appropriate chemicals into an extractor where the contaminants are dissolved. The extracted solution is then placed into a separator where the extractants and contaminants are separated for further use and treatment, respectively. This technology does not eliminate waste, it separates it from soils, resulting in a reduction in the volume to be treated. Since traces of solvent may remain on the treated soil, it is important to consider the toxicity of that solvent. This technology has been shown to be most effective in the treatment of primarily organic contaminants. Soil type and moisture content have an impact on this process. Specifically, clays will reduce extraction efficiency, thus requiring longer amounts of time within a reactor. This technology is classified as medium-term, and is best used at larger sites as capital costs can be relatively high, with total costs ranging from \$100 to \$400 per ton, depending on the volume treated.

Acid Extraction

This is a more specific case within chemical extraction where hydrochloric acid is used to treat soils with heavy metals as the primary contaminant.

Chemical Oxidation/Reduction

Using this treatment process, contaminants are converted to harmless or less toxic products through the mechanisms of oxidation and reduction. The most common oxidizing agents used are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. This is a well-established technology in the disinfection of drinking waters and wastewaters. It is a short- to medium-term technology, but it is intended for the treatment of inorganics, although it can be used against nonhalogenated volatile organic compounds, but less effectively. It is important to ensure that incomplete oxidation or the formation of more hazardous intermediate contaminants will not occur if this technology is used. Costs for this technology typically range from \$150 to \$500 per cubic yard.

Molten Salt Oxidation

In this ex situ process, combustible wastes are oxidized in a reactor containing a bath of molten salts. Organic contaminants will react with oxygen to form simpler compounds such as carbon dioxide and water, while inorganics will form residues that will be retained within the molten salt. As the salts are alkaline, any acid gases that are produced during oxidation will also be effectively scrubbed. Continuous recycling must be employed to remove residues and neutral salts from the reactor. This technology has been shown to be effective on a variety of contaminants including explosives and propellants.

UV Oxidation

Ultraviolet radiation is a process that will oxidize organic and explosive constituents in wastewaters through the use of strong oxidizers and irradiation. As with solar detoxification, this is a destruction process, not an extraction or concentration process. Almost any organic contaminant that is reactive with the hydroxyl radical can be treated by this process. Ordnance compounds such as TNT, RDX, and HMX are susceptible to destruction by UV oxidation. For this process to perform optimally, the fluid being treated must provide for good transmission of UV light. UV oxidation may be more expensive than competing technologies because of the energy requirements of this technology. Typical costs for this process are \$0.10 to \$10 per 1,000 gallons.

Solar Detoxification

This technology is based on using the ultraviolet energy of sunlight to destroy contaminants. Generally, vacuum extraction is first used to remove contaminants from soils. After being condensed, the contaminants are mixed with a semiconductor catalyst and then fed through a reactor illuminated by sunlight. The ultraviolet light from the sun activates the catalyst, resulting in the formation of radicals, which are powerful oxidizers capable of breaking down the contaminants into non-toxic by-products. One of the biggest advantages of this technology is that contaminants are destroyed instead of being moved to another media as with air stripping or carbon adsorption. The disadvantage of the process is that it is only effective with at least normal sunlight intensity.

Solvated Electron Treatment

This technology is a non-thermal chemical treatment that destroys virtually all halogenated organic compounds as well as explosives. The process uses solvated electron solutions, which, when put in contact with contaminants, strip negatively charged elements or compounds that then react with sodium ions to form salts, hydroxides, and so on, leaving these products in situ. The resulting products of explosive detoxification have been found to contain none of the targeted analytes captured in the EPA's Analytical Method 8330 and have been found to be

non-explosive. The vendor touts it as a non-thermal process equivalent to incineration and claims 99.999 percent RDX removal in treatability studies.

Separation

The purpose of separation techniques is to remove contaminants from soil or groundwater via physical and chemical means. There are many options for ex situ separation, including coagulation/flocculation/gravity separation, sieving, and magnetic separation. The target contaminants for separation are semi-volatile organic compounds, fuels, and inorganics, although the processes can also be used to a lesser effect on volatile organic compounds. Gravity separation and sieving/physical separation are well-established technologies in the treatment of wastewater, soil, sediment, and sludge. The target contaminant groups for ex situ separation processes are volatile and semi-volatile organic compounds and suspended particles.

Precipitation/ Coagulation/ Flocculation

The primary focus of precipitation/coagulation/flocculation is to transform dissolved contaminants into insoluble solids that can then be removed from wastewater via filtration, settling, or other mechanisms. Metal precipitation may be necessary as a primary treatment where the presence of metals will interfere with other treatment processes. Coagulants are used to stimulate flocculation, where particle size is increased through aggregation, allowing for easier removal by physical means. These processes are common in drinking water treatment but are likely inadequate for the treatment of explosives.

Distillation

Distillation is a chemical separation process involving vaporization and condensation of contaminants to separate components of varying volatilities. In its simplest form, distillation is a single-stage operation in which heat is applied to a liquid mixture in a still, causing a portion of it to evaporate. These vapors are then cooled and condensed, producing a liquid that contains the higher volatility components. Multiple stages are more likely to be used to obtain better separation than is possible with a single stage.

Filtration

Filtration is a physical separation process where particles in suspension are separated by forcing a fluid through a porous medium with set pore sizes, retaining particles larger than that size, and letting smaller particles and solubilized particles through.

Adsorption/Absorption

In adsorption, solutes concentrate on the surface of a sorbent material, reducing their concentration in the surrounding water. Adsorption can be sub-categorized into physical adsorption, where weak molecular forces such as Van der Waals forces

provide the driving force for adsorption; chemisorption, where chemical reactions form chemical bonds between the solute and the sorbent; and electrostatic adsorption, where ions are adsorbed through Coulombic forces. The most commonly used adsorbent is granular activated carbon. The main target contaminants of adsorption/absorption are organics, although certain inorganics will also be treated by this process. The cost of this process can be high if it is used as the primary treatment mechanism. It is not a practical option if high concentrations of oils and greases are present or where the concentration of absorbable substances is so high that the media will need to be frequently replaced, especially since contaminated media may require treatment and disposal as hazardous wastes if they cannot be regenerated.

Reverse Osmosis (Membrane Filtration)

In this process, wastewater is forced through a pervaporation module under pressure. This module contains a permeable membrane that will preferentially adsorb volatile organic compounds from the wastewater. The compounds are then diffused by vacuum from the membrane-water interface through the membrane. The treated water exits the module and the vapors travel to a condenser. The condensed organics can then be disposed of or treated.

Freeze Crystallization

In this process, a solution containing dissolved contaminants is slowly frozen and water ice crystals form on the surface, concentrating the contaminants in the remaining solution. This more concentrated solution is then generally easier to subsequently treat by other methods.

Electrokinetic Separation

Also known as electromigration, this in situ process is best used to remove organic contaminants from low permeability soil. Electrokinetic separation uses electrochemical and electrokinetic processes to desorb and then remove polar organics. The process involves applying a low-intensity direct current through soil between ceramic electrodes. Charged organics then move towards the appropriate attractive electrode. Even charge-neutral organics will migrate somewhat with water moving due to electroosmosis. This process is primarily a separation and removal technique, but two approaches can be taken in its use: 1) Enhanced Removal—contaminants are allowed to concentrate at electrodes for subsequent removal and ex situ treatment, and; 2) Treatment Without Removal—the polarity of the electrodes is periodically reversed, causing contaminants to migrate back and forth through an established treatment zone. The primary drawback of this technology is that it is not generally effective at concentrations below a few parts per million, necessitating a polishing step for many contaminants or altogether eliminating it as an option. Also, the presence of buried metallic or insulating material will induce unwanted variability in the electrical conductivity of the soil. Under the same principle, clays are the best soil type for this process because of their negative

surface charge. Additionally, redox reactions can form undesirable products if this technology is used. The cost of the process is site-specific.

Passive/Reactive Treatment Walls

Also known as in situ chemical filters and permeable reactive barriers, this technology involves installing a permeable reaction wall across the flow path of a contaminant plume. This wall will allow the water portion of the plume to move passively through the wall while prohibiting the movement of the contaminants using various agents. Contaminants at the barrier will either be degraded or retained in a concentrated form. These barriers are effective in treating volatile and semi-volatile organic compounds and inorganics. They may require replacement as they lose their reactive capacity. They are limited by subsurface lithology, as an aquitard must be present within trenching limits to prevent contaminants from migrating under the barrier.

Soil Washing

Soil washing, similar to separation, is a technology for separating contaminants from soil. Contaminants sorbed onto fine particles are separated in an aqueous-based system that may be augmented with a leaching agent, surfactant, or pH adjustment. Contaminants are either dissolved or suspended into the wash solution or are concentrated into a smaller volume of soil through particle size separation. If there are multiple target contaminants, sequential washing may be necessary so that each wash solution can be optimized for a particular contaminant or contaminant group. The wastewater created by this process is then treated appropriately. The target contaminants for this technique are semi-volatile organic compounds, fuels, and heavy metals, although it will also work on selected volatile organic compounds. It has seen relatively limited use in the United States, but is used extensively in Europe. It is classified as a short- to medium-term process. On average, the cost is about \$170 per ton of soil, including excavation.

Soil Flushing

This in situ process involves applying or injecting water, which may also contain additives to enhance contaminant solubility, into the ground. This is a developing technology that is relatively new in the United States. The theory is to leach contaminants into the groundwater that will then be extracted and treated. Another variation on the technique is to inject water so as to raise the groundwater table into the contaminated zone and then collect the contaminated water. In addition to or separately from this, cosolvent enhancement may be used, where a solvent mixture is injected into either the vadose zone, the saturated zone, or both to dissolve either the source of contamination or the plume coming from it. The solvent/dissolved contaminant mixture is then extracted downstream and treated. This process is generally short- to medium-term in length. The treatment of the recovered fluids will result in sludges that must also be properly treated, and air emissions of volatile contaminants from recovered flushing fluids may also need to be captured and treated. Residual flushing additives in the soil

may also be a concern that limits the use of this technology. The primary target for this technique is inorganics, but it has been shown to effectively treat volatile organic compounds as well, although it will generally be less cost effective than alternative technologies for these chemicals. Cost varies widely with the nature of surfactants or other additives used.

Thermal Desorption

Thermal desorption is a physical separation process that is not designed to destroy organics, but rather to volatilize water and organic contaminants with heat, which are then taken to a gas treatment system via a vacuum system. The temperatures and residence times within the thermal desorption process are designed to volatilize selected contaminants, but not to oxidize them. In addition to the off-gas treatment, thermal desorption must also have particulate removal equipment. Contaminants will most likely be removed via carbon adsorption, a secondary combustion chamber, or a catalytic oxidizer. The effectiveness of thermal desorption systems vary significantly across the spectrum of organic contaminants. Both high temperature and low temperature thermal desorption systems exist for differing circumstances. Clayey and silty soils will require longer reaction times because of their tendency to bind with contaminants. The expected time to complete the cleanup of 20,000 tons of soil is just over 4 months for a high temperature thermal desorption system.

Air-Stripping

The principle of this process is to increase the surface area of wastewater exposed to air. Volatile organic compounds will then be transferred to the air. For this reason, off-gas treatment of the air-stripping facility may be necessary. The air-stripping process is done in a packed tower. In this unit, water is distributed over the packing in a column as air is forced up the tower from the bottom. This process will not affect inorganics or organics with Henry's Law Constants lower than 0.01 atmospheres-cubic meter per mole. Low-volatility compounds may require preheating to facilitate the air stripping process. Costs of this process vary widely, being largely dependent on energy requirements, which are dictated by the nature of contaminants to be stripped and desired effluent quality.

Cascade Air-Stripping

Cascade air-stripping uses an alteration of the typical air-stripping process. Specifically, air is admitted along the full height of a packed tower instead of solely from the bottom. Currently, only pilot-scale studies of this process have been performed, but it appears to operate under the same limitations as standard air-stripping and achieves better removal efficiencies with less packing depth than conventional air-stripping when energy inputs are equal. This equates to a lower cost than conventional air-stripping for similar performance levels, although, like conventional air-stripping, cost-effectiveness will be dictated by energy requirements.

In-Well Air-Stripping

Also known as in-well aeration and groundwater circulating wells, this process entails injecting air into a double-screened well, lifting the water and forcing it out through the upper screen into the unsaturated zone. As this happens, additional water is drawn in the lower screen. This creates a hydraulic circulation and volatile organic compounds in the contaminated groundwater are stripped by air bubbles from the dissolved phase to the vapor phase. These vapors can then be drawn off by soil vapor extraction. This is still a pilot-scale technology and is currently viewed as a short to long term process, depending on contaminant concentrations, Henry's Law constants, and geohydrology.

Soil Vapor Extraction

Soil vapor extraction (SVE) can be used both in situ and ex situ. SVE used in situ is also known as soil venting, in situ volatilization, enhanced volatilization, and soil vacuum extraction. For this process, a vacuum is applied to extraction wells to create a pressure gradient that causes gas-phase volatile and some semi-volatile compounds to be removed via the extraction wells. These gases will then generally need to be collected and treated. The extraction vents can vary in depth from 5 feet to 300 feet. Air injection may facilitate the extraction of deep contamination, contamination in low-permeability soils, and contamination in the saturated zone. Treatment of contaminants in the saturated zone can also be facilitated by using groundwater drawdown pumps, as high moisture contents severely hamper the process. In situ soil vapor extraction is typically a medium to long term process, with an upper limit of about 18 months. It is typically applicable only to volatile compounds with a Henry's Law Constant greater than 0.01 or a vapor pressure greater than 0.02 inches Hg. However, because the process creates an air flow, it will also promote the biodegradation of low-volatility organic compounds in the soil. Costs for this process typically range between \$10 and \$40 per cubic yard of soil treated, depending on the number of wells needed, blower capacities, and the need for any off-gas treatment.

Ex situ soil vapor extraction follows a similar principle. A vacuum is applied to a network of above-ground pipes to encourage volatilization of organic contaminants in the excavated soil. The ex situ process forms more passageways, is no longer limited by shallow groundwater, and is more uniform and easily monitored than the in situ process. However, it also has the added costs of excavation. It is also a medium to long term process that targets volatile organic compounds. Ex situ soil vapor extraction requires a large amount of space and typically costs \$100 per ton of soil, including excavation.

Thermally Enhanced Soil Vapor Extraction

This process operates under the same principal as standard in situ soil vapor extraction, but also utilizes electrical resistance, radio frequency heating, hot-air/steam injection, or other methods to increase heat and thus facilitate extraction. Thermally enhanced soil vapor extraction may also help to overcome the high moisture content restrictions on

the standard process. The cost for this process is typically between \$25 and \$100 per cubic yard of soil treated.

Fluid/Vapor Extraction

Also known as two-phase extraction, this process uses a high vacuum system to remove liquid and gas simultaneously from low-permeability soils. Contaminants are removed both above and below the groundwater table, and the water table will also be lowered around the well, allowing better access to contaminants in this drawdown zone via soil vapor extraction. Because this process creates turbulence in extraction, most of the contaminants in the water are stripped away, so usually only polishing is needed. The estimated cost for this technology is \$160 per pound of contaminant.

Fracturing

Fracturing is an enhancement technology intended for use in low-permeability and over-consolidated soils. Using hydraulics or pneumatics for soils, or blasting where cavities in fractured bedrock need to be further expanded, passageways are opened to assist in situ processes or to increase extraction efficiencies for ex situ processes. Fracturing is typically followed by soil vapor extraction to collect gases released during the process. One concern of fracturing is that it may open new pathways for contaminants to spread more rapidly. Costs vary, although a typical range for pneumatic fracturing is \$8 to \$12 per ton of soil.

Lasagna™

Lasagna™ is an integrated in situ remedial technology, where horizontal sorption/degradation zones are created by hydraulic fracturing, and electrodes are then installed, allowing electroosmosis to transport contaminants across the treatment zone. Typical costs are \$160 to \$180 per ton of soil for remediation within one year, and \$100-\$120 per ton for remediation within three years.

Integrated Fracturing and Treatment Zones (Foremost Solutions, Inc.)

This process uses hydraulic fracturing or jet grouting to create treatment zones into which ISOLITE® spheres are then injected. ISOLITE® is a porous ceramic material inoculated with aerobic and anoxic microorganisms selected to biodegrade the target contaminants. These spheres also serve to keep created fractures open to better maintain a treatment zone, as contaminants will preferentially move through these open zones. The spheres can be left in place when remediation activities are completed. The movement of contaminants in the created treatment zones can be stimulated using soil flushing above the fracture zones. Injection wells to provide air and nutrients to microorganisms may also need to be installed. This process is aimed towards treating hydrocarbons and chlorinated solvents, but can be

applied to any biodegradable chemical. Application of the process is not limited by porosity, but higher porosities reduce its cost effectiveness. It will also have similar limitations as other bioprocesses such as reduced effectiveness at low temperatures or in the presence of toxic substances.

Directional Wells

Directional wells are an enabling technology similar in principle to fracturing. They will allow access to contaminants not accessible by vertical drilling, especially if structures are inhibiting the placement of vertical wells. However, these wells are at a greater risk for collapse, and specialized equipment is required, making this technology costly at about \$20 to \$75 per foot for hydraulic bi-directional thrust drilling and \$100 per foot for sonic drilling. Also, the technology is currently limited to a maximum depth of about 50 feet.

Incineration

This process uses high temperatures to volatilize and combust organic contaminants. The off-gases and combustion residuals from the process will also generally require additional treatment. Several combustion options exist, including a circulating bed combustor, which uses high-velocity air to create a highly turbulent combustion zone, allowing for lower temperatures than conventional incineration and more complete mix of contaminated materials. A circulating fluidized bed using high-velocity air to circulate waste particles in a combustion loop and keep them in suspension is also available. There is also an experimental unit using electrical resistance heating elements to heat material passing through a chamber on a conveyor belt. Incineration technology can be anywhere from short to long term, and is intended for use on soils contaminated with explosives or other hazardous wastes. Incineration can be done off-site if transportation costs are reasonable for about \$200 to \$1000 per ton of soil. Incineration on-site can be used to reduce transportation costs, but may not be allowed under regulations.

Open Burn/Open Detonation

This technology is used to destroy explosives through self-sustained combustion after an initial ignition. The process can be used to destroy munitions as well as media contaminated with energetics. The use of this technology may be restricted by permit emissions limitations because it is difficult to capture those emissions from this type of remediation and this technology is likely moving towards being eliminated as an option.

Pyrolysis

Also known as molten solid processing and plasma pyrolysis, the principle behind this technology is to induce chemical decomposition in organics using heat in the absence of oxygen. The organics are then transformed into gases and a solid residue (coke). The gases

will require additional treatment and a secondary combustion chamber may be used and the remaining gases then be partially condensed. This process also requires particulate removal equipment such as wet scrubbers. The kilns used for pyrolysis are similar to those used for incineration, but operate at a lower temperature and with less air supply. This technology requires that the soil being treated have a low moisture content, so drying prior to pyrolysis may be necessary. The expected cost for remediating 20,000 tons of contaminated soil is approximately \$300 per ton.

Hot Gas Decontamination

This technology is based on raising the temperature of contaminated material for a specified period. The off-gassing from the material is then treated in an afterburner system to destroy all volatilized contaminants. The costs of this method are higher than for open burning, and the rate of decontamination is also slower. This technology is used more for decontaminating equipment than for soil remediation activities.

Excavation, Retrieval, and Off-site Disposal

This alternative is not a treatment perse, although some pretreatment may still be required before contaminated materials can be moved to permitted disposal facilities. The primary factors in considering this option are distance to the disposal site and depth and composition of the contaminated media. Depending on the nature of materials, costs for this option typically range from \$270 to \$460 per ton.

Deep Well Injection

This is a liquid waste disposal technology whereby liquid wastes are injected into geologic formations that will not allow migration of contaminants in the waste into potential drinking water supplies. Extensive assessments will be required before regulatory authorities will approve this option.

Landfill Cap

A landfill cap can be used to contain waste while treatment is being applied, especially as it prevents percolation of rainwater through the soil. It can also help to control gas emissions from underlying waste. Because of their ability to stop percolation and thus significantly slow the migration of contaminants to deeper depths, landfill caps are best used when a contaminant has not already entered groundwater. Landfill caps cost roughly \$175,000 to \$225,000 per acre.

Landfill Cover Enhancements

The purpose of these enhancements is to additionally reduce or eliminate the migration of contaminants below the cover. This is most commonly accomplished by harvesting water runoff to prevent infiltration or adding vegetative cover to reduce soil moisture via plant uptake and evapotranspiration.

Monitored Natural Attenuation

Also known as intrinsic remediation, bioattenuation, intrinsic bioremediation, natural recovery, and natural assimilation, this process is not a technology in the sense that the other options in this report are. Rather, it is based on allowing natural mechanisms such as dilution, dispersion, volatilization, adsorption, and chemical reactions with soil materials to reduce contaminant concentrations. The consideration of this process requires significant evaluation of site data and extensive modeling to show that natural processes will indeed reduce the presence of contaminants to acceptable levels. For regulatory purposes, this option is not the same as “no action,” and it has only been selected as an option where contaminants are not migrating and where it has been determined that active remedial processes would not significantly increase the speed of remediation.

Phytoremediation

Also known as vegetation-enhanced bioremediation, this process is based on using plant life to remove, stabilize, or destroy contaminants in soil. Although it is considered to be a very cost-effective process, it also suffers from several limitations. It will not affect contaminants at anything more than shallow depths without excavation, it may be a seasonal process, depending on the plants used, it may transfer contaminants to a different media, and it is still a new technology, lacking large amounts of performance data; from a regulatory standpoint, it is not an accepted technology.

Constructed Wetlands

A constructed wetland uses the chemical and biological processes inherent in a wetland system to accumulate and remove many types of contaminants from influent waters. Remediation is accomplished through biodegradation in the saturated root zone and in surface waters and through filtration through the saturated root zone. However, the long term effectiveness of constructed wetlands is not known, they cannot remediate contaminants at anything more than shallow depths, and they do not allow for easy land reclamation once remedial activities are complete.

Off-gas Treatment

Several of the treatment options detailed above involve the mass-transfer of contaminants from the aqueous phase to the vapor phase. Because of this, off-gas treatment may be required for those technologies. Most off-gas treatment options are similar to wastewater treatment options, except that the generally greater ease in treating contaminants in the vapor phase make them cheaper than their wastewater treatment equivalents.

Biofiltration

In biofiltration, vapor-phase organic contaminants are pumped through a soil bed, where they sorb to the surface of the soil particles and are subsequently degraded by microorganisms. As opposed to activated carbon adsorbers, biofilters keep the maximum adsorption capacity available at all time. Also, the filter does not require regeneration and the required bed length is significantly shorter. Also, whereas activated carbon treatment of off-gases is intended to separate contaminants from the air, biofiltration will destroy the contaminants. The drawback to biofiltration is that its efficiency is dependent on the biodegradability of the contaminants being treated, including reduced efficiency at low temperatures. Typical costs are \$2.25 to \$4.50 per pound of contaminant.

High Energy Destruction

This process uses high-voltage electricity to destroy volatile organic compounds and is effective against almost every volatile or semi-volatile organic compound. Continued research on the efficiency of this process is still being done, and current cost estimates are at about \$10 per pound of contaminants.

Membrane Separation

This technology uses the preferential transport of organic compound vapors through a gas separation membrane by diffusion. The primary limitation of this process is a relative inability to deal with fluctuations in concentrations and a sensitivity to moisture. Costs of this technology are also quite high as compared to other options.

Oxidation

Internal Combustion Engine Oxidation

This technology uses the organic contaminants in off-gases as fuel in an internal combustion engine. When contaminant concentration is low, auxiliary fuel will need to be added to facilitate oxidation.

Thermal Oxidation

In this process, organic contaminants are destroyed at high temperatures (1,800°F and above). This option is generally more costly than alternatives, but provides permanent, efficient destruction of organics within a relatively short time.

Catalytic Oxidation

This process uses the addition of a catalyst to accelerate the rate of oxidation, necessitating much lower temperatures than required by standard thermal oxidation (approximately 450°F). This option has evolved as an alternative for the treatment of organics in the vapor phase only relatively recently, but is still considered a mature, viable technology. Typically, metal oxides are used as the catalyst.

UV Oxidation

UV oxidation of off-gases operates under the same principles as UV oxidation of wastewater. The complete conversion of an organic contaminant to basic products such as carbon dioxide and water is not likely.

Vapor Phase Carbon Adsorption

This alternative involves pumping off-gases through a series of activated carbon filters to which organics will adsorb. It will be necessary to periodically replace saturated carbon and the material removed may need to be treated as a hazardous waste. Other options are more preferable for high-contaminant concentrations, and vapor phase carbon adsorption works best as a polishing step.

Brayton-cycle Heat Pump

This relatively recent technology involves using a Brayton-cycle heat pump to condense volatile organic compounds from an air stream.

Appendix C
Acronyms and Initialisms

Appendix C

Acronyms and Initialisms

AO	Administrative Order
AOC	Areas of Concern
ARARs	applicable or relevant and appropriate requirements
C-4	RDX with plasticizer
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
COC	Contaminants of Concern
DNT	dinitrotoluene
EBCT	empty bed contact time
E_h	reduction/oxidation potential
EPA	U.S. Environmental Protection Agency
FRB	fluidized bed reactor
FS	Feasibility Study
GAC	granular activated carbon
H_2O_2	hydrogen peroxide
HMX	His Majesty's Explosive
ISRM	In Situ Redox Manipulation
$KMnO_4$	potassium permanganate
mg/kg	milligrams per kilogram
mg/l	milligrams per liter
mm	millimeter
MMR	Massachusetts Military Reservation
$\Phi g/l$	micrograms per liter
$NaMnO_4$	sodium permanganate
O_3	ozone
ppm	parts per million
PRB	permeable reactor barrier
RAO	Remedial Action Objective
RDX	Royal Demolition Explosive
TAG	Technical Advisory Group
TNT	trinitrotoluene
UXO	unexploded ordnance
UV	ultraviolet
WERC	A Consortium for Environmental Education and Technology Development
yd^3	cubic yard
ZVI	zero-valent iron