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ENGINEERING AND EXPEDITIONARY WARFARE CENTER

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ATTENUATION PATHWAYS FOR MUNITIONS CONSTITUENTS IN SOILS AND GROUNDWATER

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14. ABSTRACT
The objective of this report is to provide an understanding of natural and enhanced attenuation processes for munitions constituents (MC) in soils and groundwater. Recent research findings related to MC attenuation pathways are summarized, along with lessons learned from monitored natural attenuation (MNA) and bioremediation applications for MC at Department of Defense (DoD) and other sites. The scope of this report includes MC issues; physical, chemical and biological attenuation pathways; technology applications; and case studies.

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ACRONYMS AND ABBREVIATIONS

2,4-DNT	2,4-dinitrotoluene
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CSIA	compound specific isotope analysis
DAT	diaminotoluene
DMM	discarded military munitions
DNG	dinitroglycerin
DNT	dinitrotoluene
DNX	hexahydro-1,3-dinitroso-5-nitro-1,3,5- triazine
DoD	Department of Defense
DON	Department of the Navy
EDTA	ethylenediaminetetraacetic acid
EOD	explosive ordnance disposal
EVO	emulsified vegetable oil
GDN	glycerol dinitrate
GMN	mononitrate
HMX	oxtahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
ITRC	Interstate Technology Regulatory Council
LOE	line of evidence
MBT	molecular biological tool
MC	munitions constituents
MDNA	methylene dinitramine
MNA	monitored natural attenuation
MNG	mononitroglycerin
MNX	hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine
MRP	Munitions Response Program
NAC	natural attenuation capacity
NAVFAC	Naval Facilities Engineering Command
NC	nitrocellulose
NG	nitroglycerin
NQ	nitroguanidine
OD/OB	open detonation/open burn
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
RPM	remedial program manager

T2	Technology Transfer
TAT	triaminotoluene
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TNX	hexahydro1,3,5-trinitroso-1,3,5-triazine
UXO	unexploded ordnance
VOC	volatile organic compound

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1.0 OVERVIEW OF MUNITION CONSTITUENT ISSUES

The objective of this report is to provide an understanding of natural and enhanced attenuation processes for munitions constituents (MC) in soil and groundwater. Recent research findings related to MC attenuation pathways are summarized, along with lessons learned from monitored natural attenuation (MNA) and bioremediation applications for MC at the Department of Defense (DoD) and other sites. The scope of this report includes the following:

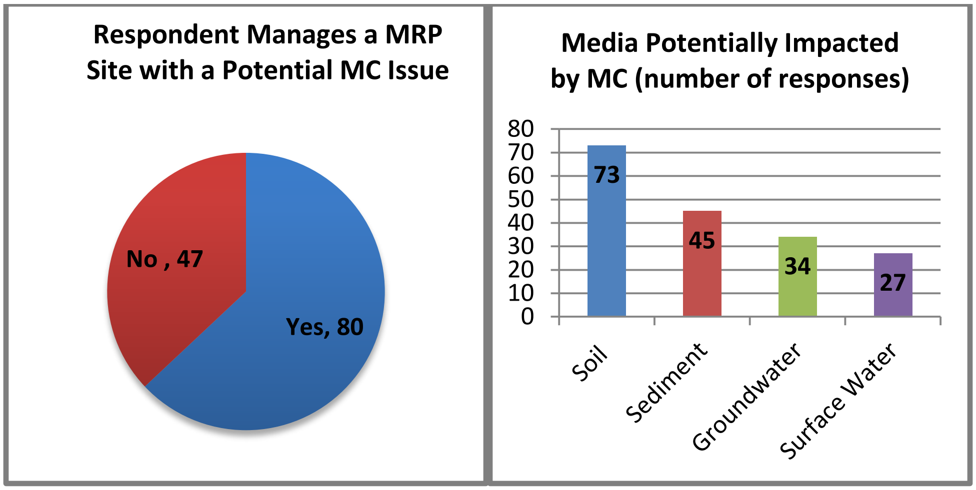
- Section 1: Overview of MC Issues
- Section 2: Physical Attenuation Pathways
- Section 3: Chemical Attenuation Pathways
- Section 4: Biological Attenuation Pathways
- Section 5: Technology Applications
- Section 6: Lessons Learned from Case Studies
- Section 7: Conclusions

1.1 Munitions Constituents Definition

MC are "any materials originating from unexploded ordnance (UXO), discarded military munitions (DMM), or other military munitions, including explosive and non-explosive materials and emission, degradation, or breakdown elements of such ordnance or munitions (10 U.S.C. 2710(e)(3))".

Based on responses to the Naval Facilities Engineering Command (NAVFAC) Technology Transfer (T2) Survey (see Figure 1-1), the majority of survey respondents (63%) indicated that they managed a Munitions Response Program (MRP) site with a potential MC issue. The vast majority (91%) indicated that soil is a potentially impacted media, but sediment (56%), groundwater (43%) and surface water (34%) are also potentially impacted media. In addition, the state-of-technology for MNA and bioremediation of MC was of interest based on the T2 survey results and because of their lower environmental footprints in line with the goals of the Navy's Optimization Policy [1] and Green and Sustainable Remediation Guidance [2].

MNA is a remedy that utilizes the capacity of the natural environment to mitigate contamination. Pathways for MNA include degradation (biotic and abiotic), abiotic transformation, sorption and advection. The acceptance of MNA as a groundwater remedy has been firmly established for petroleum hydrocarbons [3] and chlorinated solvent groundwater plumes [4]. While MNA has been applied at nitroaromatic explosive sites [5] and perchlorate sites [6], this report was undertaken to compile a summary of the state-of-technology of MNA for all MC categories. The report also serves as a technical resource for NAVFAC Remedial Project Managers (RPMs) in understanding natural attenuation pathways for MC in soil and groundwater.


Respondent Manages a MRP Site with a Potential MC Issue

Media Potentially Impacted by MC (number of responses)

Figure 1-1. T2 Survey Responses Concerning Frequency and Media Impacted by MC

1.2 MC Categories

MC can be divided into three main categories:

- Explosives,
- Propellants and
- Metals.

Both explosives and propellants are often referred to as energetic compounds given their role in military ordnance. For high explosives, the main sources of MC include the projectile body, cartridge case, filler and propellant, whereas minor sources of MC could originate from the fuze, primer and/or booster [7]. MC are also included in a variety of secondary explosives (such as boosters), chemical agents, riot control agents and pyrotechnics (e.g., incendiaries).

Explosives: Explosive formulations commonly used by DoD include Composition B, Composition C4 and 2,4,6-trinitrotoluene (TNT). The chemical constituents of these formulations rely on the combinations of the following chemicals: TNT, 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) and oxtahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Table 1-1 provides the compounds, uses and formulations for typical explosives, while Figure 1-2 presents structural and toxicity information for each explosive constituent.

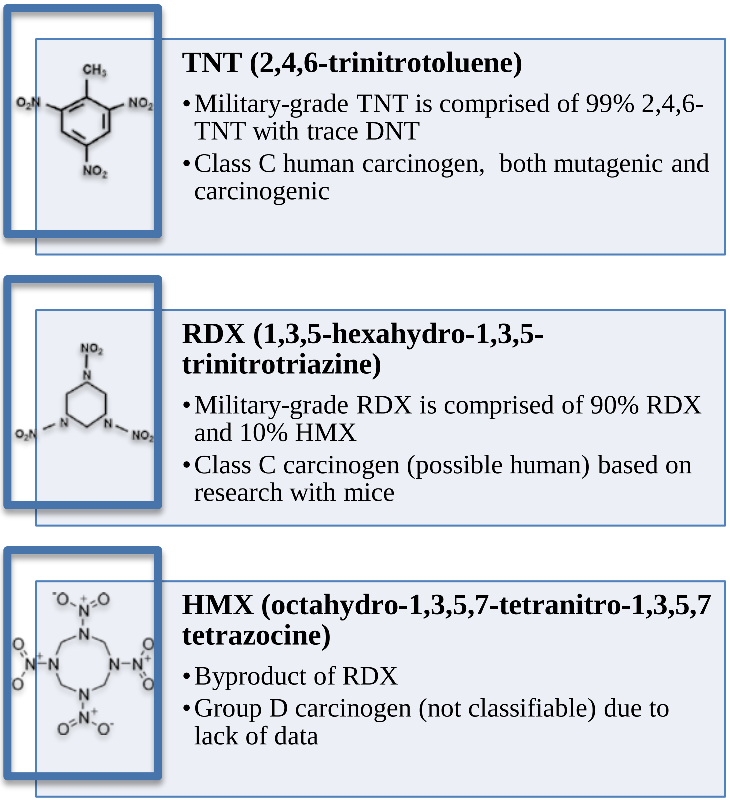
In general, TNT is well characterized because of its prolific use in military and industrial explosives. A TNT byproduct, 2,4-dinitrotoluene (DNT), has been used in explosives as a component of Composition C series [8-11]. RDX typically serves as the base in explosive formulations such as Composition A, Composition B and Composition C, whereas HMX is used in plastic explosives and rocket fuels due to its rapid violent explosive properties at high temperatures. Additionally, HMX is formed as a byproduct when manufacturing RDX. Thus, HMX is a co-contaminant with RDX. In terms of toxicity, the three explosive compounds can be ranked as follows:

TNT > RDX > HMX

with TNT having the largest impact to human health and the environment.

Table 1-1. Typical Explosive Compounds, Uses and Formulations for Military Munitions Constituents

Compound	Uses	Formulations
Composition B	Artillery, mortar	60% military-grade RDX, 39% military grade TNT and 1% wax
Composition C4	Demolition explosive	91% military-grade RDX
Composition A4	40-mm grenades	Military-grade RDX
TNT	Artillery	Military-grade TNT
Composition H6	Bombs	Military-grade RDX, TNT; aluminum



TNT (2,4,6-trinitrotoluene)

- Military-grade TNT is comprised of 99% 2,4,6-TNT with trace DNT
- Class C human carcinogen, both mutagenic and carcinogenic

RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine)

- Military-grade RDX is comprised of 90% RDX and 10% HMX
- Class C carcinogen (possible human) based on research with mice

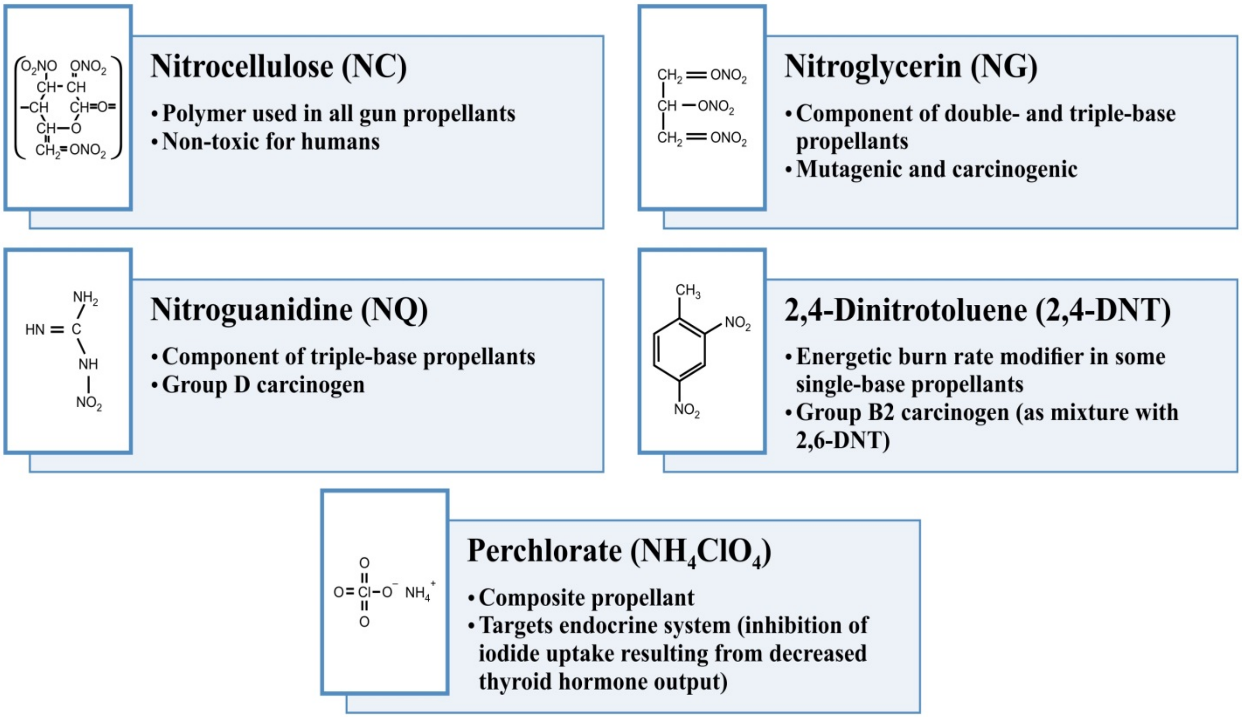
HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine)

- Byproduct of RDX
- Group D carcinogen (not classifiable) due to lack of data

Figure 1-2. Key Explosive Constituents

Propellants: In addition to explosives, military gun propellants can generate MC residues. Propellants are designed to burn at a controlled rate and rapidly produce gases, thus providing energy to deliver a munition to its target. The main difference between explosives and propellants is their reaction rate. While explosives react rapidly, resulting in breaking apart munition's casings, propellants react slowly, providing sustained energy to propel a munition.

Propellants, such as nitrocellulose, nitroglycerin, nitroguanidine, 2,4-dinitrotoluene and perchlorate, are found in cartridge cases (small arms, medium caliber munitions, some artillery), projectile externals (mortars, some artillery), rocket motors and explosive charges. Additionally, DoD munitions, munition components and training devices often contain perchlorate. Such devices can include [12]: signal flares, mines, solid fuel rockets, smoke-generating compounds, parachute flares, torpedo warheads, fuzes, and training simulators. Typical propellants are listed in Figure 1-3 along with their structures, uses and toxicity information. Depending on the size of the munition, the propellant formulation will vary from single-base through triple-base or as a composite.



Nitrocellulose (NC)

- Polymer used in all gun propellants
- Non-toxic for humans

Nitroglycerin (NG)

- Component of double- and triple-base propellants
- Mutagenic and carcinogenic

Nitroguanidine (NQ)

- Component of triple-base propellants
- Group D carcinogen

2,4-Dinitrotoluene (2,4-DNT)

- Energetic burn rate modifier in some single-base propellants
- Group B2 carcinogen (as mixture with 2,6-DNT)

Perchlorate (NH_4ClO_4)

- Composite propellant
- Targets endocrine system (inhibition of iodide uptake resulting from decreased thyroid hormone output)

Figure 1-3. Key Propellant Constituents

Metals: In addition to energetic chemicals, metals are found in nearly all military munitions [8]. Uses of metals in munitions include casings, bullets, projectile cases, projectiles, bomb bodies and fillers. Table 1-2 presents the most commonly occurring metals, along with their roles in munitions and toxicity. Although metals such as lead, antimony, copper and zinc can be found in trace amounts, lead is often the primary metal contaminant of concern at MRP sites. As aluminum, iron and magnesium are not defined as Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) hazardous elemental metals, further discussion will be limited to lead, antimony, copper and zinc with an emphasis on lead.

Table 1-2. Commonly Occurring Metals in MC [7]

Metal Contaminant	Use	Toxicity
Aluminum (Al)	Incendiaries, composition explosives, propellants, pyrotechnics and alloys in rocket cases	Not a CERCLA hazardous elemental metal
Antimony (Sb)	Lead-based alloys in small arms bullets and pyrotechnics	Toxic metal that targets cardiovascular and respiratory systems
Copper (Cu)	Brass cartridge cases, bullet jackets, pyrotechnics and bronze gun barrels	Toxic metal that targets gastrointestinal, hematological and hepatic systems
Iron (Fe)	Steel projectiles, incendiaries, and pyrotechnics	Not a CERCLA hazardous elemental metal
Lead (Pb)	Small arms bullets, primary explosives, primer compositions	Group B2 carcinogen, toxic metal that targets cardiovascular, developmental, gastrointestinal, hematological, musculoskeletal, neurological, ocular, renal and reproductive systems
Magnesium (Mg)	Incendiaries, pyrotechnics (photoflash), tracers and armor piercing bullets	Not a CERCLA hazardous elemental metal
Zinc (Zn)	Cartridge cases (brass) bullet jackets (e.g., gilding metal), hexachloroethane smoke-filled munitions and pyrotechnics	Toxic metal that targets gastrointestinal, hematological and respiratory systems

1.3 MC Fate and Transport

While most munitions undergo high order detonation and deposit little energetic residue, some munitions undergo low order detonation or fail to detonate before impact. In these circumstances, the munition may contain significant quantities of unexploded fill in addition to residual propellant and casing materials. Thus, MC source material or free product is present in the environment and can serve as a point source for contamination of soils or groundwater. For example, MC may be present on the ground surface at firing ranges. Table 1-3 highlights the typical terrestrial areas where MC contamination can be found at Department of the Navy (DON) installations. In the case of underwater UXO, contaminants can be present in a variety of media: water body (fresh water and saline environments) and sediments.

At most ranges, the type of MC depends on where the weapons are fired and where detonations have occurred. Generally, MC at impact areas are comprised of high explosives from the munition warheads while energetic residues found at firing points originate from propellants.

Table 1-3. Typical Terrestrial Areas of MC for the Navy

Areas of MC Contamination	Predominant Characteristics of Contaminated Areas
Impact Areas	• Not only do impact areas differ by ordnance, but their MC residues also differ on whether a high or low order detonation was achieved. • Although RDX predominates in the residue from detonations of items containing Composition B and C4, typical contaminants are TNT, RDX and HMX (in this order). • Metals are the primary contaminant detected in soils near berms at small arms ranges, but they are also detected as contaminants in soil at artillery and mortar range targets, anti-tank rocket ranges, open detonation/open burn (OD/OB) areas and explosive ordinance disposal (EOD) demolition areas [11]. • Perchlorate may be present at artillery and mortar range targets and in soil and groundwater at OB/OD and EOD demolition areas. In contrast to metal contaminants, perchlorate is highly mobile in the aqueous phase and therefore has more potential to leach into groundwater [11, 13].
Firing Point Areas	• MC residue from propellants is deposited close to the firing position and can be estimated if the total number of rounds of a given type of ordnance is known. • Most often, propellant residue includes nitroglycerin (NG) or 2,4-DNT associated with particles of nitrocellulose (NC). Note: NC in soil does not pose health risks. Thus, the predominant contaminants are NG and 2,4-DNT. • Metals have been found in surface soils near artillery and mortar firing positions and contamination appears highly localized [11].

As highlighted in Table 1-3, source zones for MC are the surface soils at either the impact areas or firing point areas at ranges. Movement from solid MC residuals into the environment begins with processes such as erosion and dissolution facilitating contaminant transport from surface soil to groundwater and/or surface water. For example, transfer from solid MC residuals to aqueous-phase contaminants often is a result of rainfall. In addition, composition of military explosives influences the relative dissolution rate of the various constituents. However, the primary variable controlling the release of contaminants into the water-soluble phase is the point source size of MC residuals. Once in the aqueous-phase, the MC differ in ease of transport based on a variety of mechanisms such as sorption, advection, diffusion and transformation.

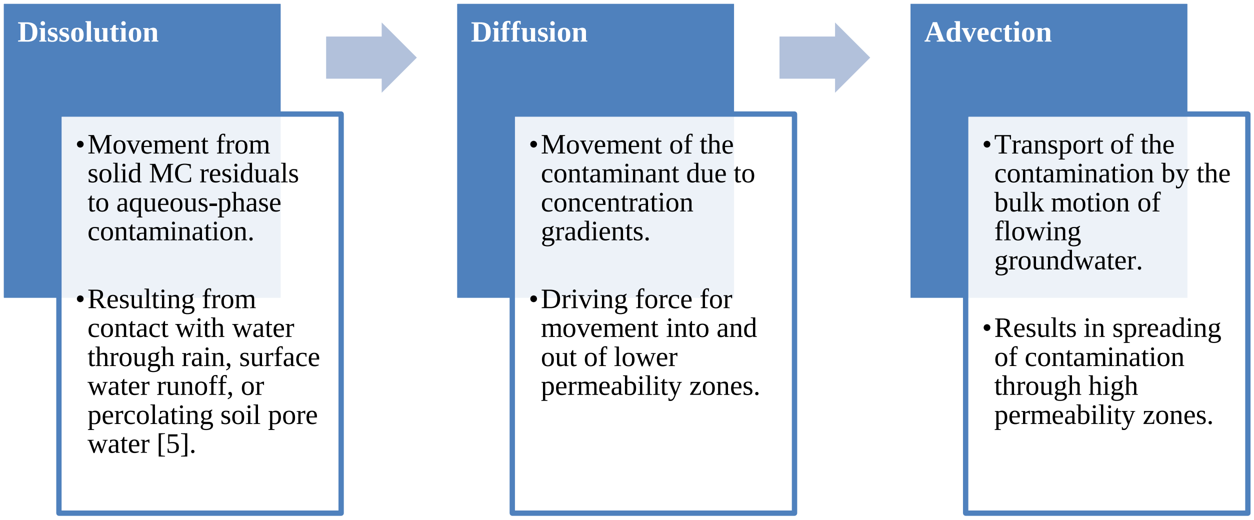
Following the initial release of MC into the environment, the fate of MC in groundwater is dependent on the contaminant, subsurface geochemistry and microbial community. For example, the lithology of the site affects contaminant fate in the subsurface due to the contaminant's affinity for sorption with organic matter. Additionally, biological degradation pathways impact the fate of MC with the redox environment of the soil or groundwater contributing to the rate of biotransformation. As shown in Table 1-4, these attenuation processes are summarized into three main categories: physical, chemical and biological pathways. Each pathway is reviewed in subsequent sections of this report.

Table 1-4. Summary of Attenuation Pathways Applicable to MC in Soil and Groundwater

Pathway	Mechanism	Description
Physical	Advection	Movement of contaminant within groundwater
	Diffusion	Mass transfer of contaminant into or out of matrix due to concentration gradient
	Phase Transfer	Dissolution and/or volatilization
Chemical	Sorption	Reversible interactions between aquifer matrix and contaminant
	Abiotic Transformation	Reactions between mineral and contaminant
	Photolysis	Transformation of contaminant due to sunlight exposure in surface soils only
Biological	Microbial Processes	Biotically-mediated reactions
	Biogeochemical Transformation	Coupled biotic and abiotic reactions

2.0 PHYSICAL ATTENUATION OF MUNITIONS CONSTITUENTS

Knowledge of the physical transformation properties of MC is fundamental to an understanding of the fate and transport of MC at a site. Figure 2-1 summarizes the primary physical attenuation processes in order of their impact on fate and transport. While volatilization is listed under phase transfer in Table 1-4 as a potential attenuation pathway, energetic compounds are classified as semi-volatile organics and other common MC are classified as non-volatile inorganics. Therefore, volatilization[1] is not a significant attenuation pathway for MC.



Dissolution

- Movement from solid MC residuals to aqueous-phase contamination.
- Resulting from contact with water through rain, surface water runoff, or percolating soil pore water [5].

Diffusion

- Movement of the contaminant due to concentration gradients.
- Driving force for movement into and out of lower permeability zones.

Advection

- Transport of the contamination by the bulk motion of flowing groundwater.
- Results in spreading of contamination through high permeability zones.

Figure 2-1. Summary of the Physical Attenuation Process for MC

An understanding of the physical attenuation pathways is important in accurately predicting the environmental fate of MC. Dissolution is the first step in introducing organic energetics and other MC into the environment. The controlling mechanisms for dissolution include factors such as quantity of free product at the point source (low order and high order detonation), solubility[2] (of the individual constituents separately and as part of a compound), soil type at the site, affinity for sorption of the MC and mass transfer coefficients. Once the MC moves into the aqueous phase, a variety of factors influence contaminant fate and transport. Although physical attenuation mechanisms (e.g., diffusion and advection) do not contribute to contaminant degradation, physical attenuation mechanisms, such as matrix diffusion, can contribute to the longevity of aqueous-phase contamination. Overall, mobility-limiting rates are dependent on dissolution and solubility. These mass transfer processes impose limits on the mass loading of MC into the environment due to rainfall events. These properties can be used to estimate the total

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[1] These characteristics are evenly exploited during collecting, preparing and sub-sampling potentially contaminated soils. Soil samples for analysis of these constituents can be processed without substantial loss due to volatilization.

[2] Solubility of a MC is defined by its saturation point concentration, the concentration above which precipitation is thermodynamically favored. The rate of solubilization in turn describes the kinetics of dissolution, which is dependent on factors such as the surface area of the solid and concentration gradient of the solution.

mass surface loading and to aid in modeling contaminant transport in the vadose (unsaturated) zone or in groundwater.

2.1 Physical Attenuation of Energetics

Once released, through detonation, shell cleavage or corrosion, the first step for energetics to enter into the environment is through dissolution as noted above. This is the most substantial mechanism behind the mobility of explosives: dissolution and the associated downward movement of contaminants through soils or via overland flow. Results for neat explosives, found in Table 2-1, indicate the following trend for dissolution rates: TNT > HMX > RDX. Additional information on physical attention mechanisms specific to explosives is provided below:

- **TNT:** TNT may remain as free product, dissolve into aqueous media, sorb onto particulates, or partition into dissolved organic matter. Nitro groups (NO_2^-) located on the TNT ring's structure are polarizing and form hydrogen bonds with water. This characteristic increases the aqueous solubility of TNT and its affinity for charged surfaces. In addition, research has shown that TNT transport is enhanced when colloids (e.g., fine fractions) are present in the system due to TNT's affinity for surfaces with high cation exchange capacities such as clays [14].

- **RDX:** RDX has a substantially lower polarity and therefore a much lower aqueous solubility and dissolution rate than TNT. Once dissolved, however, RDX can migrate through the vadose zone and contaminate underlying groundwater aquifers, especially on training ranges that have permeable soils, a shallow groundwater table and abundant rainfall.

- **HMX:** Because HMX has a low aqueous solubility and slow dissolution rate, HMX tends to remain on the soil surface. Due to the lower sorption ability, HMX does not, however, strongly interact with soils after dissolution and can be carried through the vadose zone to underlying groundwater aquifers.

Table 2-1. Aqueous Solubility and Dissolution Rates for Energetics [11]

Compound	Aqueous Solubility (mg/L; [8])	Dissolution Rate (mg cm^{-2} s^{-1}; [15])
TNT	88.5 at 20 °C	0.00063 at 30°C
RDX	59.9 at 25 °C	0.00032 at 30°C
HMX	5 at 25 °C	0.000097 at 30°C

With the exception of NG, the major energetic compounds used by the DoD as propellants are solids at ambient temperature and are deposited on ranges as particles of solid material (Table 2-2). Therefore, as with explosives, dissolution is a major factor in determining the mobility of propellants. While some propellants, such as NC, are insoluble and present no hazard to human health in soils, others, such as nitroguanidine (NQ) and perchlorate, are highly soluble. Source type is a significant factor in the overall mobility of propellants. For example, NC is an ingredient in single-, double- and triple-base propellants. As such, polymeric NC matrices bind other energetic compounds such as DNT, NG, NQ and HMX and limit their dissolution and mobility when compared to each energetic as a free product.

Table 2-2. Aqueous Solubility for Propellants [16]

Compound	Aqueous Solubility (mg/L)
NC	Insoluble
2,4-DNT	270 at 25 °C
2,6-DNT	206 at 25 °C
NG	1800 at 25 °C
NQ	4,400 at 25 °C
Perchlorate	10,000 to 2,000,000 at 20 °C

The dissolution of explosives and propellants has historically been studied at the laboratory scale with soil column tests [17], batch studies [18] and neat or reagent-grade compounds [19]. However, there is some conflict as to how well laboratory-scale studies can accurately reflect field conditions. As Table 2-3 shows, dissolution of energetic MC has many contributing variables and cannot be characterized by one parameter. For example, research found that utilizing reagent-grade compounds might not appropriately reflect the dissolution properties observed in the field. Clausen [19] conducted experiments with NG-containing soil originating from unfired or fired propellants. The results of these experiments produced soil partitioning values of propellants higher than those of reagent grade material. In addition, research found that using distribution coefficients from batch studies for pure explosives in solution could underestimate transport of mixtures [20]. Researchers continue to evaluate whether laboratory-scale studies can effectively predict the dissolution properties of military-grade MC mixtures in the field. Models and codes to link variables concurrently have been developed to predict the fate and transport of MC [17, 21, 22].

Table 2-3. Factors that Impact the Dissolution of MC

Factor	Impact on Dissolution	Reference
pH	Dissolution rate not affected by pH in range of 4.2 to 6.2	[15]
	Elevated pH (>11) can cause rapid dissolution	[23]
Temperature	Dissolution rates increase with temperature (3.1 to 33.3°C)	[15]
Soil Type	Dissolution is impacted by the sorption of MC to certain soil types	[24]
	Dissolution is greater in soils with low total organic carbon, surface area and percent fines, as MC exhibit less sorption	[24]

Table 2-3. Factors that Impact the Dissolution of MC (continued)

Sorption	Surface attachment of MC particles may cause long-term sources of spreading contamination because of the unexposed surface area of the particle to water	[25]
Solubility of individual constituent	Solubility of individual constituent is impacted by reversible sorption, irreversible attenuation and degradation	[20]
Solubility of multi-component compounds	For multi-component MC, the solubility of the individual components controls the dissolution	[26]
	Solubility of a compound can be limited by diffusion of an individual constituent from the interior of the compound	[21]
	The dissolution rate is often determined by the compound with the slowest dissolution rate	[22, 27]
Low order or high order denotation	Low order (incomplete) detonation can leave large quantities of explosive residue on the site, whereas high order (complete) detonations have smaller point source contamination	[10]
Fractures in compound	Explosive residue resulting from field detonations are fractured and produce conduits by which water could access the interior of the residue, resulting in faster dissolution	[26]
Water flow rate	Dissolution can be enhanced under conditions with higher flow rates	[17]

2.2 Physical Attenuation of Metals

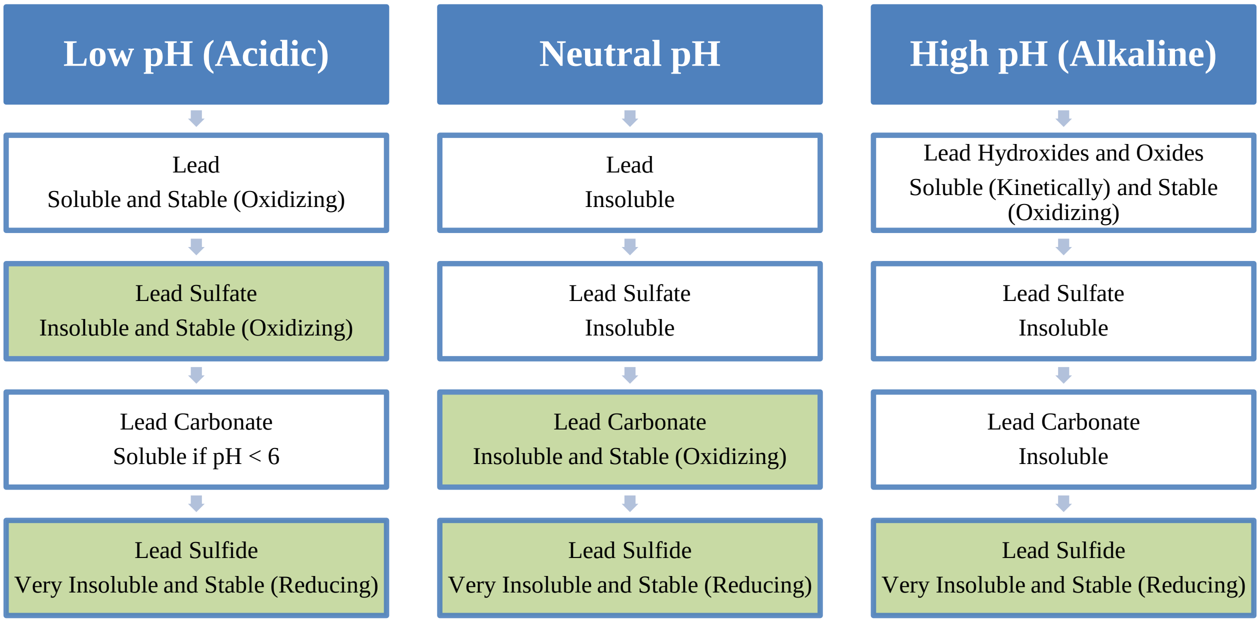
Metals released to soils from MC are generally not bioavailable (they are typically in bulk forms such as bullets or casings); however, weathering and dissolution over time may lead to mobility of contamination to surface water, pore water and groundwater. While attenuation processes can potentially destroy other contaminants, attenuation of metals relies on immobilization processes that limit their bioavailability. These processes are generally reversible and dependent on the geochemistry of the affected media. Most notably the pH and oxidation-reduction (redox) potential of the aqueous system (quantified by Eh) can dictate the valence state of the metal contaminants [13]. Mobility is also dependent on properties of the contaminated soil, including soil moisture, degree of weathering and type of organic matter present [28]. In addition, physical attenuation routes for metals include precipitation, co-precipitation and complexation (Figure 2-2) [29]. For each metal, certain species dominate under specific geochemical states. Therefore, understanding the geochemistry of the impacted media and the associated mobility of the dominant species is key to assessing physical attenuation mechanisms for metals.

Precipitation	Co-precipitation	Complexation
Removes metals from solution. System pH strongly influences solubility of precipitates (carbonate, oxide, hydroxide and sulfide) with higher pH generally promoting precipitation.	Occurs when a metal contaminant is bound within a solid formed by major ions, affecting mobility similarly to precipitation.	Complexation of metals with inorganic and organic ligands affects solubility and sorption processes compared to dissolved ions. Metals are more likely to exist in complexes in aqueous environments.
Carbonate, hydroxide and sulfide are the most common naturally occurring anions that precipitate with metal contaminants. Metal sulfides are especially insoluble and are an effective immobilization mechanism.	Iron minerals co-precipitate with a number of metals, including lead (to galena), zinc and aluminum (to goethite) and arsenic (to iron oxide).	Metals can complex with organic ligands including humic and fulvic acids, low molecular weight acids, proteins and man-made chemicals (such as ethylenediaminetetraacetic acid). These complexes retard precipitation and can increase metal mobility.

Figure 2-2. Physical Attenuation Pathways for Metals

- **Lead:** Lead, with a rather complex natural attenuation pathway, is of primary focus among metal MCs. While lead is increasingly mobile in low pH ranges and oxidizing conditions, its aqueous solubility at near neutral to alkaline pH is slow. As highlighted in Figure 2-3, lead forms stable aqueous complexes with hydroxyl species, carbonate, sulfate and sulfide. Lead complexes are most stable with chloride and sulfate at near neutral to low pH. At neutral to moderately alkaline conditions, lead complexes with carbonate are stable and predominate. Once high pH is reached, hydroxyl species dominate stable lead complexes. In sulfate-reducing conditions, lead sulfide will precipitate to form an insoluble complex.

  Dissolved organic carbon may also form stable complexes with lead, but little research has been conducted on this subject. Lead can also be highly mobilized by organic ligands such as ethylenediaminetetraacetic acid (EDTA). Determining the presence of these complexing ligands and the geochemical state of the media can indicate whether lead is anticipated to be in a highly mobile state or unavailable in a solid phase.



Low pH (Acidic)	Neutral pH	High pH (Alkaline)
Lead Soluble and Stable (Oxidizing)	Lead Insoluble	Lead Hydroxides and Oxides Soluble (Kinetically) and Stable (Oxidizing)
Lead Sulfate Insoluble and Stable (Oxidizing)	Lead Sulfate Insoluble	Lead Sulfate Insoluble
Lead Carbonate Soluble if pH < 6	Lead Carbonate Insoluble and Stable (Oxidizing)	Lead Carbonate Insoluble
Lead Sulfide Very Insoluble and Stable (Reducing)	Lead Sulfide Very Insoluble and Stable (Reducing)	Lead Sulfide Very Insoluble and Stable (Reducing)

Figure 2-3. Summary of Lead Complexation under Low, Neutral and High pH Conditions

A brief description of natural physical attenuation pathways for other common MC metals is included below.

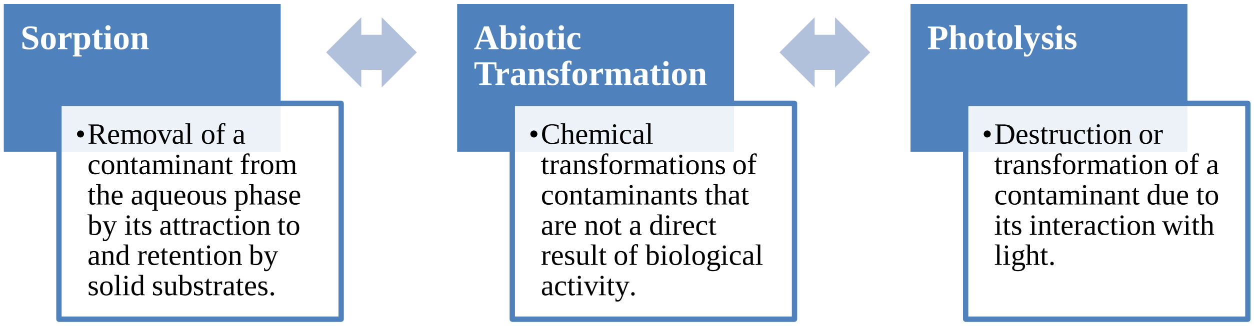
- **Antimony:** Sb(V) is assumed to be favored in water, while Sb(III) is only stable in anaerobic or moderately reducing conditions. Soluble forms are assumed to be very mobile with basic, oxidizing conditions favoring increased mobility (in contrast with other metals). Insoluble forms tend to sorb to clay, soil and sediments where they are bound to extractable iron and aluminum [30].

- **Copper:** Cu(II) is the most common soluble oxidation state of copper, which is more mobile at highly oxidizing acidic systems. Copper is bound to ammonia at mildly acidic to basic conditions and can be strongly complexed by dissolved organic material, which increases mobility. In moderately oxidizing neutral systems, the mineral malachite is stable. In neutral to alkaline systems, copper oxides are stable with low bioavailability. In highly reducing and sulfidic environments, copper sulfides are stable and highly insoluble [31].

- **Zinc**: Zn(II) is the most common state of zinc, which forms complexes with a number of anions, amino acids and organic acids. Zinc is one of the most mobile heavy metals because a number of its compounds are soluble in acidic and neutral pH waters. Zinc precipitates readily with hydroxide, carbonate and sulfide, which are favored at basic, reducing conditions and co-precipitates with hydrous oxides of iron or manganese [28].

3.0 CHEMICAL ATTENUATION OF MUNITIONS CONSTITUENTS

Chemical attenuation pathways are defined by the chemical transformation or immobility of MC, as highlighted in Figure 3-1. These attenuation processes include sorption, abiotic transformations and photolysis. As with physical attenuation pathways, chemical attenuation pathways are dependent on multiple parameters and can serve as measures of the effectiveness of natural immobility and destruction of MC.



Sorption

- Removal of a contaminant from the aqueous phase by its attraction to and retention by solid substrates.

Abiotic Transformation

- Chemical transformations of contaminants that are not a direct result of biological activity.

Photolysis

- Destruction or transformation of a contaminant due to its interaction with light.

Figure 3-1. Summary of Chemical Attenuation Processes for MC

Sorption can be described as either adsorption (sorption only to the surface of the solid substrate) or absorption (sorption within the substrate). The sorbent (the solid substrate onto which the contaminant is sorbed) has an equilibrium capacity that is affected by a number of system parameters (such as pH). Sorption is a reversible process and desorption results in dissolution; this partitioning is continuous, with constant movement to and from sorption sites. The process of sorption is typically described using partition coefficients. Next to precipitation, sorption is the most significant factor on dissolution and therefore the mobility of MC.

When reactive minerals are present, energetics can be chemically transformed, resulting in less hazardous substances. Typically, abiotic degradation involves reduction of the contaminant by the reactive mineral. In addition, biogeochemical transformation (abiotic degradation coupled with biotic attenuation pathways) may also provide a complete degradation pathway for MC. MC can also react with other aqueous constituents to form benign products, including arylamines, arylhydroxylamines and condensed azoxy and azo compounds. This pathway can lead to the complete destruction of some MC and is typically facilitated by dissolution, which increases the availability of reactants.

Photolysis refers to the destruction or transformation of a contaminant due to its interaction with light. Photons impart energy to chemical bonds upon striking a target molecule; specific wavelengths of light can provide the energy required to induce a chemical reaction resulting in photodecomposition. Photolysis can be a significant attenuation pathway for explosives and propellants. For solid explosives, photodecomposition reactions occur only on the surface, the products of which can be washed off – often producing a halo of reddish brown residue on the soil surface surrounding the bulk particles. This pathway, like abiotic pathways, can lead to reduction of contaminant mass by degradation. Photolysis does not occur when the MC is under soil surfaces and in groundwater due to the absence of light.

3.1 Chemical Attenuation of Energetics

Sorption. Sorption pathways for energetics are dominated by adsorption processes. Preferences for sorption range from practically non-existent (e.g., perchlorate) to very strong (e.g., TNT) depending on the sorbent type and geochemistry. This preference is defined by the partition coefficient K_d, which describes the equilibrium between sorbed and free contaminants. Where soil K_d values might not be empirically determined for all sorbents, other partition coefficients exist that comparatively describe soil transport properties, including octanol-water coefficients (K_{ow}) and organic carbon normalized partition coefficients (K_{oc}). These coefficients for energetics are summarized in Table 3-1. A description of the sorptive properties of energetics is included below.

- **TNT:** Adsorption of nitroaromatics to clays, specifically phyllosilicates, dominates sorptive processes in soil and groundwater. As such, studies have shown that the mobility of TNT is limited [18]. In addition, measurements of soil-phase TNT levels have shown that steady-state conditions between solid and aqueous phase contamination is not always reached because TNT biotransforms, especially under anaerobic conditions [32]. Therefore, understanding the relative contribution of the sorption pathway and biological pathways is not always easy in the field [24].

- **RDX:** Although RDX is less soluble than TNT, RDX has a lower sorption potential. This leads to increased RDX contamination of and migration in groundwater. This behavior was observed by Pennington et al. [9, 10] as they reported RDX-contaminated groundwater at DoD sites and confirmed the potential for RDX transport in groundwater. Therefore, the low sorption potential, especially for organic matter, suggests that sorption is not a significant attenuation process for RDX in aquifer systems [33].

- **HMX:** In general, HMX has the potential to sorb more than RDX, but less than TNT [34] and can be found attached to dust and other air particles. HMX has the longest half-life in the environment. At training ranges with shallow groundwater and permeable soils, groundwater may be contaminated with both HMX and RDX.

- **Organic Propellants:** After dissolving or leaching from the polymeric NC matrix, sorption of DNTs and NG to soil further limits their mobility [11]. For both 2,4- and 2,6-DNT and NG, the potential for sorption to aquifer soils is similar to TNT, with values for adsorption to pure clays higher for 2,4-DNT than for 2,6-DNT [8]. Conversely, NQ does not sorb strongly to soil surface and is mobile. As such, it is expected that NQ may travel through the vadose zone and can contaminate groundwater.

- **Perchlorate:** Sorption of perchlorate to soil materials is typically assumed to be negligible. Partitioning coefficients describing sorption of perchlorate to geologic materials are usually found to equal zero [6], however there is some evidence of soil organic-perchlorate complexes.

Table 3-1. Partition Coefficients for Energetics ([16] unless noted otherwise)

Compound	Log K_{ow}	Log K_{oc}	K_d
TNT	1.6	37.4	0.04 – 413
RDX	0.090	6.26	0.06 – 8.4
HMX	0.17	1.15	0.12 – 17
2,4-DNT	1.98 – 2.01 [35]	88.48 [35]	2.34 – 15.3 [35]
2,6-DNT	2.02 – 2.28 [35]	116.0	0.27 – 2.49 [35]
NG	1.62 [36], 1.62 – 2.81 [35]	39.20	≈0 [37], 0.26 – 1.41 [35]
NQ	-0.89 – 0.156 [35]	0.13	0.14 – 0.61 [35]
Perchlorate	-	-	Negligible

Abiotic Degradation. Abiotic degradation of energetics is a promising attenuation pathway that can lead to the complete destruction of a contaminant. Abiotic degradation of energetics occurs in the presence of ferrous iron, which is obtained through intrinsic or engineered processes that reduce the iron naturally abundant in the aquifer solids. Abiotic degradation rates are typically faster than biodegradation rates and are generally uniform over mildly acidic to alkaline (from 6 to 10) pH ranges [38].

- **TNT:** Complete mineralization of TNT can occur by abiotic transformation. The first two steps include producing 2-hydroxylamino-4,6-dinitrotoluene (4-HA-2,6-DNT) then generating 4-ADNT (4-amino-2,6-dinitrotoluene) as shown in Figure 3-2. The second step in the abiotic process, 4-ADNT, is also a typical biotransformation product (see Section 4.1 for discussion on biotransformation). Therefore, presence of 4-ADNT does not indicate a specific transformation mechanism (e.g., abiotic or biotic transformation). TNT can be completely mineralized under abiotic conditions, whereas biotic transformations cannot completely mineralize TNT [6, 26, 32].

- **RDX:** Unlike TNT, RDX is not completely degraded via abiotic transformation processes. Rather, a combination of abiotic and biological degradation is required for complete mineralization of RDX. Abiotic transformation of RDX to methylene dinitramine (MDNA) is known to have a short half-life on the order of minutes to hours [38]. Then, MDNA undergoes an acid hydrolysis reaction to formate. This reaction is slower in highly reduced groundwater because reduced sediment tends to be more alkaline (pH 8.5 to 9.2), but the rate of transformation increases with higher water to soil ratios. Formate mineralization to CO_2 is the biological rate-limiting step in the complete mineralization of RDX.

- **HMX:** Abiotic transformation of HMX is similar to the abiotic transformation of RDX. In highly reduced environments, HMX can be degraded abiotically when in the presence of a reductant. The abiotic transformation mechanism of HMX occurs via sequential reduction of the four nitro groups forming mono-, di-, tri- and finally tetra-nitroso-HMX before ring cleavage.

- **Organic Propellants:** For organic propellants, NG (and others) can be abiotically reduced by iron [36]. For NG, abiotic reduction includes production of 1,2- and 1,3-dinitroglycerins (DNGs) and 1- and 2-mononitroglycerins (MNGs); nitrite is produced at each step. The nitrite is further reduced to dinitrogen gas. NG can be also reduced to nitroguanidine and aminoguanidine by catalytic hydrogenation and by zero valent iron under anaerobic conditions.

- **Perchlorate:** No clear evidence exists to support occurrence of perchlorate abiotic attenuation, however few studies indicate that anaerobic conditions may favor perchlorate degradation [6]. Decreased concentrations of perchlorate loss occurred in treatments with microscale zero-valent iron after a few hours, but the decline was associated with biodegradation rather than abiotic reactions.

In addition to the natural abiotic processes described above, a research project under the Navy Environmental Sustainability Development to Integration (NESDI) program (Project Number 445) validated the use of hydrated lime to treat and remove residual RDX remaining in surface soils at air-to-ground ranges. This could be a best management practice to mitigate RDX transport to groundwater.

Photolysis. Energetic residue containing TNT, RDX and HMX on the surface of soil can undergo photolysis or chemical decomposition by natural light. While these reactions are limited to direct interaction with natural light, this degradation process produces byproducts that can then be transported into groundwater. For example, TNT is also particularly subject to photodegradation, leading to a complex array of degradation products. A primary product known as 1,3,5-trinitrobenzene (TNB) [8] is also a manufactured explosive. Once released, TNB is further subject to photolysis and transformation; TNB undergoes sediment transformation and reductive transformation to dinitroaniles or amino-dinitrobenzenes.

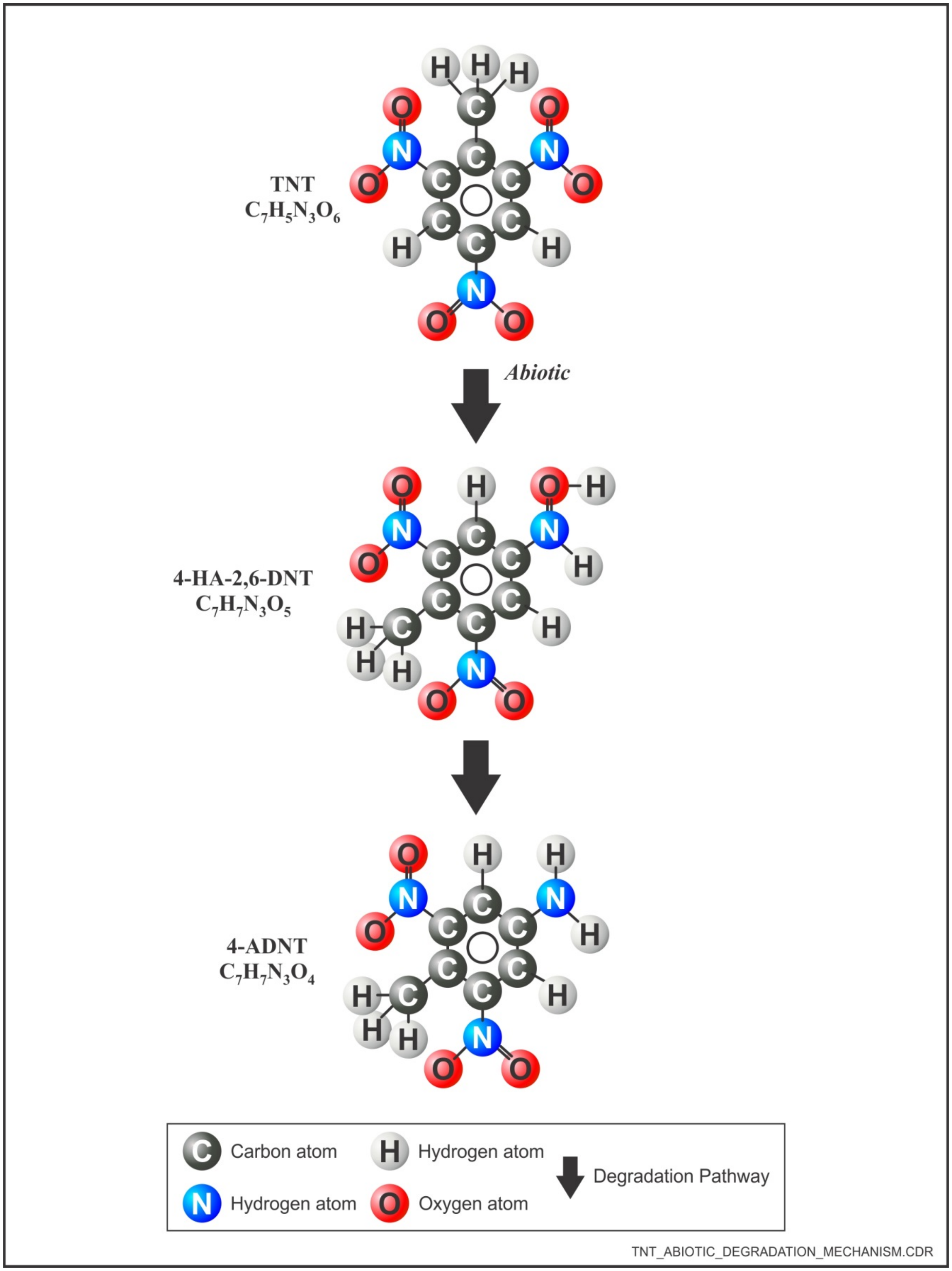


Figure 3-2. First Two Steps of the Abiotic Transformation of TNT

3.2 Chemical Attenuation of Metals

Abiotic pathways are typically negligible for metals; however, sorption is a significant attenuation pathway. Sorption of metals takes place when either a metal or a complexed ligand is attracted electrically to charged groups in minerals or solid organic materials. Adsorption is much more significant than absorption as an attenuation pathway although absorption of metals is kinetically less reversible than adsorption. Generally, low pH favors sorption of ligands while high pH favors sorption of metal ions. Ion exchange adsorption reactions also occur in the presence of surface-exchanging cations (such as Ca^{2+} and Na^{2+}) and are kinetically dependent on the concentration of surface-exchanging cation sites and on competing species rather than pH. Sorption capacity is also dependent on soil particle size distribution: fine soil particles have greater surface area than coarser material and therefore have a greater capacity for immobilizing metal contaminants [28]. Most importantly, adsorption processes for metals can be reversible if geochemical conditions change [29]. Therefore, the longevity of this attenuation mechanism should be considered when evaluating the applicability of MNA for metals.

A brief description of attenuation by sorption for MC-related metals is included below:

- **Lead**: The adsorption of lead is highly dependent on pH, with increasing pH favoring sorption. Lead adsorbs more strongly than most divalent metal ions onto hydrous ferric oxide, other ferric oxides, hydrous oxides, aluminum oxides, oxyhydroxides, clay minerals and iron and aluminum containing hydroxypolymer coatings on natural aquifer sediments. In reducing systems, lead adsorbs to and co-precipitates with iron sulfide [28]. Uptake of lead in natural systems is irreversible due to its strong retention and small likelihood of transport to surface waters or groundwater.

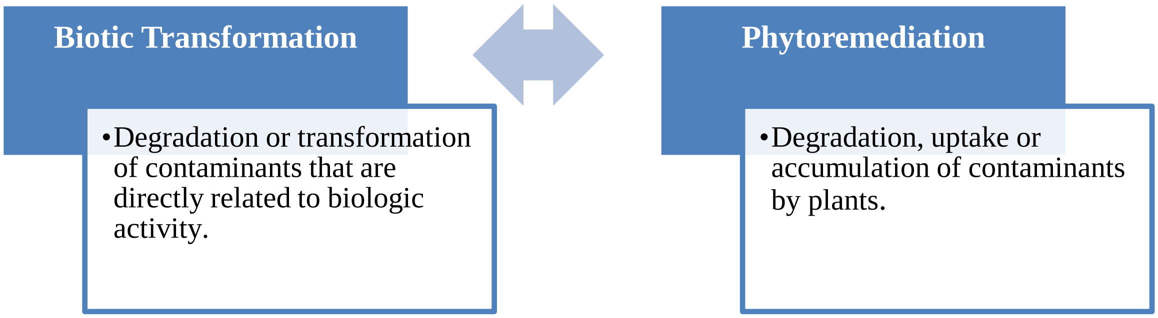
- **Antimony:** Insoluble forms of antimony tend to sorb to clay, soil and sediments, where they are bound to extractable iron and aluminum and antimony readily adsorbs to iron oxides and oxihydroxides [30].

- **Copper:** Low pH soils are less effective in retaining Cu(II) compared to neutral and calcareous soils, with a high degree of reversibility of sorption processes at low pH. Redox conditions have little impact on solid copper stability: copper has a strong affinity for the surfaces of iron oxides and hydroxides, clays, sulfides and organic matter and is more strongly sorbed to mineral substrates than zinc, nickel and cadmium [31].

- **Zinc:** Zinc readily sorbs to sediments and suspended solids such as hydrous iron and manganese oxides, clay minerals and organic matter. The sorption affinity of zinc increases with increasing pH and decreasing salinity [28].

4.0 BIOLOGICAL ATTENUATION OF MUNITIONS CONSTITUENTS

Biological attenuation pathways are defined by the biologically mediated transformation or immobilization of MC. These attenuation processes include biotransformation and phytoremediation and are summarized in Figure 4-1.



Biotic Transformation

- Degradation or transformation of contaminants that are directly related to biologic activity.

Phytoremediation

- Degradation, uptake or accumulation of contaminants by plants.

Figure 4-1. Summary of Biological Attenuation Processes for MC

Naturally occurring microorganisms (such as bacteria and fungi) can transform hazardous chemicals to either substances that are less toxic or completely benign. These processes are defined as either biodegradation or biotransformation. Biodegradation is a treatment process that occurs through aerobic or anaerobic chemical degradation of organic matter or contaminants, while biotransformation consists of partial transformation and production of intermediates. Contaminant transformation may also occur through direct metabolism, in which energy gain comes directly from the transformation process. Conversely, co-metabolic pathways result from a fortuitous reaction where the microorganisms do not receive energy from the transformation reaction and require a primary energetic substrate to facilitate sustained contaminant biotransformation. Bioremediation may be applied in situ or ex situ to treat both soil and groundwater. Often, site conditions need additional adjustment to enhance a contaminant’s degradation rate and to provide an optimal environment to sustain the growth and performance of microbial populations.

Phytoremediation offers an innovative and cost-effective option to address recalcitrant environmental contaminants. The use of plant products, algae or entire plants as a tool to restore or stabilize contaminated sites gives an opportunity to extract, store or degrade a variety of organic and inorganic compounds. The ability to cultivate high plant biomass with a high content of toxic chemicals in a contaminated soil determines successful remediation. Phytoremediation pathways include the following three aspects:

- Phytodegradation: The active uptake and biotransformation of the contaminant.
- Phytoextraction/Phytoaccumulation: The uptake and accumulation, possibly hyperaccumulation, of the contaminant is limited by the uptake and efficiency of plant roots. Phytoextraction targets a variety of heavy metals and organic substrates.

- Rhizodegradation: The degradation or transformation of contaminants within the root zone of the plants.

The selective removal of ions represents a unique plant quality utilized for uptake, regulation and distribution of metals in a soil medium. Absorption dominates as a major rhizosphere uptake mechanism due to the presence of additional protective barriers, which prevent plants from metal toxicity during phytoaccumulation. A plant with hyperaccumulating abilities exhibits an ability to yield 0.1% chromium, cobalt, copper or nickel or 1% zinc or manganese in the aboveground shoots on a dry weight basis [39]. The aboveground shoots are usually harvested for metal removal and subsequently disposed as hazardous waste after the phytoaccumulation process is completed.

Given the prevalence of soil contamination from MC, a number of plant-based research projects have been conducted for MC treatment. Within the DoD, transgenic grasses were engineered to uptake and degrade RDX and TNT. The project investigated the ability of the transgenic grasses to withstand drought in addition to disruption by live-fire ammunition and heavy equipment [40]. Additionally, the DoD has supported several studies as part of the Remediation Management of Distributed Sources of Munitions Constituents on Ranges Program. Those efforts included a large-scale lysimeter study, a bench-top study and an investigation of the effects of explosive-degrading plants on the rhizosphere and soil microbial population [40].

4.1 Biological Attenuation of Energetics

Biological attenuation of energetic contaminants depends on the biodegradation potential of microbial populations present in the environment. Cyclic nitramine explosives, such as TNT, RDX and HMX, contain multiple nitro groups (R-NO_2) attached onto aromatic or heterocyclic rings providing protection from an oxidative degradation. The chemical structure of energetics suggests that their primary biotransformation process is reductive in nature and initiated by nitroreductases. Catalysis of nitro groups requires a co-substrate and can occur either under aerobic or anaerobic conditions. Furthermore, intermediates of energetics such as TNT can potentially be more toxic than the parent energetic compound. Therefore, monitoring for intermediates is required as part of a MNA strategy. Depending on the levels of the intermediates, enhanced biodegradation (an active remedial strategy) may be needed to obtain complete mineralization.

TNT: TNT biodegradation has been reported for a wide variety of bacterial isolates such as *Pseudomonas*, *Desulfovibrio sp.*, *Bacillus sp.* and *Staphylococcus sp.* cultured from freshwater or terrestrial environments. Biotransformations of TNT can take place under aerobic or anaerobic conditions and are typically co-metabolic in nature. A common finding is that the nitro groups of the TNT are reduced to anilines (aromatic R-NH_2). Figure 4-2 illustrates this reductive process where TNT is biotransformed in a stepwise manner:

- One of the nitro groups (shown in red and blue) is reduced through biotic reaction to a hydroxylamime (-NHOH) group. Note the two additional hydrogens on either 2-hydroxylamino-4, 6-dinitrotoluene (2-HADNT) or 4-hydroxylamino-4, 6-dinitrotoluene (4-HADNT).

- Next, (following the 2-HADNT pathway), the recently formed hydroxylamine group is further reduced to generate 2-amino-2,6-dinitrotoluene (2-ADNT). Both 2-ADNT and 4-ADNT are the most common intermediates of TNT biotransformation and can be generated in oxic or anoxic conditions.

- Under strict anoxic conditions, enzymes can continue the reductive process and remove the remainder of two nitro groups. First, 2,6-diamino-6-nitrotoluene (2,6-DANT) is produced.

- Finally, the last nitro group can be reduced to form 2,4,6-triaminotoluene (TAT), which is highly reactive and can polymerize or irreversibly bind to the organic soil matrix.

TNT has been utilized by heterotrophic bacteria as a sole nitrogen source or carbon source via nitrobenzene with both carbon and nitrogen incorporated into macromolecules [6]. Additionally, white-rot fungi and litter degrading fungus (e.g., *Phanerochaete chrysosporium*) have been observed to completely biodegrade TNT [36].

RDX: RDX biotransformation occurs via co-metabolic processes under anaerobic conditions. As with most other cases, the co-metabolic degradation rate of RDX is much slower than the direct metabolism of the compound [41, 42]. Shown in Figure 4-3, RDX can be biotransformed in a stepwise process by the sequential reduction of its three nitro groups:

- First, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX) is formed.

- Then, hexahydro-1,3-dinitroso-5-nitro-1,3,5- triazine (DNX) is produced.

- Finally, all three nitro groups are reduced and hexahydro1,3,5-trinitroso-1,3,5-triazine (TNX) is formed.

The metabolites may undergo further reduction prior to ring cleavage and transform into hydroxylamino-RDX intermediates, which in another ring cleavage reaction may yield formaldehyde, methanol, hydrazine, 1,1-dimethylhydrazine and 1,2-dimethylhydrazine.

HMX: While aerobic degradation of HMX appears to be negligible, the similarities in structure with RDX make HMX susceptible to anaerobic biotransformations. For example, HMX degrades to methane and chloroform under anaerobic conditions when a mixed microbial consortium is present [43]. When under specific electron-accepting conditions, the order of the biotransformation rate is highest starting as follows: sulfate-reducing, fermenting, methanogenic and nitrate-reducing conditions [43].

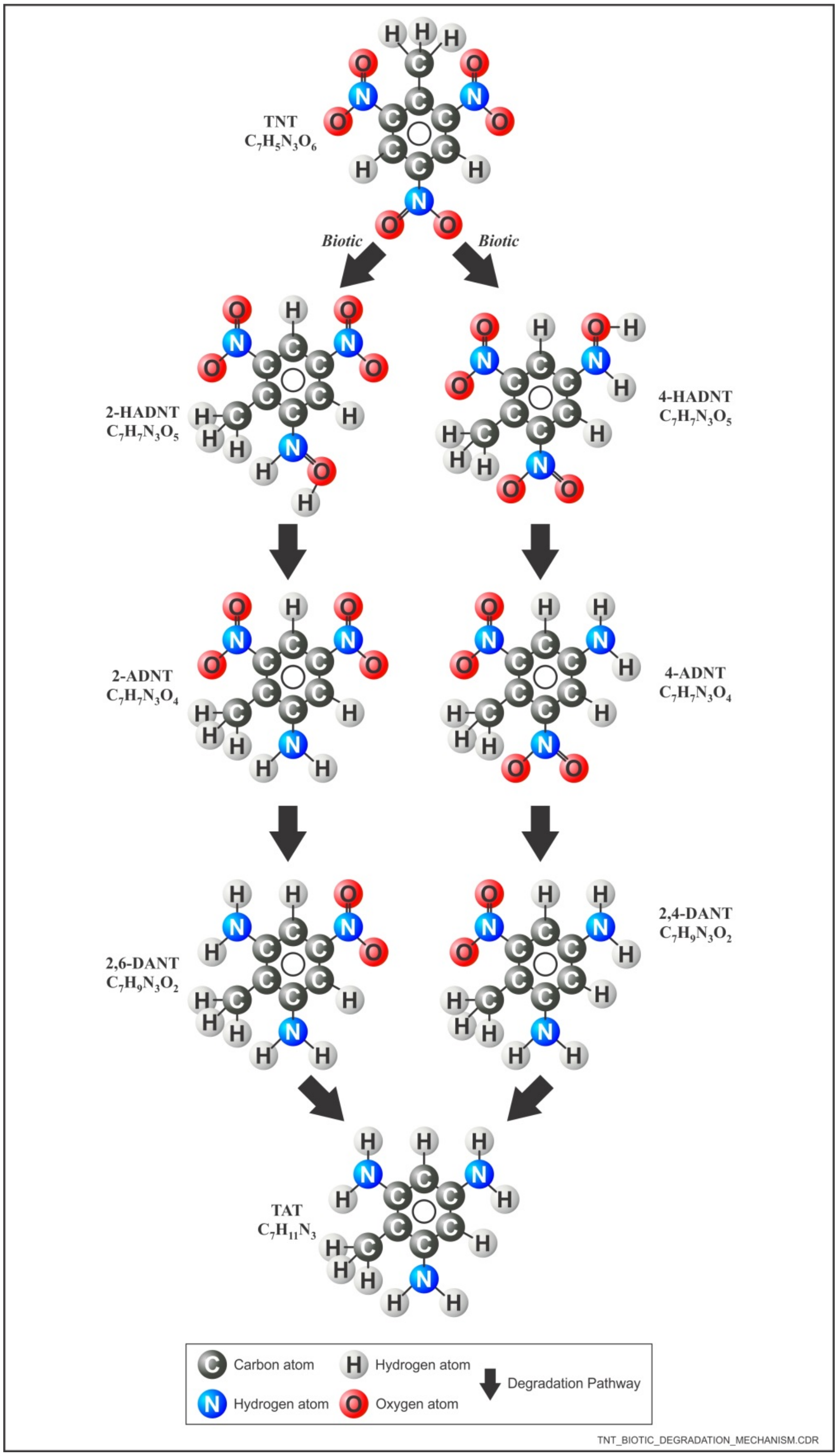


Figure 4-2. Biodegradation of TNT

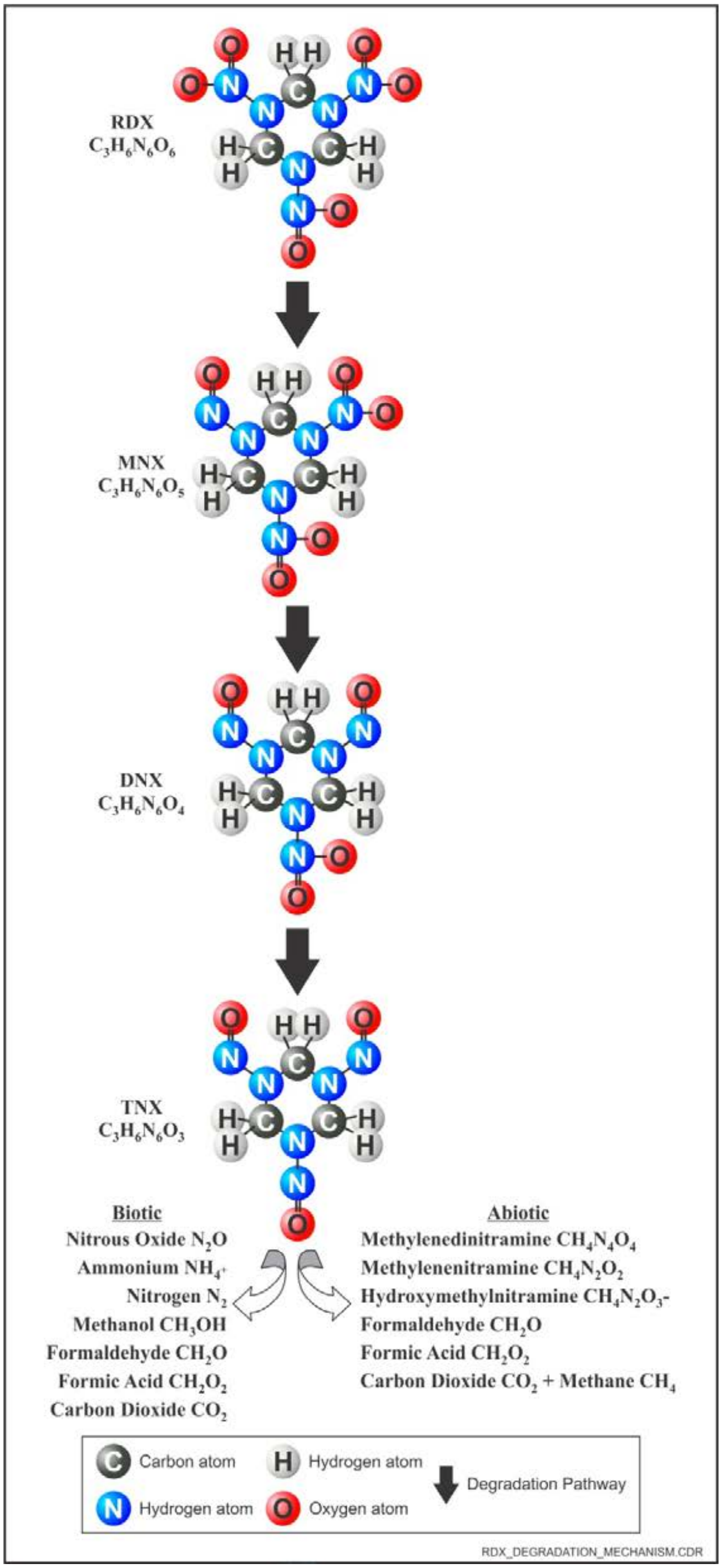


Figure 4-3. Biodegradation of RDX

4.2 Biological Attenuation of Propellants

Organic Propellants. Similarly to explosives, organic propellants are susceptible to biotransformation.

- **DNTs:** Studies have shown that both 2,4-DNT and 2,6-DNT can be mineralized through an oxidative pathway [44] with DNTs serving as the sole source of nitrogen, carbon and energy [45]. Biotransformation under anoxic conditions does not result in complete degradation of these contaminants. Rather, the reductive pathway produces corresponding diaminotoluenes (DATs), which appear recalcitrant to further microbial degradation in an anoxic environment. Overall, both DNTs tend to undergo biotransformation and, if not in oxic environments, irreversibly binding to aquifer solids.

- **NG:** NG is biodegraded both aerobically and anaerobically, serving as a sole source of nitrogen to a variety of microorganisms (*P. putida, P. fluorescens, Klebsiella, Rhodococcus, G. candidum, P. chrysosporium*) [36, 46]. It has been reported that NG can be co-metabolically transformed to glycerol dinitrates (GDNs) and mononitrates (GMNs) with concomitant production of nitrite and nitrate [47, 48]. The aerobic degradation results in nitrate release, whereas anaerobic conditions release ammonia [49]. The glycerol generation through the removal of the last nitro group is consistently the slowest and the most difficult step [47, 50] in NG biotransformation. As a result, once glycerol is formed, it is biologically transformed to carbon dioxide and water.

- **NQ:** Very little information is available concerning the biotransformation of NQ. The limited data indicate that it does not biodegrade [44]. Recent studies have shown NQ biotransformation in aerobic microcosms after a carbon source was supplied [51], however NG was persistent in unamended microcosms or under anaerobic conditions. When *Variovorax* strain VC1 was isolated from soil microcosms containing NQ as the sole nitrogen source, its degradation was still inhibited in the presence of a more favorable source of nitrogen. Mineralization of NQ by VC1 produced ammonia, nitrous oxide and carbon dioxide as final products [51].

Perchlorate. Perchlorate reducing bacteria are ubiquitous in the environment, and several perchlorate degrading pure cultures have been isolated to date. Most perchlorate reducing species belong to the genera *Dechloromonas* and *Azospira* (formerly called *Dechlorosoma*) [52] and utilize perchlorate as an electron acceptor while using different organic substrates as electron donors and the carbon source. Perchlorate biodegradation is governed by microbially mediated redox reactions, whereby perchlorate serves as the electron acceptor and is reduced via chlorate and chlorite to chloride, oxygen and carbon dioxide (Figure 4-4). Both chlorate and chlorite are transient intermediates and are typically not observed during in situ perchlorate reduction (reaction rates for these intermediates are typically too rapid for detection). The geochemical conditions required for biological perchlorate degradation include pH between 6.5 and 7.5, an oxidation reduction potential between 0 and –100 mV, low or minimal oxygen concentrations and low nitrate levels [52].

Typical co-contaminants present at perchlorate sites include volatile organic compounds (VOCs), halogenated solvents and explosive compounds such as TNT, RDX and HMX [6]. The microorganisms and conditions for optimal removal of perchlorate may differ from those capable of degrading the co-contaminants. However, in some situations, the presence of co-contaminants may rather promote favorable conditions for perchlorate degradation.

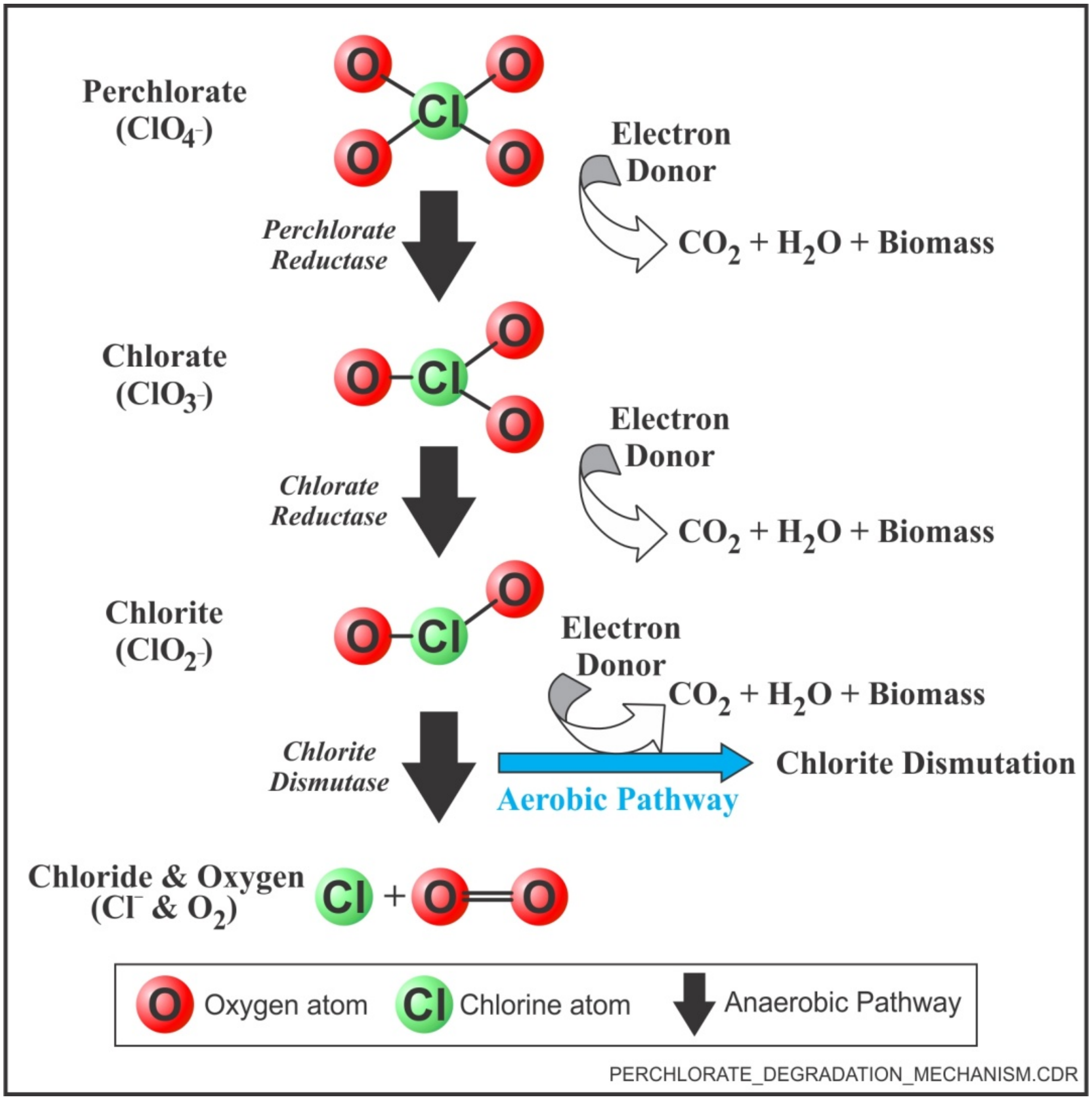


Figure 4-4. Biodegradation of Perchlorate

4.3 Biological Attenuation of Metals

Geochemistry of the particular site and the metal chemistry govern the microbial interactions with the given metal of interest. The biotic cycling of naturally occurring elements, especially iron and manganese, also affects the behavior of many toxic elements. There are generally two pathways for natural attenuation by biological processes: precipitation and adsorption leading to metal sequestration and changes in geochemical condition due to microbial respiration, including changes in redox potential and pH, leading to reversible changes in solubility.

Microbial degradation of organic matter can be coupled to many metabolical pathways, for example sulfate reduction that results in the production of hydrogen sulfide. Metals such as copper form extremely insoluble copper sulfide complexes, such that no complexing ligand can compete with hydrogen sulfide or metal sulfide for copper. Moreover, complexes of lead with sulfide are highly insoluble and stable, enhancing lead properties to co-precipitate with iron particles. For this reason, in situ bioremediation has been proposed as a remedial technology with a goal to promote bacterial sulfate reduction and consequent precipitation [31, 53].

Decomposition of organic matter depletes dissolved oxygen, leading to increased solubility of iron. However, iron oxidation processes are mediated by specific microorganisms and have been proposed as an iron removal technique for groundwater treatment [54]. Research indicates that biotic processes also contribute to the metastability of Sb(III) in aqueous solutions despite being thermodynamically unfavorable [55].

5.0 TECHNOLOGY APPLICATIONS

5.1 MNA of MC

A DoD RPM considering the suitability of natural attenuation for MC in the environment has several factors to consider, as shown in Figure 5-1. This includes evaluating the site-specific lines of evidence (LOEs) related to the physical, chemical and biological attenuation pathways as discussed in Sections 2 through 4. Under favorable conditions, the attenuation of MC will proceed without human intervention to reduce mass, toxicity, mobility, volume, or concentrations of contaminants in soil or groundwater [4]. This means that the source term of the contamination is equal to or less than the natural attenuation capacity (NAC) of the environment. As illustrated in Figure 5-1, the source terms consist of mechanisms that can contribute mass to the environment, whereas the NAC consists of all mechanisms that reduce the mass, toxicity, mobility, volume, or concentrations of contaminants in the system.

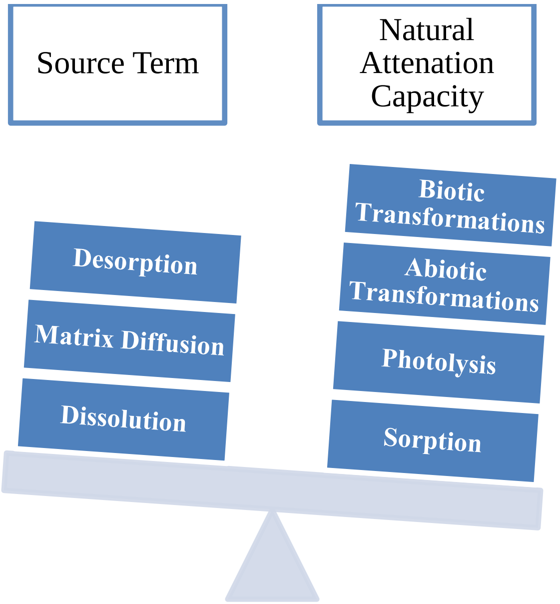


Figure 5-1. MNA Suitability Factors

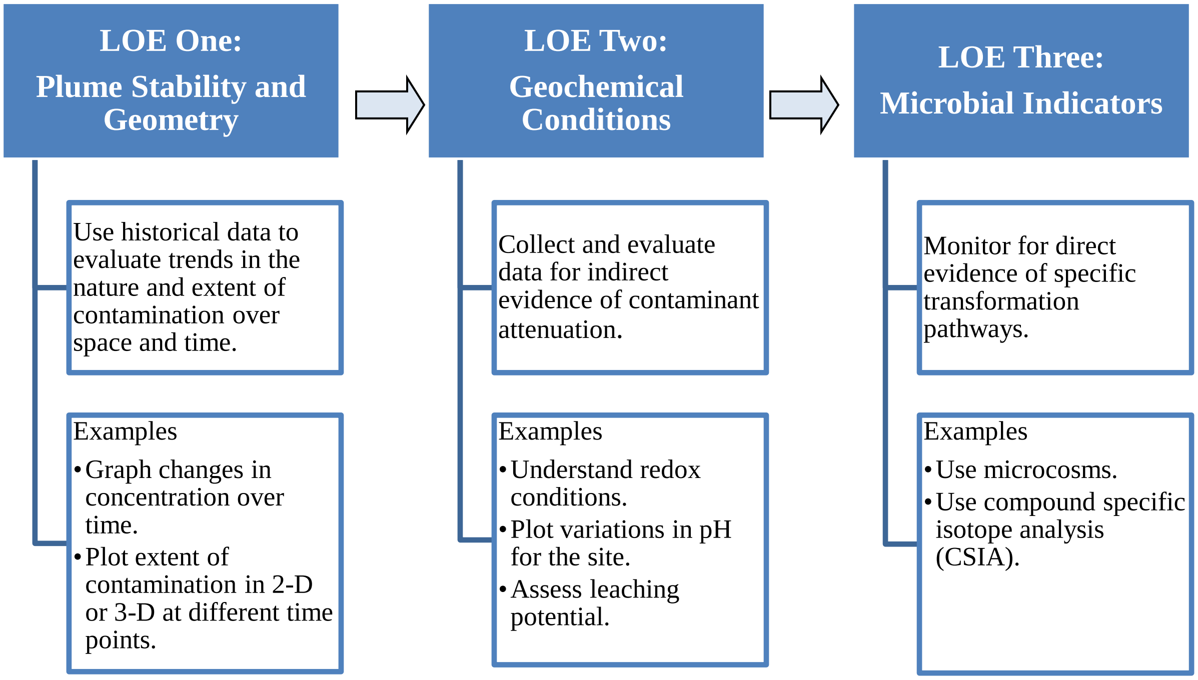
However, the effectiveness of these processes must be confirmed for MNA to be a timely and realistic remedial strategy and not simply a “no action” solution. This confirmation involves the identification of favorable conditions at which MNA is taking place and the documentation of attenuation pathways that mitigate fate and transport processes that would otherwise increase toxicity or mobility of contaminants.

Figure 5-2 summarizes a method for the identification and documentation of the active pathways outlined by the U.S. Army Corps of Engineers [56]. The protocol recommends a tiered analysis that provides LOEs to support evaluation of MNA. The LOEs are shown in Figure 5-2, along with a general description of the LOE and sample ways to identify and document attenuation pathways.

- **First Line of Evidence**. For the first LOE, a decreasing or stable trend in the nature and extent of contamination should be observed. Trend analysis can be conducted using regression analysis or a non-parametric statistical test such as Mann-Kendall. Consideration should be given to transformation products and contamination in various phases (aqueous phase, solid phase, vapor phase and non-aqueous phase [if appropriate]). If the LOE analysis shows that the nature and extent of contamination is increasing, then an MNA strategy may not be appropriate for the site at that time (see Section 5.2 for potential of enhanced MNA).

- **Second Line of Evidence**. In the second LOE, the geochemical data at the site are evaluated to ascertain which processes may be contributing to contaminant attenuation. This step includes recognizing all potential attenuation mechanisms (e.g., physical, chemical and biological) for the contaminants of concern and determining whether the environment can support these pathways. The results of this analysis rely on interpreting data to demonstrate indirectly which MNA attenuation mechanisms could be active at the site. If sufficient evidence exists for attenuation processes, then direct measure of the pathway(s) is recommend and the third LOE can be pursued.

- **Third Line of Evidence**. The third LOE provides direct evidence of the attenuation processes responsible for contaminant reduction. For MCs, LOE examples include detecting necessary enzymes, establishing soil mineralization potentials and documenting microbial community composition. Typically, the third LOE focuses on verifying biotransformation potential.



Use historical data to evaluate trends in the nature and extent of contamination over space and time.

Examples
- Graph changes in concentration over time.
- Plot extent of contamination in 2-D or 3-D at different time points.

Collect and evaluate data for indirect evidence of contaminant attenuation.

Examples
- Understand redox conditions.
- Plot variations in pH for the site.
- Assess leaching potential.

Monitor for direct evidence of specific transformation pathways.

Examples
- Use microcosms.
- Use compound specific isotope analysis (CSIA).

Figure 5-2. Line of Evidence Process for Evaluating Whether MNA is Appropriate for a Site

For additional information on microbial indictors, please reference the Environmental Molecular Diagnostic tool (http://www.itrcweb.org/emd-2/) which includes discussion on molecular biological tools (MBTs) and CSIA.

Although chemical, geochemical and microbiological evidence may exist, most regulatory agencies consider a stable or shrinking plume to be the critical LOE for determining whether natural attenuation alone is an appropriate remedy. In some cases where there are no sensitive receptors in the plume path even though the plume is expanding, a “monitoring only” approach may be followed for a time if there is evidence that attenuation rates are increasing while loading rates are decreasing. However, a “monitoring only” phase is typically only an interim measure to see whether further action is required.

5.2 Enhanced MNA of MC

The objective of enhanced MNA is to increase the NAC of the system such that the enhancement(s) achieve a balance between source term and NAC. This would lead to plume stabilization followed ultimately by plume shrinkage over time. Effective enhancements provide sufficient longevity to maintain the plume stability/shrinkage such that an enhancement is no longer needed to reduce contamination. Figure 5-3 illustrates three types of options for enhancing MNA.

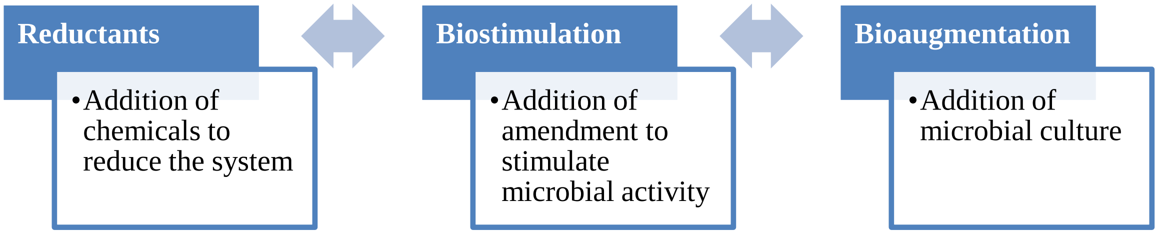


Figure 5-3. MNA Enhancement Options

A coupled abiotic/biotic remediation technology appears to produce the fastest rate of complete mineralization for energetics [38] with the exception of perchlorate which degrades rapidly through biogenic processes. This technology creates iron-reducing conditions by initially injecting a chemical reductant such as dithionite followed by the injection of a carbon source such as lactate. The chemical reductant dithionite reduces naturally occurring Fe(III) oxides to Fe(II). The Fe(II) is present as sorbed Fe(II), siderite (Fe(II) carbonate) and/or FeS. The Fe(II) produced is sorbed quickly from pH 6.8 and up, low ionic strength water and therefore does not leach from the sediment. The Fe(II) forms a reactive zone that is available for transformation.

One of the most widely used bioremediation procedures is biostimulation. As defined in Figure 5-3, biostimulation is the addition of amendments to stimulate indigenous and introduced microorganisms. These amendments can include substrates, electron donors, salts with buffer capacity, inorganic macro- and micro-elements and vitamins. If indigenous microbial communities are not present or significant in numbers, then bioaugmentation can provide the enhancement needed to promote MC biodegradation and thus stabilize/shrink the plume.

6.0 LESSONS LEARNED FROM CASE STUDIES

Both laboratory and pilot-scale studies have been undertaken to further the understanding of how MC can be degraded in situ through MNA or enhanced MNA (bioremediation) technologies. A literature survey was conducted for studies addressing TNT, HMX, or RDX contamination with either MNA or bioremediation as part of the remedy. Since case studies for perchlorate are already summarized by the Interstate Technology Regulatory Council (ITRC) in its perchlorate technology overview [57], sites with perchlorate contamination were not included in the literature survey. Case studies at DoD installations identified through the literature survey were then selected for review. Table 6-1 summarizes the selected sites in terms of study type, contaminant, treatment technology, amendment, maximum contaminant concentration and maximum realized removal. Detailed site backgrounds, remedial approaches and outcomes for each of these case studies are included as Appendices A through H.

Biostimulation, via the injection of liquid substrates, was the most commonly used technology to treat MC in groundwater among the identified case studies. Carbon substrates including ethanol, lactose, cheese whey, soybean oil and emulsified vegetable oil (EVO) have been used to stimulate naturally occurring perchlorate, RDX and TNT-degrading microorganisms. The liquid substrate injections occurred as direct injections, recirculation and a biobarrier configuration. Mulch was used in one instance as the electron donor in a biowall configuration.

For the collected case studies shown in Table 2-1, RDX has been found at DoD sites at groundwater concentrations ranging from less than 100 µg/L to 2,000 µg/L (ppb). RDX concentrations at sites where bioremediation has been applied decreased significantly in response to substrate amendments (often to below site cleanup goals); this was followed by the appearance of RDX daughter products DNX and TNX, the concentrations of which subsequently decreased. A similar phenomenon was observed when TNT was present at the biostimulated sites: the concentration of TNT degradation product 4-ADNT increased after biostimulation, but this was followed by a decrease in concentration.

Injection of an electron donor led to the degradation of RDX, TNT and their degradation products at the studied sites. This suggests that the microorganisms are capable of degrading RDX and TNT may be ubiquitous in the environment. The microorganisms may merely require a reduction in the redox conditions of the contaminated groundwater before RDX biodegradation can occur.

RDX appears to be recalcitrant under oxic conditions, unless the contaminated groundwater is augmented with specific microorganisms. Since RDX has been documented to be persistent under oxic conditions, it can be concluded that aerobic microorganisms capable of degrading RDX may not be commonly found in soil and groundwater. The U.S. Army Corps of Engineers is currently conducting studies into the potential for bioaugmentation to facilitate aerobic biodegradation of RDX plumes [58]. In contrast to anaerobic biostimulation, the potential benefits of the aerobic bioaugmentation approach would include: significantly less bioremediation substrate required, which translates to reduced substrate cost; minimal-to-no impacts to groundwater quality such as mobilization of redox-sensitive metals or the formation of sulfide or methane; and minimal-to-no formation of toxic nitroso-RDX derivatives associated with anaerobic biostimulation. Testing is ongoing to determine if this is a feasible approach.

Two of the nine sites were identified as Navy sites including Naval Submarine Base Bangor, WA and Naval Surface Warfare Center, Dahlgren, VA. At the Naval Submarine Base Bangor, a large dilute plume is present with RDX concentrations over 2,000 µg/L (ppb) [59]. At the Naval Surface Warfare Center Dahlgren, shallow groundwater is contaminated with RDX, HMX and perchlorate up to 200 µg/L (ppb). Initial results from the field trial (which is ongoing) suggest that an emulsified oil biobarrier with pH buffering can be a viable alternative to remove perchlorate and explosives from shallow groundwater [60]. Further details are available in Appendices A through H on the case study results and lessons learned at each site.

Table 6-1. Summary of MC Groundwater Case Studies

Case Study Number	Field Site	Study Type	Contaminant	Treatment Technology	Amendment	Max Concentration (µg/L, ppb))	Max Removal
1 (Appendix A)	**Naval Submarine Base Kitsap-Bangor, WA**	Field	RDX	Pump-and-Treat	N/A	2,000	111 g/day
				Push-Pull Biostimulation Pilot Study	Corn Syrup Ethanol Lactose	(in process)	
		Laboratory	RDX	Biostimulation	Oxygen Nitrate Iron (III) Manganese (IV) Acetate	330	100%
2 (Appendix B)	**Umatilla Chemical Depot, OR**	Laboratory and Field	RDX	Aerobic Bioaugmentation	KTR9 RHA1 Strain IC cells	300	N/A
3 (Appendix C)	**Naval Surface Warfare Center, Dahlgren, VA**	Field	RDX HMX Perchlorate	Biostimulation	EVO Buffer	200	to <5 µg/L
4 (Appendix D)	**Picatinny Arsenal, Dover, NJ**	Field	TNT	Biostimulation	Cheese Whey	105	99%
			RDX			68	92%
5 (Appendix E)	**Pantex Plant, Amarillo, TX**	Field	RDX	Biostimulation	Soybean oil Lactic acid	NA	97%
6 (Appendix F)	**Iowa Army Ammunition Plant, Middletown, IA**	Field	RDX	Biostimulation, MNA and ICs	Acetate	>100	99%
7 (Appendix G)	**Former Nebraska Ordnance Plant, Mead, NE**	Field	RDX	Biostimulation	Acetate	450	98%
8 (Appendix H)	**Pueblo Chemical Depot, Pueblo, CO**	Field	RDX	Biowall	Mulch/Gravel	268	95%

7.0 CONCLUSIONS

Recent research findings were summarized related to natural and enhanced attenuation processes for MC in soil and groundwater. Ultimately, the fate and transport of MC is affected by a variety of mechanisms such as dissolution, sorption, dilution, advection, dispersion, diffusion and degradation.

For high explosives, the main sources of MC include the projectile body, cartridge case, filler and propellant whereas minor sources of MC could originate from the fuze, primer and/or booster. MC is also included in a variety of secondary explosives (such as boosters), chemical agents and pyrotechnics (e.g., incendiaries). Propellants are found in cartridge cases (i.e., small arms, medium caliber munitions and some artillery), rocket motors and explosive charges, as well as external to the projectile (e.g., mortars). In addition to energetic chemicals, metals are found in nearly all military munitions. Uses of metals in munitions include casings, bullets, projectile cases, projectiles, bomb bodies and fillers.

MC contamination in soils is the predominant impact at terrestrial MRP sites. Often, the size of a point source of solid-phase MC is the primary variable controlling the release of contaminants into the water-soluble phase and facilitating contaminant transport from surface soil to groundwater. Movement of contaminants through the subsurface depends on their retardation coefficients or affinity for sorption with organic matter. For example, RDX is less soluble than TNT, but RDX also has a lower sorption potential. This leads to an increased potential for RDX contamination of and migration in groundwater. Additionally, biological transformation pathways impact the fate of MC. For biotransformation, the redox environment of the soil or groundwater is the controlling variable for transformation pathways. If natural attenuation is suspected, the fate and transport of MC in soil and groundwater can be further assessed through the LOE approach using site-specific data to evaluate the natural attenuation capacity of the system via biotic transformation, abiotic transformation, sorption and other processes.

Biodegradation and biotransformation appear to be promising pathways for the attenuation of energetics. Sites commonly contain some if not all geochemical conditions to facilitate the reduction of energetics. Adjusting redox conditions or providing substrate to contaminated aqueous media appears to be sufficient in most cases to accelerate attenuation processes. Recent research also suggests that coupled abiotic and biotic processes can be an effective means for achieving the mineralization of energetics.

Conversely, immobilization by sorption or precipitation appears to be the most promising pathway for natural attenuation of metals. Adjusting redox conditions or the pH of contaminated aqueous media can be sufficient to change geochemical properties to favor immobilization of metal contaminants.

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APPENDIX A

NAVAL BASE KITSAP-BANGOR

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Biostimulation for MC-Contaminated Groundwater at Naval Base Kitsap-Bangor Site F

Site Background: The groundwater at Site F Naval Base Kitsap Bangor, WA is contaminated with RDX, TNT, 2,6-DNT and 2,4-DNT. Cleanup levels for these constituents are 0.8, 2.9, 0.13 and 0.13 µg/L (ppb), respectively. The geology consists of a shallow 6 m thick seasonal, high-permeability aquifer perched atop a low-permeability glacial till and an underlying, 60-m thick moderate- to low-permeability unit of silty, sandy, glaciolacustrine ice-contact deposits. The site has a large dilute mixed plume at 100 to 200 feet below the ground surface under the dense glacial till. The perched and shallow aquifers contain RDX concentrations up to 1,000 ppb and 660 ppb, respectively. The shallow aquifer consists of predominantly anoxic (dissolved [O_2] <0.5 mg/L [ppm]), Mn (IV)-reducing conditions.

Technology Approach: Monitored natural attenuation (MNA) and biostimulation were evaluated in microcosm studies for this site (Bradley and Dinicola, 2005) and a field trial of biostimulation is planned in the near future (King, 2013). Biostimulation is currently being evaluated as a potential full-scale remedial strategy for the RDX plume as an alternative to the existing pump-and-treat system.

A 600 gallon per minute (gpm) groundwater pump-and-treat system has been in operation since 1996 with the goal of plume containment and mass removal. Concentrations at each extraction well have shown asymptotic trends well above cleanup levels. Recently, the system treated 265 million gallons per year and only removed an estimated 80 pounds (lbs) of RDX, 15 lbs of TNT and 0.93 lbs of DNT. The pump-and-treat system is nearing the end of its useful life and will require significant upgrades in the near future if the treatment system is to continue to operate. Due to the length of time and estimated cost for clean up by pump-and-treat, alternative remedial methods are under consideration.

The Unites States Geological Survey conducted a microcosm study at this site to investigate the potential for RDX biodegradation in aquifer sediments under metal reducing conditions (Bradley and Dinicola, 2005). Microcosms were amended with either oxygen, nitrate, iron (III), manganese (IV) or were left unamended. Acetate was added to a few nitrate reducing and unamended microcosms. RDX concentrations of 330 ppb were spiked in the microcosms followed by monitoring for headspace concentrations of N_2, N_2O, CH_4, $^{14}CH_4$, CO_2 and $^{14}CO_2$. The liquid phase was analyzed for ^{14}C-RDX and its potential nitroso degradation products (^{14}C-MNX, ^{14}CDNX and ^{14}C-TNX) and short-chain organic acid. $^{14}CO_2$ and $^{14}CH_4$ in the liquid phase was estimated using Henry's law. Henry's law defines that at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. Microbial analyses were carried out on the microcosms for the presence of *Geobacter*.

Outcome: The results of the microcosm study are shown in Table A-1. During the microcosm study, no significant ^{14}C-RDX biodegradation was observed in aquifer microcosms under oxic conditions. Under anoxic conditions, the predominant terminal electron accepting process was Mn(IV) reduction as evidenced by the significant increase in Mn(II) and the increase in the Mn/Fe(II)-reducing microbial population. Table A-1 shows the percent C-14 labeled RDX remaining and percent CO_2 formed in microcosms at different terminal electron accepting conditions both naturally and after amendments were added. No significant reduction of RDX was found in the autoclaved microcosms. Although RDX concentrations were found to decrease in the microcosm study under manganese-reducing conditions, due to the migrating plume and the persistence of intermediate daughter products (MNX, TNX and DNX) at the field site, it was not possible to implement MNA as the treatment approach at the site.

Table A-1. Percent RDX Remaining and CO_2 Formation in Microcosms

Electron Acceptor Amendment	**Carbon Addition**	**Live Microcosms**		**Autoclaved Microcosms**
		% ^{14}C RDX	**% $^{14}CO_2$**	**% ^{14}C RDX**
O_2	-	72	-	69
NO_3	-	-	100	97
NO_3	Acetate	16	90	-
Mn (IV)	-	-	104	-
Fe(III)	-	-	88	98
Unamended	-	-	89	98
Unamended	Acetate	-	95	-

Note: Unamended microcosms were at manganese reducing conditions

A push-pull pilot study is currently planned at this site that involves the injection of a non-reactive tracer and a reactive carbon substrate (King, 2013). Figure A-1 shows the location of the four push-pull well locations within the RDX groundwater plume. The objectives of this pilot study are to: 1) determine *in situ* contaminant transformation rates for each carbon substrate tested and (2) identify the carbon substrate that supports complete contaminant transformation at the fastest rate. Potential substrates to be tested include corn syrup, ethanol and lactose. The push pull test will be conducted in three phases as follows: 1) transport tests to determine in situ dilution rates and retardation factors for RDX, 2) injection of carbon substrate to support growth of indigenous microorganisms and 3) push-pull tests to quantify the rate of RDX transformation.

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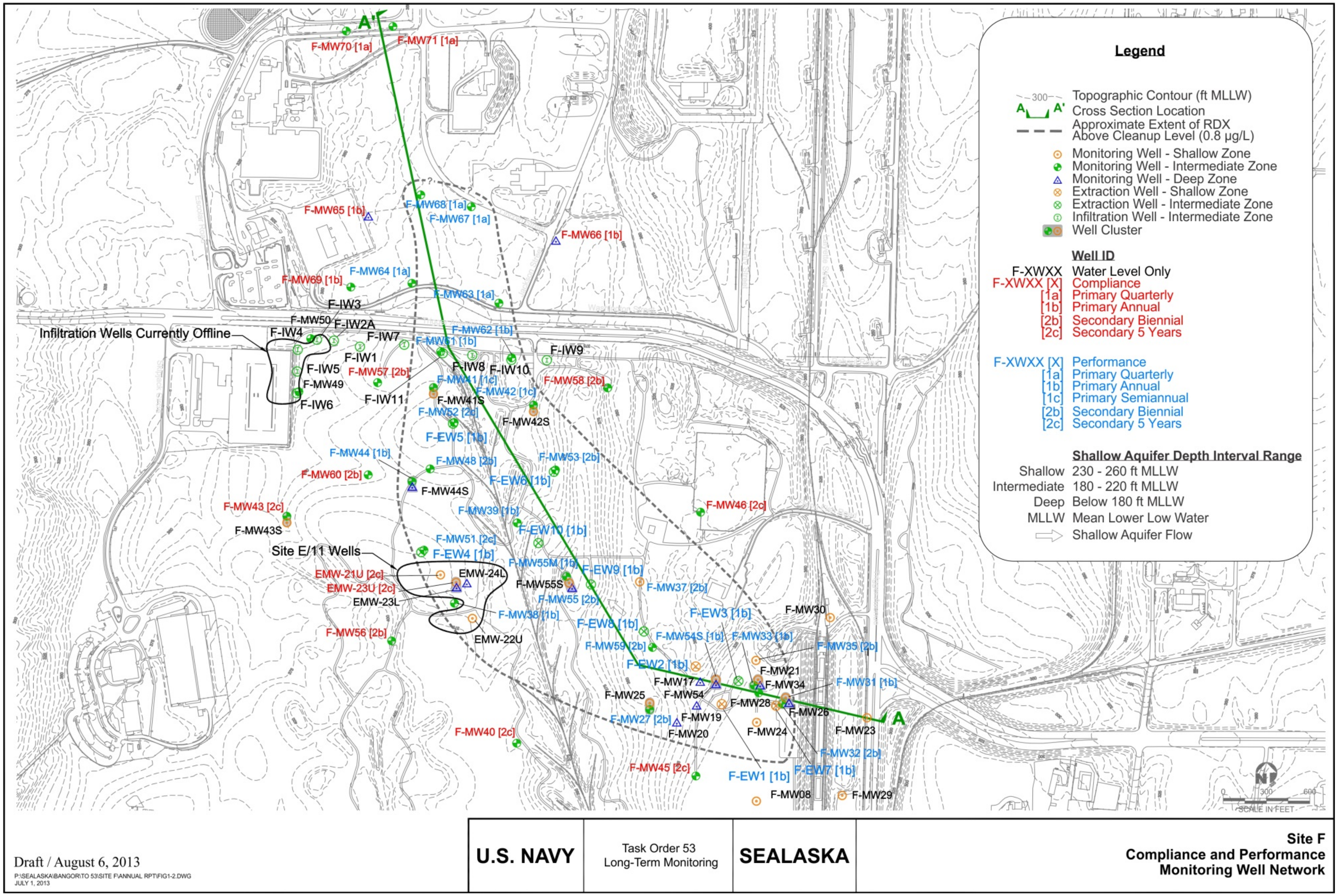

Figure A-1. Location of Push-Pull Test (PPT) Wells at Site F

APPENDIX B

UMATILLA CHEMICAL DEPOT

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Bioaugmentation for Aerobic Bioremediation of RDX-Contaminated Groundwater at Umatilla Chemical Depot

Site Background: Umatilla Chemical Depot (UMCD) has RDX concentrations ranging from 2 to 300 µg/L over a 200 acre, aerobic plume.

Technology Approach: This project was initiated to demonstrate bioaugmentation as an innovative, aerobic approach to RDX-contaminated groundwater remediation. A series of laboratory column tests performed using UMCD aquifer material and artificial groundwater showed that bioaugmented cells could: (a) be effectively transported through UMCD aquifer material; and (b) retain viability and RDX-degrading capability following periods of starvation intended to simulate a potential field-scale bioaugmentation strategy (Figure B-1). In order to confirm the ability to transport bioaugmented cells *in situ* at the field-scale, a cell transport test was conducted by amending UMCD site groundwater (11,400 L total) with chloride (100 mg/L) as a conservative tracer and KTR9, RHA1and Strain IC cells (1×10^9 cells/mL each). The cells and tracer solution were injected in to well DW-2, followed by time-series monitoring downgradient to obtain breakthrough curves. Extraction well EW-4 was continuously operated at 1,100 gpm to control groundwater flow direction during the cell transport test.

Outcome: Results at one well, located approximately 10 feet down gradient from the injection well, confirmed breakthrough of the cells very rapidly with nearly 1×10^8 *xplA* gene copys/ mL detected only hours after the test began (Figure B-2). Viable cell counts remained above 1×10^4 CFU/mL near the end of the 5 day cell transport test. Laboratory column tests and *in situ* cell transport results collectively suggest bioaugmentation could be an effective *aerobic* remediation strategy for RDX-contaminated groundwater. In contrast to anaerobic biostimulation, benefits of the *aerobic* bioaugmentation approach include: significantly, less bioremediation substrate required, which translates to reduced substrate cost; minimal-to-no impacts to groundwater quality such as mobilization of redox-sensitive metals, formation of sulfide or methane; and minimal-to-no formation of toxic nitroso-RDX derivatives associated with anaerobic biostimulation. The demonstration of next steps include a series of push-pull tests to quantify the rate and extent of RDX removal during *aerobic* bioaugmentation compared to biostimulation.

References

Michalsen, M., Crocker, F., Indest, K., Jung, C., Fuller, M., Hatzinger, P. and J. Istok. 2012. Bioaugmentation for Aerobic Bioremediation of RDX-Contaminated Groundwater. Eighth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2012).

Personal Communication with Mandy Michalsen. 2014.

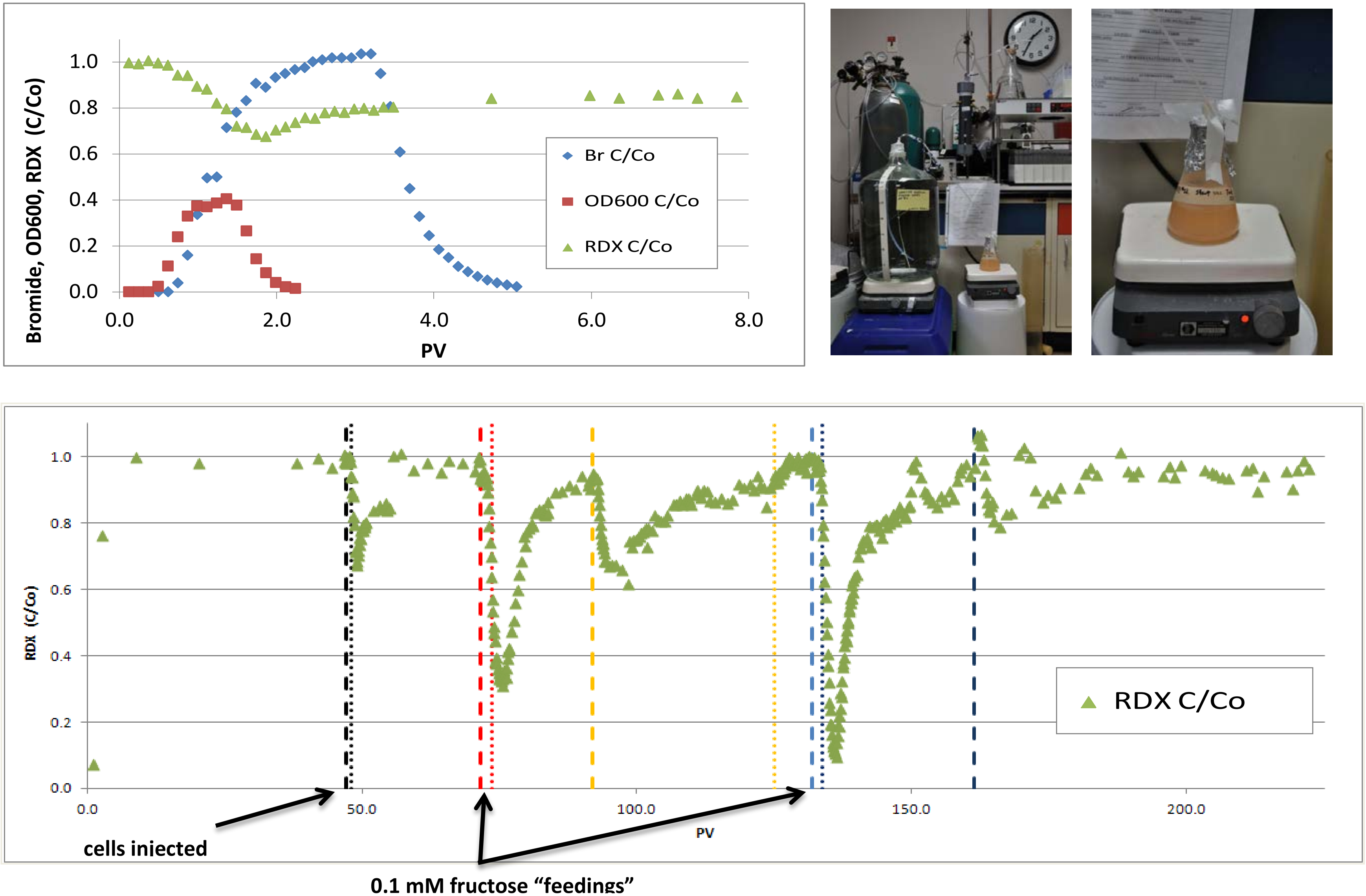

Figure B-1. Breakthrough curves for bromide, optical density and RDX concentrations during column inoculation with KTR9 only (upper left); photos of KTR9 suspension and column set up in the laboratory (upper right); time series RDX concentrations in column effluent prior to and following single bioaugmentation event at 50 pore volumes. RDX-degrading activity resumed following each fructose “feeding”.

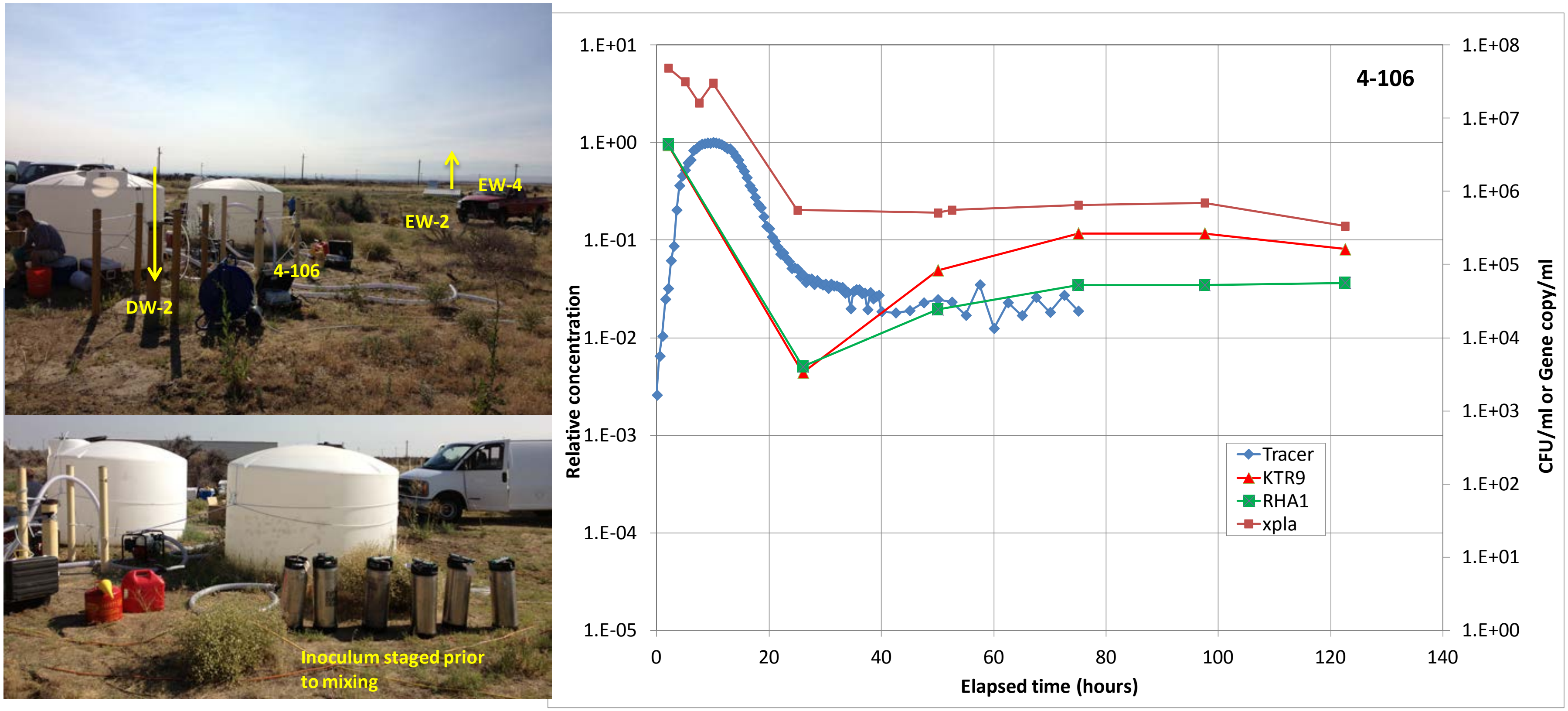

Figure B-2. Locations of test wells (left); and breakthrough curves measured during the *in situ* cell transport test relative (right).

APPENDIX C

NAVAL SURFACE WARFARE CENTER DAHLGREN

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Passive Biobarrier for Treating Comingled Perchlorate and RDX in Acidic Groundwater at an Active Range

Site Background: The Naval Surface Warfare Center, Dahlgren (NSWC Dahlgren) is located in King George County, VA along the Potomac River approximately 40 miles south of downtown Washington, DC. NSWC Dahlgren, which was originally established in 1918 as a testing site for naval ordnance, is presently focused on research, development, test and evaluation (RDT&E) of ordnance, integrated warfare systems, weapons and ammunition. The Churchill Range of NSWC Dahlgren, where this demonstration was conducted, includes OB/OD areas as well as a fast cook-off area and other facilities for ordnance and energetics testing. RTD&E activities on the Churchill Range have resulted in contamination of shallow perched groundwater at some locations with RDX, HMX and perchlorate, generally at 10 to 200 μg/L. At the demonstration location, the groundwater was observed to be aerobic and generally has a low pH (< 5). Treatability studies suggested that the addition of an organic substrate and buffering was necessary to promote perchlorate and explosives biodegradation *in situ*.

Technology Approach: This project was undertaken through the DoD ESTCP program to investigate the feasibility of using a passive emulsified oil biobarrier to remediate co-mingled perchlorate, RDX and HMX at the Churchill Range. The approach selected was designed to minimize impacts to routine range activities. A 100 ft long biobarrier consisting of emulsified vegetable oil and a buffer was emplaced in early 2012 using 20 temporary wells (Figure C-1). A series of upgradient and downgradient monitoring wells were installed to measure dissolved perchlorate, explosives and other relevant groundwater parameters before and after biobarrier installation. Monitoring will continue into 2015.

Outcome: A zone of increased pH and decreased DO was quickly established after installation of the biobarrier. Perchlorate, RDX and HMX were observed to decrease markedly in the downgradient centerline monitoring wells (MW1-MW6) compared to upgradient groundwater after barrier installation. Each compound was generally detected at < 5 μg/L in the centerline wells 6 months after the oil and buffer were injected. Perchlorate biodegraded most rapidly, followed by RDX and then HMX. Nitroso breakdown products, MNX, DNX and TNX were observed from RDX, but only TNX persisted at > 2 μg/L after 6 months. Initial results from the field trial (which is ongoing) suggest that an emulsified oil biobarrier with pH buffering can be a viable alternative to treat perchlorate and explosives in shallow groundwater at this and other range sites with minimal impacts to typical range activities.

References

Fuller, M., Hatzinger, P., Hedman, P. and C. Condee. 2014. Bioremediation of Co-Mingled Perchlorate and Nitramine Explosives in an Acidic Aquifer at an Active Military Range. Proceedings of the Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. (Monterey, California; May 19-22, 2014).

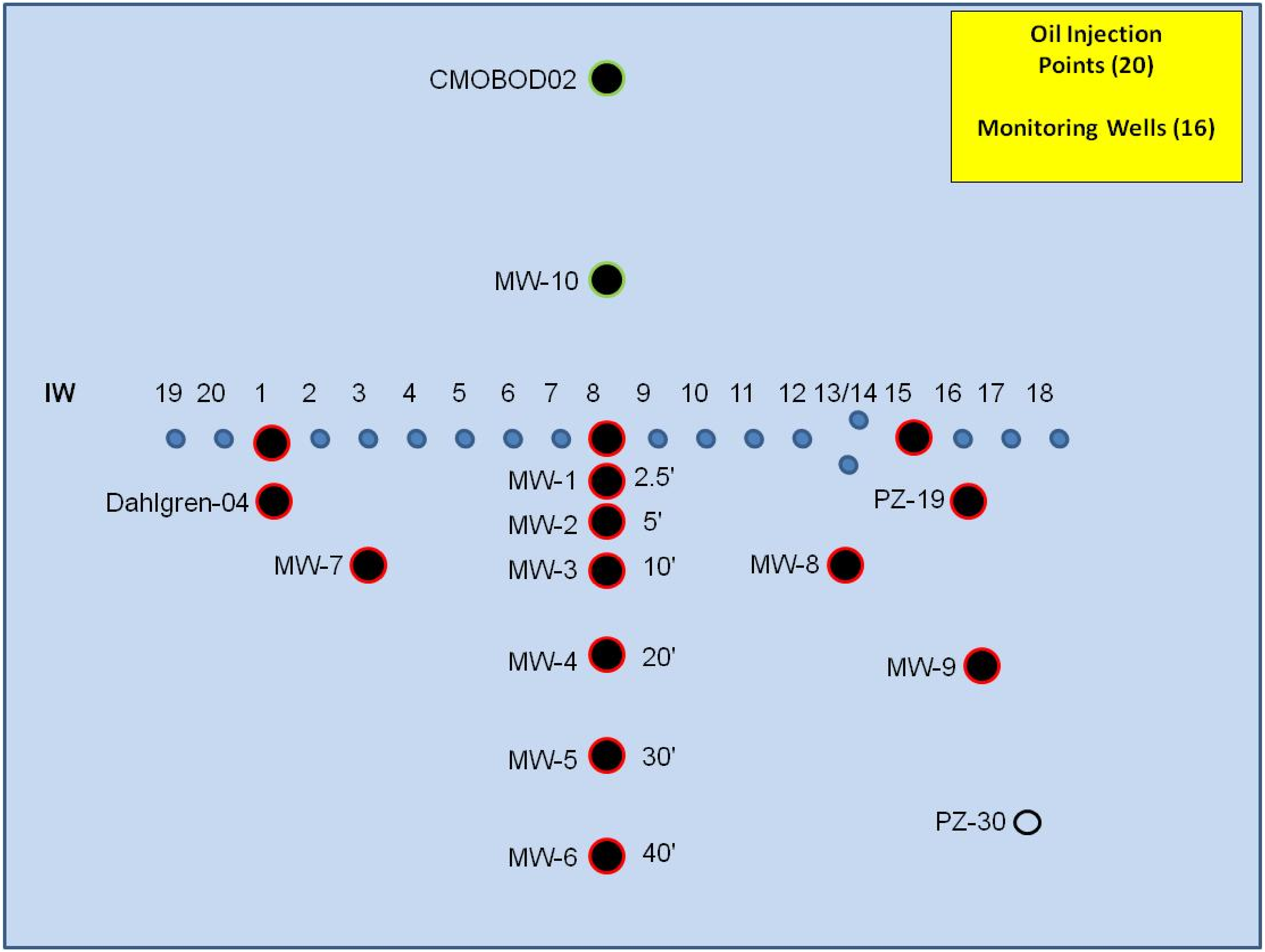

Figure C-1. Demonstration Plot Design

APPENDIX D

PICATINNY ARSENAL

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In Situ Bioremediation of RDX and TNT at Picatinny Arsenal Site 157

Site Background: A location at Picatinny Arsenal characterized by shallow groundwater (< 35 ft bgs) was contaminated with RDX, HMX, TNT, 2,4-DNT and 2,6-DNT (Figure D-1). The groundwater TNT concentrations ranged from below detection (below PQL of 0.5 µg/L) to 105 µg/L, RDX levels ranged from 15 µg/L to 68 µg/L and HMX concentrations ranged from 7.5 µg/L to 69 µg/L. The pH of groundwater ranged from 5.2 to 6.2. In addition to these parent explosives, two TNT degradation products, 2-Amino-4,6-dinoitrotoluene (2A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT) were detected in groundwater at concentrations ranging from 3 µg/L to 51 µg/L. Picatinny Arsenal is owned and operated by the U.S. Army. The source of the contamination results from those periods when Picatinny was involved in the production of explosives, rocket and munitions, propellants, pyrotechnic signals and flares, fuses and metal components. The redox of the groundwater was mildly reducing to oxidizing.

Technology Approach: A recirculation system was designed and installed to introduce cheese whey into the treatment area. The recirculation system consisted of two groundwater extraction wells and one groundwater injection well installed perpendicular to groundwater flow. After the groundwater was extracted it was amended with cheese whey and then re-injected through a single injection well. Cheese whey was selected as the substrate based on the results of a microcosm study in which several different substrates were evaluated for their ability to promote naturally-occurring microorganisms to degrade the energetic compounds. Cheese whey and yeast amended microcosms showed the most amount of degradation, but degradation was more rapid in the presence of cheese whey.

Outcome: Within 62 days after the injection, TNT concentrations declined to below analytical detection limits (PQL = 0.25 µg/L) in all of the treatment zone monitoring wells (TZMWs) except one well that was only impacted slightly by the cheese whey. Two common TNT daughter products, 4-amino-4,6-dinitrotoluene (4-ADNT)**)** and 2-amino-2,6-dinitrotoluene (4-ADNT) were also detected from ~ 1 to 120 µg/L. Within 148 days after the initial injection of cheese whey. RDX concentrations were < 5 µg/L in all six of the TZMWs. RDX daughter products MNX, DNX and TNX increased only slightly. The data from this DoD ESTCP pilot study show that a bioremediation approach can be a viable alternative to treat a complex mixture of energetics in groundwater.

References

Hatzinger, P., Lippincott, D. 2012. In Situ Bioremediation of Energetic Compounds in Groundwater. ESTCP ER-200425. http://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-200425/ER-200425

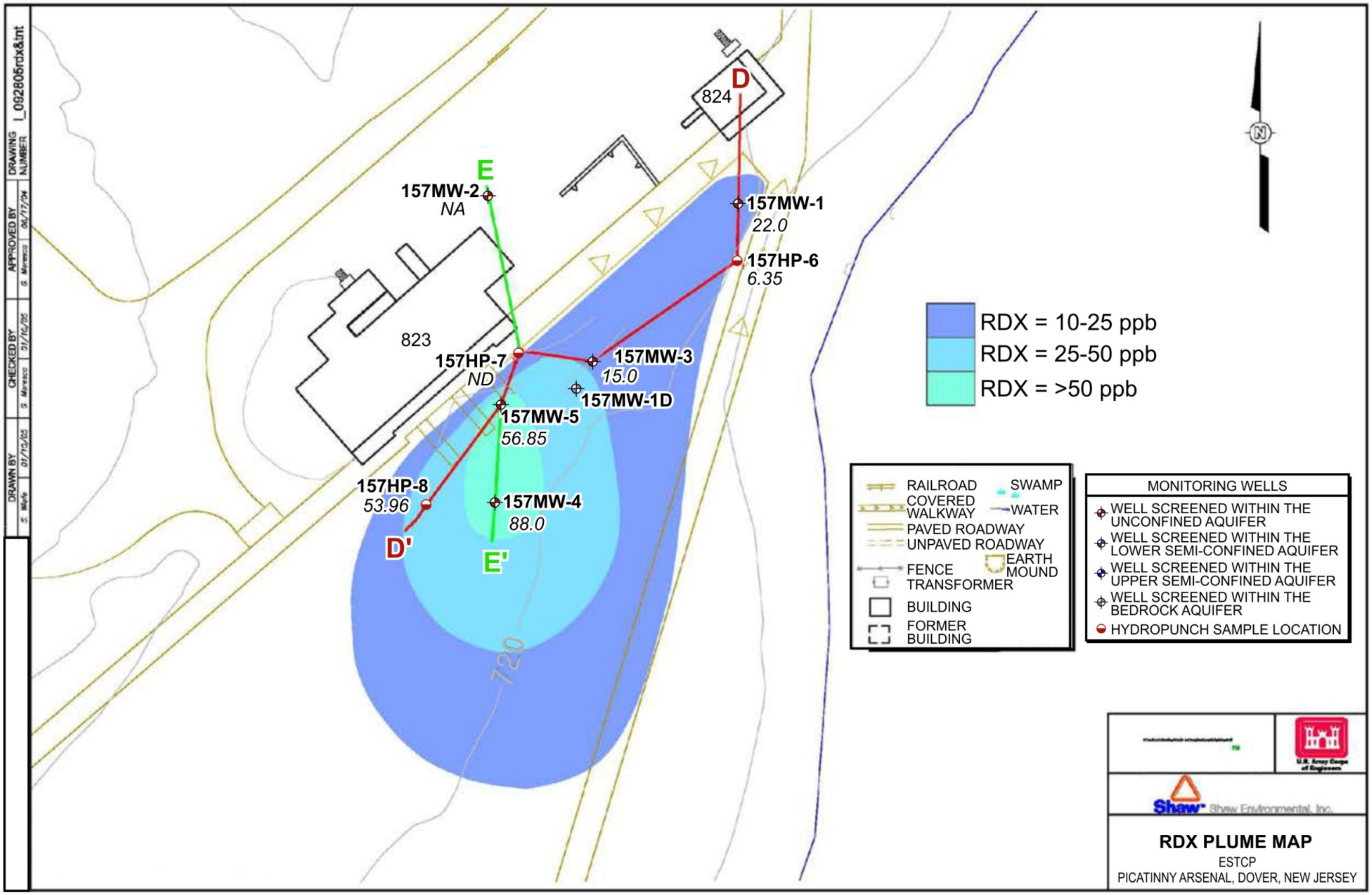

Figure D-1. RDX Plume at Picatinny Arsenal, Dover New Jersey

APPENDIX E

PANTEX PLANT

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In Situ Reductive Biological Treatment of High Explosives at Pantex Plant, Amarillo TX

Site Background: An interim corrective measure (ICM) pilot test of in-situ reductive biological treatment of RDX was carried out at the U.S. Department of Energy (DOE) Pantex Plant, located in Amarillo, Texas.

Technology Approach: A carbon source consisting of soybean oil and lactic acid was injected into a perched aquifer to adjust the geochemical conditions and stimulate the resident bacteria to degrade RDX. A total volume of 315,800 gallons of carbon source containing 13,100 gallons of Newman Zone® amendment was injected in two events over a two year period.

Outcome: Total organic carbon concentrations decreased with a half-life of 19 to 48 days, while volatile fatty acid concentrations increased. RDX was reduced by 52% to 89% within 8 months in three of four monitoring wells. A temporary increase in nitroso derivatives (MNX, DNX, or TNX) followed by degradation of these products was observed. Following the second injection event, groundwater monitoring indicated RDX concentrations continued to decline to less than 97% of the baseline concentrations in the treated wells.

References

Seitz, S., Holmes, V., Marvin, B.K., Clayton, W.S. Biggs, T. 2007. Successful In Situ Reductive Biological Treatment of High Explosives. In Situ and On-Site Bioremediation—2007. Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium (Baltimore, Maryland; May 7–10, 2007).

APPENDIX F

IOWA ARMY AMMUNITION PLANT

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Remediation of RDX Groundwater Contamination through In Situ Bioremediation at Iowa Army Ammunitions Plant

Site Background: Iowa Army Ammunition Plant (IAAAP) is a 19,000-acre government-owned, production facility located in Middletown, Iowa. Historical production practices in the Brush Creek headwaters resulted in significant volumes of RDX-contaminated wash water entering a stream. A shallow alluvial aquifer has been contaminated by Brush Creek surface water at levels exceeding the health advisory level of 2 µg/L. Groundwater is generally 3 to 25 feet below ground surface with high groundwater flow velocities, estimated at 200 to 450 feet per year resulting in an RDX plume area over 26 million square feet (600 acres). Stagnation of the groundwater in a certain area has allowed higher concentrations of RDX to adsorb to a low permeability unit immediately below the shallow aquifer. Desorption from this unit has served as a long-term source of continuing contamination. Concentrations of RDX have historically been higher than 100 ppb in this area.

Technology Approach: The remediation approach for this site has three components: 1) an enhanced degradation system to actively treat RDX to less than 50 µg/L within 5 years, 2) MNA to reduce RDX to less than 2 µg/L within 40 years and 3) institutional and engineering controls. The objective of this project was to inject electron donor into the flow stagnation area to promote enhanced in situ bioremediation. Eleven injection wells and eight performance monitoring wells were installed at varying distances down gradient of the injection area (Figure F-1). Injections of sodium acetate were completed in Fall 2007.

Outcome: Results of the pilot study indicate that injection of sodium lactate can decrease RDX concentrations to below the target 50 µg/L (Table F-1).

Table F-1. Percent Decrease in RDX in Extraction and Monitoring Wells at Iowa Army Ammunition Plant

Well	Highest RDX concentration (µg/L) and Year	RDX Concentration (µg/L) in 2011	% Decrease in RDX concentration
EMW-02	81.4 (2009)	0.55	99
MW-309	192 (2006)	1.2	99
MW-123	6.3 (2008)	1.4	78
MW-408	6.5 (2008)	2.8	57
MW-510	24 (2002)	10.2	58
MW-513	26 (2002)	2.8	89

References

Caldwell, B., Amseth, R., Britto, R., Muffler, S. 2008. Four Case Studies of Enhanced Biodegradation of RDX, TNT, Chlorinated VOCs and Freon-113 in Similar Geology Using Identical Carbon Amendment. Remediation of Chlorinated and Recalcitrant Compound. Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2008).

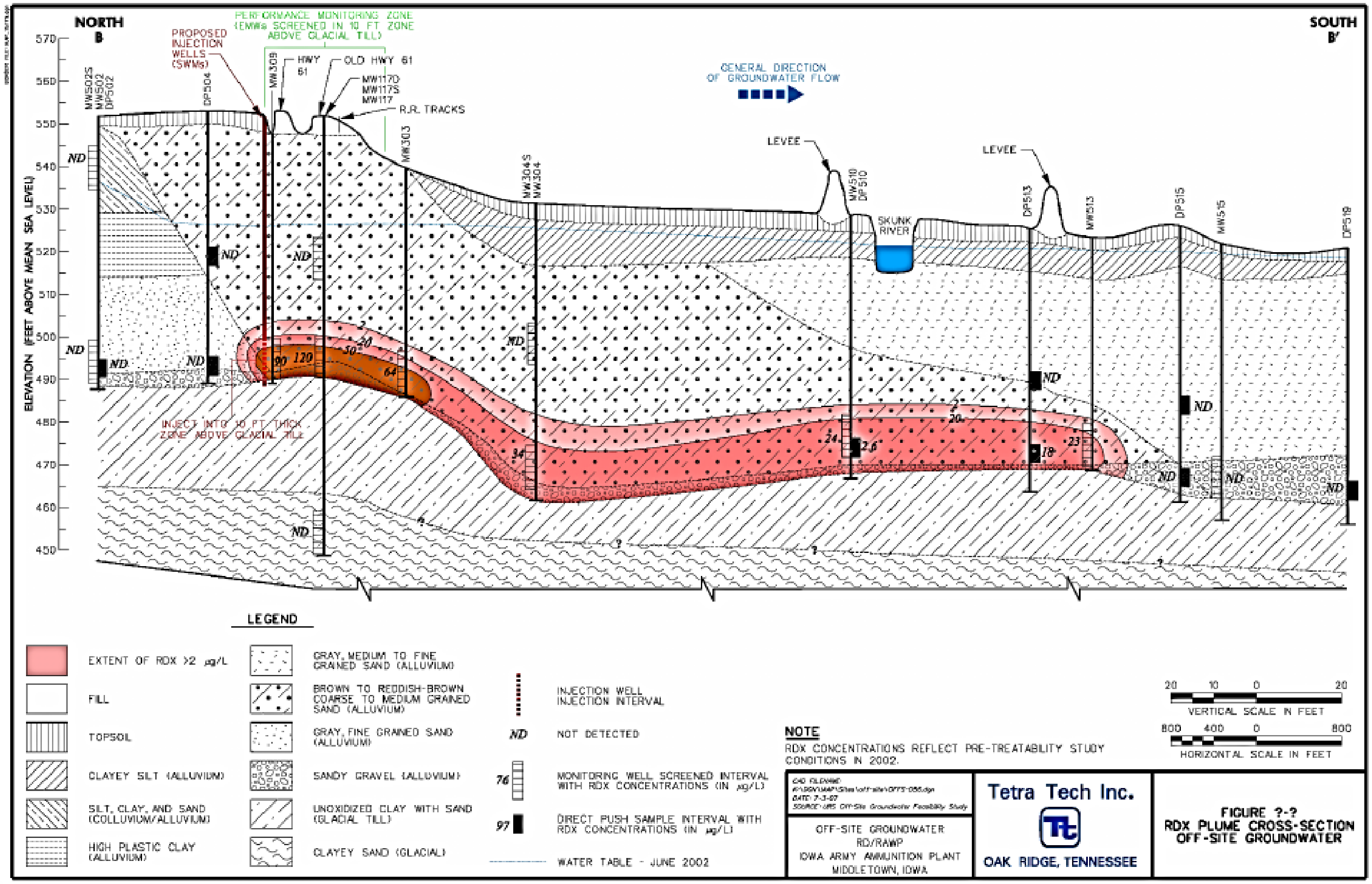

Figure F-1. Cross Section of the Iowa Army Ammunition Plant showing Location of Contamination, Pilot Study and Monitoring Wells.

APPENDIX G

NEBRASKA ORDNANCE PLANT

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Biologically Active Zone Enhancement (BAZE) for In Situ RDX Degradation in Groundwater at Nebraska Ordnance Plant

Site Background: The former Nebraska Ordnance Plant (NOP) was a load, assemble and pack facility, which produced bombs, boosters and shells, which led to RDX contamination. Prior to applying the treatment technology the RDX concentrations in the soil varied between 60 and 300 µg/L at the test site. RDX concentrations in ground water ranged from non-detect to 450 µg/L. The water table varies between 45-55 feet (14-17 m) bgs at the test site and contamination was found at depths between 55 and 75 feet (16.8 to 22.9 m) bgs.

Technology Approach: The overall objective of this demonstration was to validate the ability of sodium acetate injection to enhance indigenous biological activity in order to cost-effectively remediate RDX-contaminated groundwater. A recirculation system consisting of one extraction well and two injection wells (Figure G-1) was operated monthly for 8 to 10 hours each time for 12 months so that one pore volume of amended liquid was recirculated during each injection event. Eleven monitoring wells were installed to monitor the effect of the acetate injections with one being an upgradient monitoring well. The injection and monitoring wells were screened in the area of highest contamination to a depth of 60 linear feet (18.3 m) below ground surface.

Outcome: RDX concentrations were reduced by a range of 74% to 98% in the treatment area within 300 feet downgradient of the injection well (Table G-1).

Table G-1. RDX Concentration and Percent Reduction in Monitoring Wells at the Nebraska Ordnance Plant

Monitoring Well	Distance from Injection well	RDX Concentration (µg/L)		% Reduction
		Baseline	After 20 months	
1	100 LF upgradient	313	189	40%
4	100 LF downgradient	89.9	6.42	93%
7	150 LF downgradient	233	4.28	98%
10	300 LF downgradient	115	30.2	74%
11	500 LF downgradient	70	75.6	-8%

LF = linear foot

References

Wade, R., Davis, J.L., Wani, A.H., Felt, D. 2010. Biologically Active Zone Enhancement (BAZE) for In Situ RDX Degradation in Ground Water. ESTCP ER-0110 http://www.serdp.org/content/download/4116/62993/file/ER-0110-FR.pdf

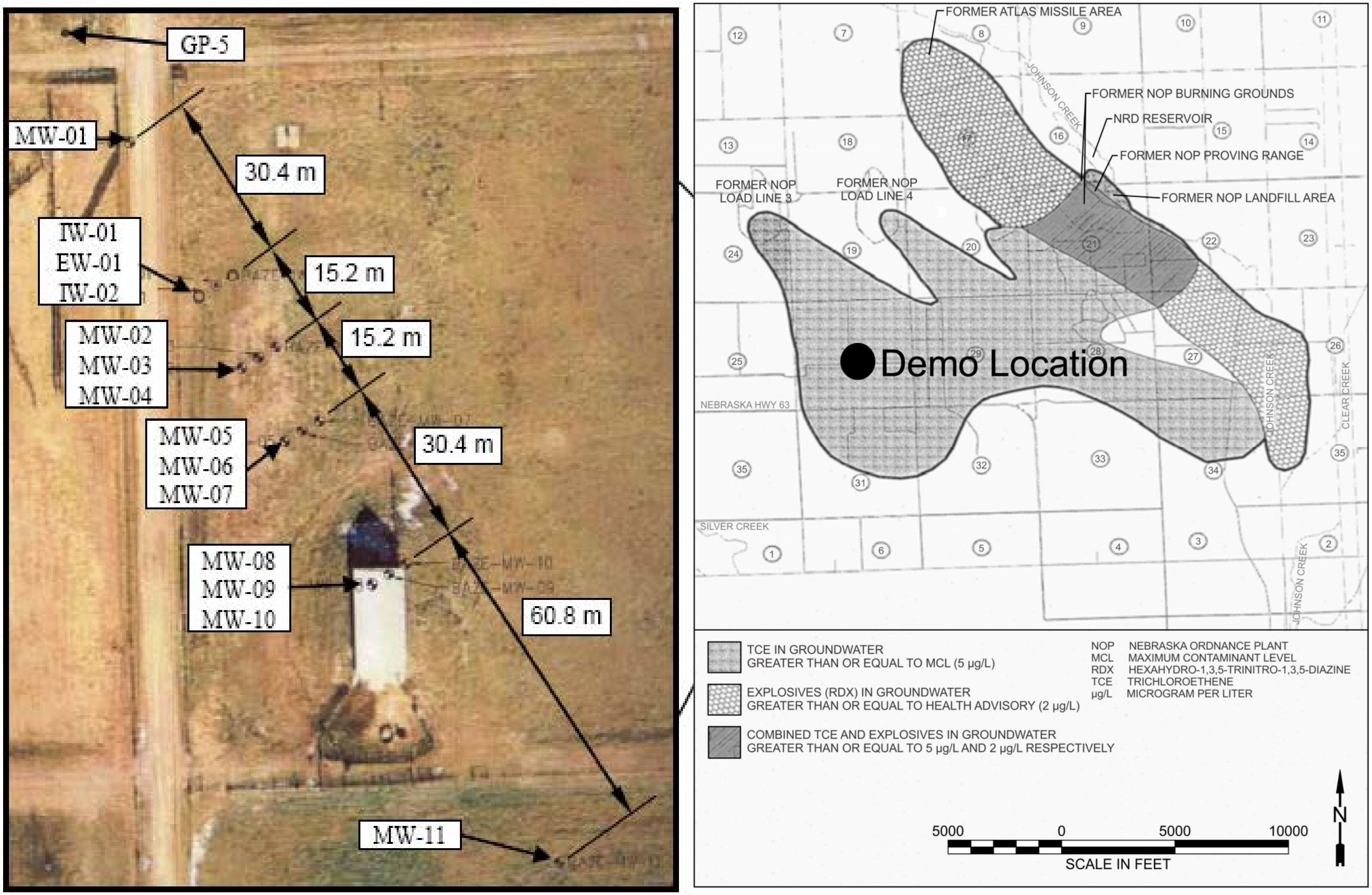

Figure G-1. Location of Pilot Study Injection, Extraction and Monitoring Wells

APPENDIX H

PUEBLO CHEMICAL DEPOT

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Treatment of RDX and HMX Plumes Using Mulch Biowalls at Pueblo Chemical Depot

Site Background: Pueblo Chemical Depot (PCD) was chosen as the site for a mulch permeable reactive barrier (PRB) technology field demonstration. The munitions contamination in groundwater at PCD emanates from the SWMU-17 area, where a TNT "Washout Facility" for shell packing operations was active from the 1940s until 1974. This site contained contamination of RDX and HMX in shallow groundwater (<30 ft below-ground-surface [bgs]). Baseline concentrations of RDX ranged from 2.68 ppb to 1.30 ppb in the Row R1A Wells upgradient of the proposed location of the biowall and 2.08 to 0.61 ppb in the Row R3A Wells downgradient of the location of the proposed biowall. All RDX concentrations were above the CDPHE regulatory threshold of 0.55 ppb**.** The HMX cleanup levels set by CDPHE is 602 ppb.

Technology Approach: The overall purpose of the pilot study was to demonstrate and validate the performance of a mulch PRB for remediating explosives contamination in groundwater. The mulch PRB was approximately 105 ft long and 2 ft thick and filled with a 33%:67% (volume:volume) pea gravel:mulch fill mixture. The mulch selected had a high cellulose-to-lignin ratio. Four rows of three monitoring wells each parallel to the PRB were used to test the performance of the PRB. One row was upgradient of the PRB. Three monitoring wells were also installed within the PRB. A 30-ft long and 2-ft thick soil-bentonite impermeable wall was tied into the eastern end of the biowall to serve as a hydraulic control for the eastern end of the mulch biowall and help to funnel groundwater through the biowall. The impermeable wall was oriented approximately 30-35 degrees north of the biowall orientation (Figure H-1).

Outcome: Elevated TOC concentrations were detected in the R2A, R3A monitoring wells with concentrations reaching as high as 807 mg/L in the R2A wells. Geochemical conditions indicated a reduction in redox conditions. Metals appeared to be mobilized by the spike in iron and arsenic in the downgradient wells. By 31 weeks after installation of the PRB, RDX concentrations were below detection in the R2A and R3A wells (Table H-1). After 15 months of operation of the biowall, no breakthrough of RDX was observed indicating that the wall was still operating.

Table H-1. Concentration of TOC and % RDX Removal After Installation of PRB

		Concentration of TOC and % RDX removal at intervals after installation of PRB							
		2.5 weeks		**31 weeks**		**7 months**		**15 months**	
Well Row	**Distance from PRB**	**Average TOC (mg/L)**	**Average RDX (% removal)**	**Average TOC (mg/L)**	**Average RDX (% removal)**	**Average TOC (mg/L)**	**Average RDX (% removal)**	**Average TOC (mg/L)**	**Average RDX (% removal)**
R1A	-15	0.5	0	0.5	0	0.5	0	0.5	0
R2A	10	536	92.73	7.37	93.18	4.2	93.8	5.33	96
R3A	25	188.27	38.08	5.17	93.18	2.93	93.8	2.6	96
R4A	40	1.13	54.75	2.43	86.36	2.03	84.07	2.03	89

References

Newell, C. 2008. Treatment of RDX & HMX Plumes Using Mulch Biowalls. ESTCP ER-0426. http://www.estcp.org/Technology/upload/ER-0426-C&P.pdf

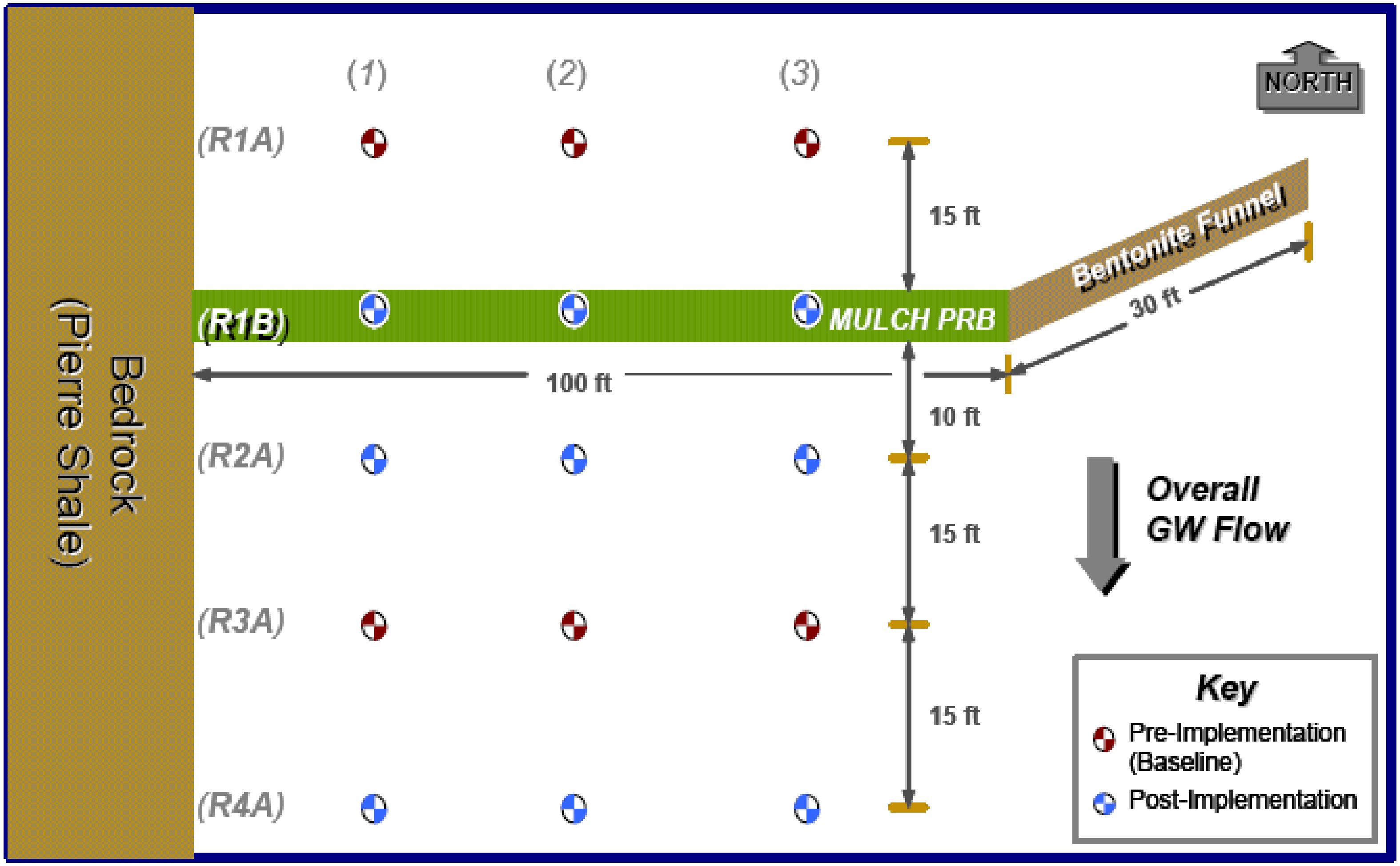

Figure H-1. Pilot Study Well Configuration at Pueblo Chemical Depot Mulch Biowall