NAVFAC RPM Tech Update: Munitions Constituents (MC) Attenuation Pathways

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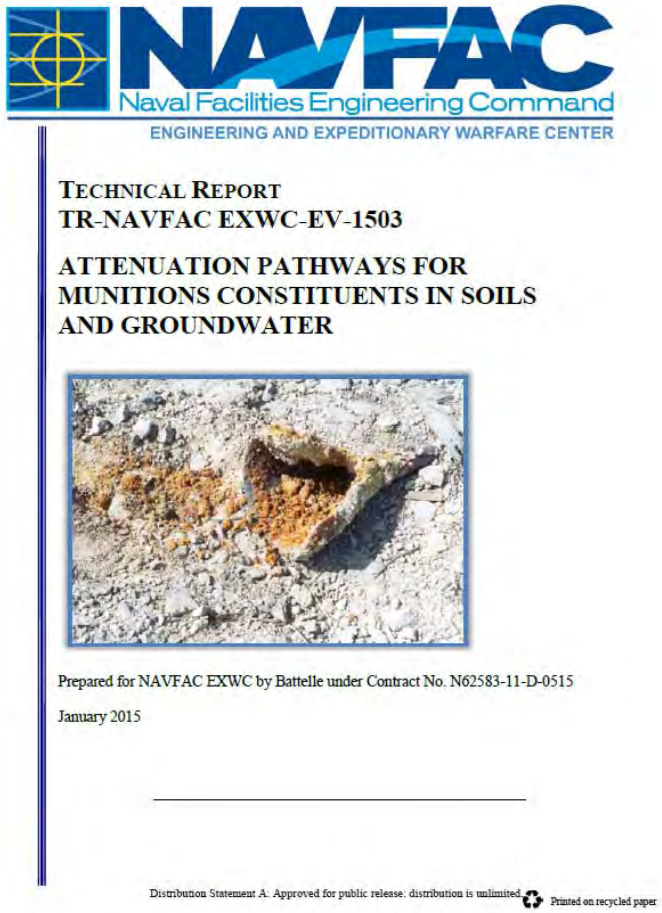
Overview of MC Issues

- Overview of MC issues
- Physical attenuation
- Chemical attenuation
- Biological attenuation
- Technology applications
- Case studies



NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

TECHNICAL REPORT
TR-NAVFAC EXWC-EV-1503

ATTENUATION PATHWAYS FOR MUNITIONS CONSTITUENTS IN SOILS AND GROUNDWATER

Prepared for NAVFAC EXWC by Battelle under Contract No. N62583-11-D-0515

January 2015

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Overview of MC Issues

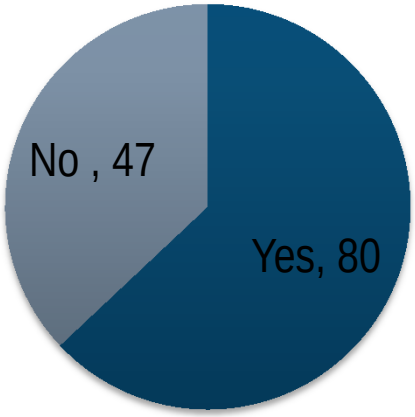
- MCs are "any materials originating from unexploded ordinance (UXO), discarded military munitions (DMM), or other military munitions, including explosive materials and emission, or breakdown elements such as ordnance or munitions."

- MC can be divided into three main categories:
  - Explosives
  - Propellants
  - Metals

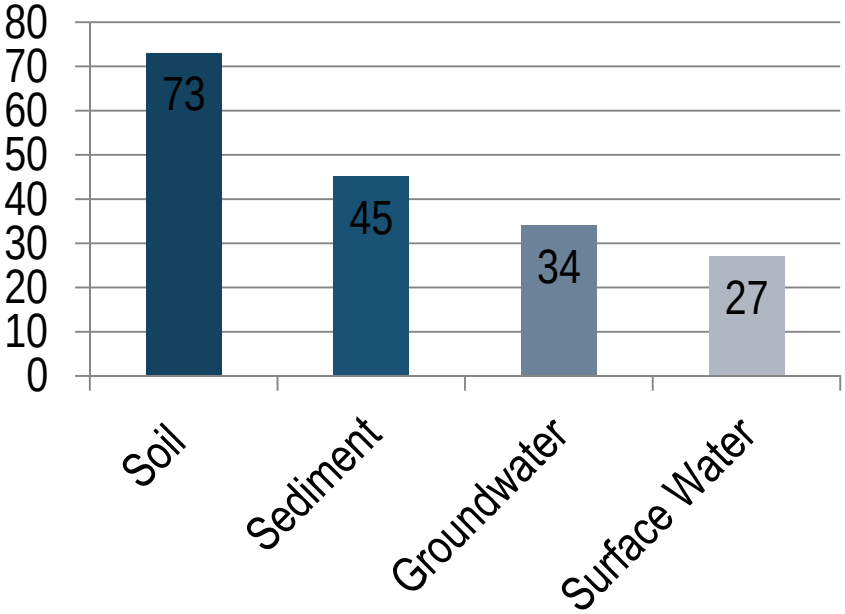
Compound	Uses	Formulations
Composition B	Artillery, mortar	60% military-grade RDX, 39% military grade TNT and 1% wax
Composition C4	Demolition explosive	91% military-grade RDX
Composition A4	40-mm grenades	Military-grade RDX
TNT	Artillery	Military-grade TNT
Composition H6	Bombs	Military-grade RDX, TNT;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

Overview of MC Issues

Respondent Manages a MRP Site with a Potential MC Issue



Media Potentially Impacted by MC (number of responses)



Overview of MCs Issues

Attenuation pathways applicable to MC in soil and groundwater

Pathway	Mechanism
Physical	Advection
	Diffusion
	Phase Transfer
Chemical	Sorption
	Abiotic Transformation
	Photolysis
Biological	Microbial Processes
	Biogeochemical Transformation

Physical Attenuation of MCs

- Understanding physical attenuation pathways is important in predicting the environmental fate of MC
- Dissolution is the first step in introducing organic energetics and other MC into the environment
- Results for neat explosives indicate the following trend for dissolution rates: TNT > HMX > RDX

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.

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.

Physical Attenuation of Energetics

- First step for energetics to enter the environment is through dissolution
  - TNT: TNT may remain as free product, dissolve into aqueous media, sorb onto particulates, or partition into dissolved organic matter
  - RDX: Once dissolved, can migrate through the vadose zone to underlying groundwater aquifers
  - HMX: Because of a low aqueous solubility and slow dissolution rate, tends to remain on the soil surface

Compound	Aqueous Solubility (mg/L)	Dissolution Rate (mg cm^{-2} s^{-1})
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

Major energetic compounds used by the DoD as propellants are solids at ambient temp and are deposited on ranges as particles of solid material. For explosives, dissolution is a major factor in determining the mobility of propellants.

Chemical Attenuation of MCs

- 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

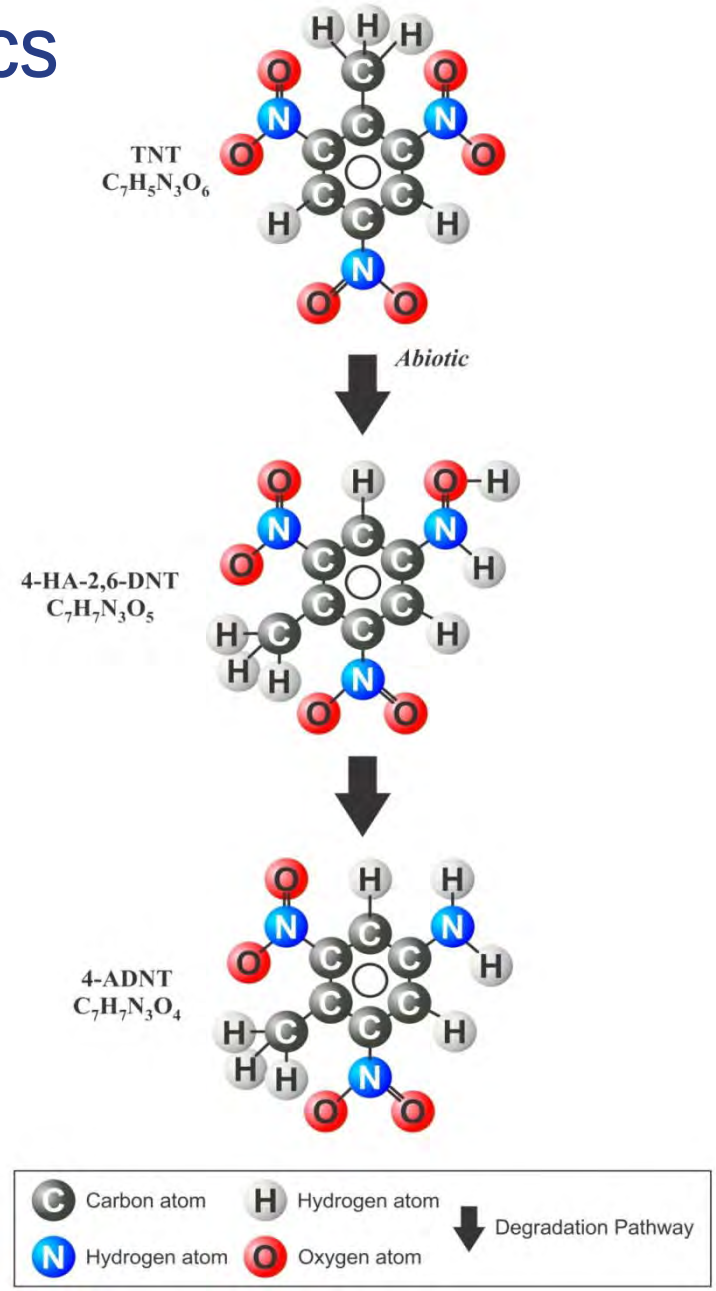
- Chemical transformations of contaminants that are not a direct result of biological activity.

Photolysis

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

Chemical Attenuation of Energetics

- Abiotic degradation of energetics occurs in the presence of ferrous iron
- 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)



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Chemical Attenuation of Metals

- Low pH favors sorption of ligands, while high pH favors sorption of metal ions
- Sorption is a significant attenuation pathway
- Longevity of this attenuation mechanism should be considered when evaluating the applicability of MNA for metals

Biological Attenuation of MCs

Biotic Transformation

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

Phytoremediation

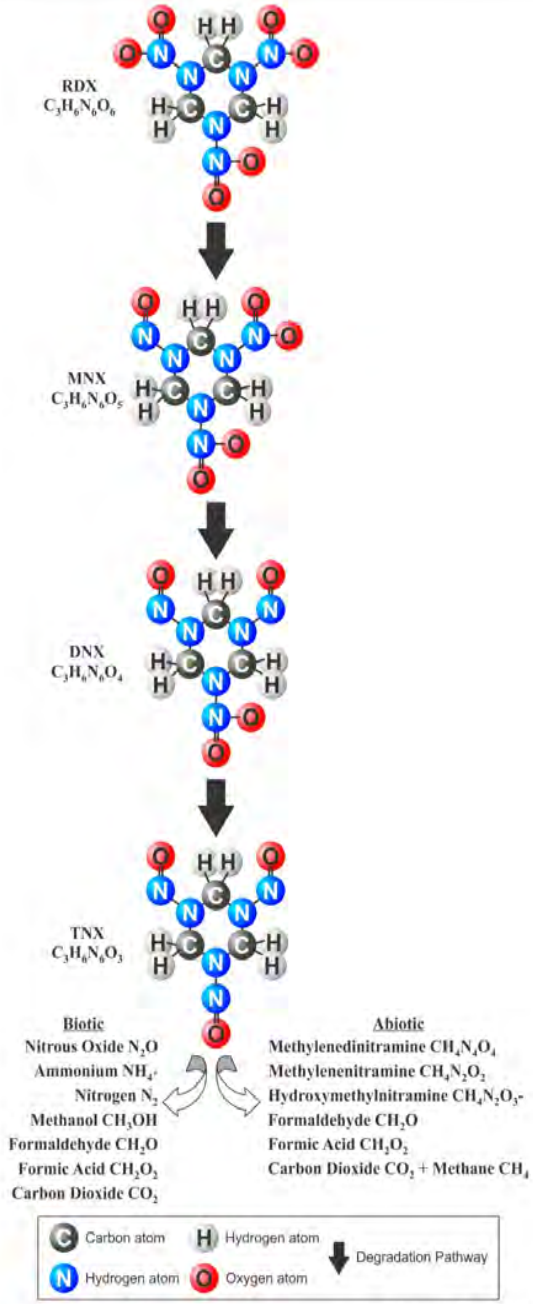
- Degradation, uptake or accumulation of contaminants by plants.

- Biological attenuation pathways are defined by the biologically mediated transformation or immobilization of MC

- Naturally occurring microorganisms (such as bacteria and fungi) can transform hazardous chemicals to either substances that are less toxic or completely benign

Biological Attenuation of MCs (cont.)

- Bacteria and fungi can transform hazardous chemicals to either substances that are less toxic or completely benign
- RDX biotransformation occurs via co-metabolic processes under anaerobic conditions in a stepwise process by the sequential reduction of its three nitro groups
  - hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX) is formed
  - hexahydro-1,3-dinitroso-5-nitro-1,3,5- triazine (DNX) is produced
  - all three nitro groups are reduced and hexahydro1,3,5-trinitroso-1,3,5-triazine (TNX) is formed



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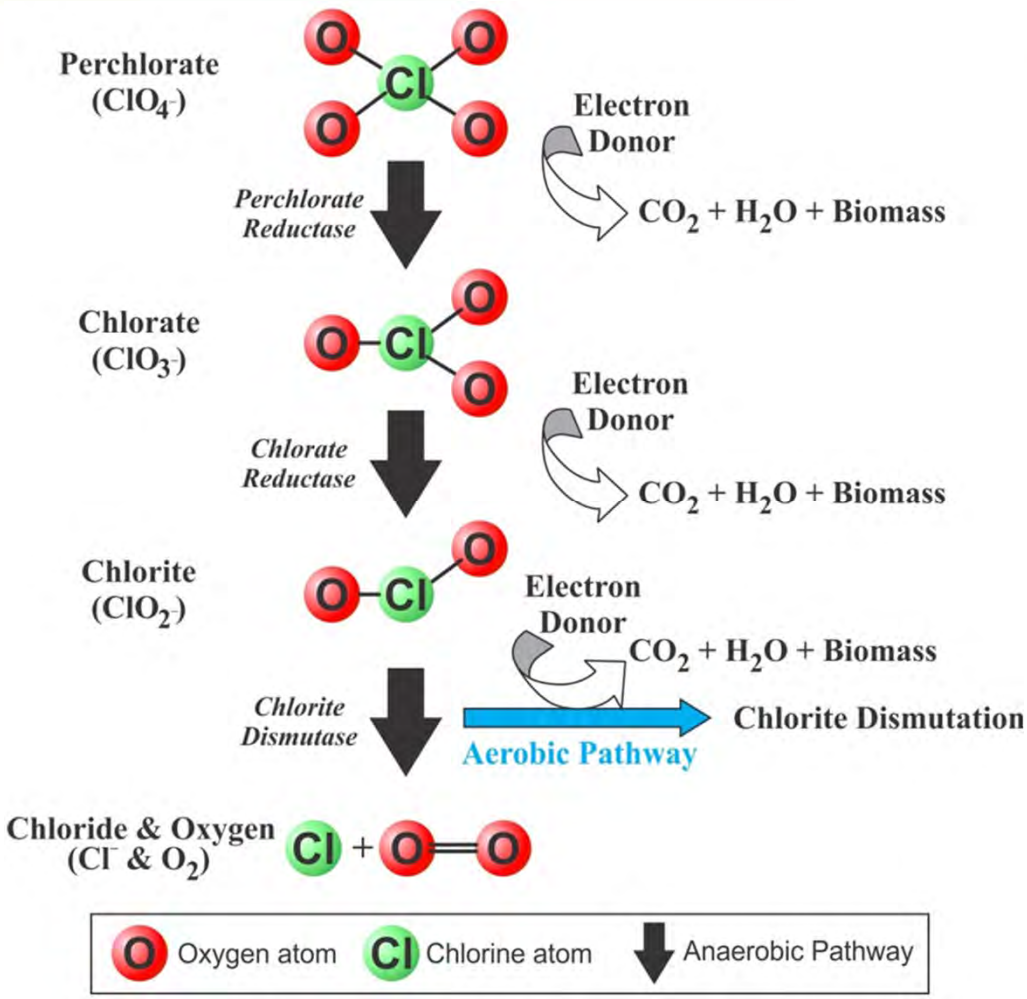
Biological Attenuation of Propellants

- Propellants are susceptible to biotransformation
- Perchlorate degradation via <u>perchlorate reductase</u> and <u>chlorite dismutase</u> reactions results in production of less toxic compounds: water, carbon dioxide and chloride
- Perchlorate degradation is governed by anaerobic bacteria from genera of *Dechloromonas* and *Azospira*



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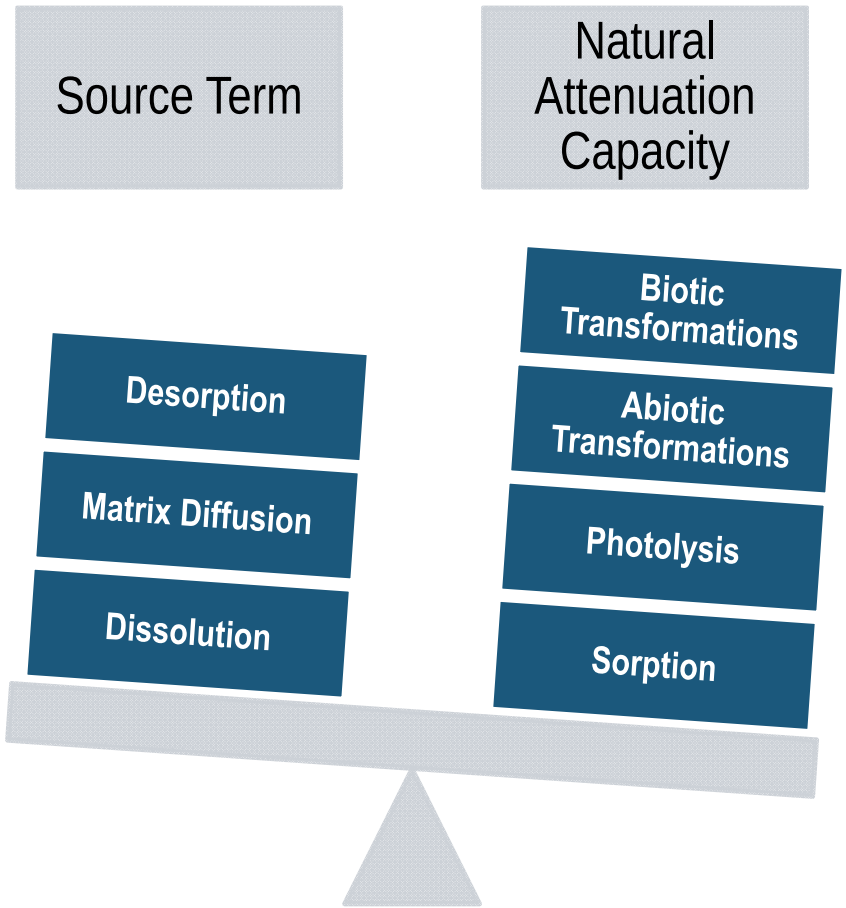
Technology Applications



- The effectiveness of the NAC processes must be confirmed for MNA to be a timely and realistic remedial strategy
- This confirmation involves:
  - Identification of favorable conditions for MNA
  - Documentation of attenuation pathways that mitigate fate and transport processes

Technology Applications (cont.)

LOE One: Plume Stability and Geometry

Use historical data to evaluate trends in the nature and extent of COCs 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

LOE Two: Geochemical Conditions

Collect and evaluate data for indirect evidence of COC attenuation

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

LOE Three: Microbial Indicators

Monitor for direct evidence of specific transformation pathways

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

Line of Evidence Process for Evaluating Whether MNA is Appropriate for a Site

Case Studies

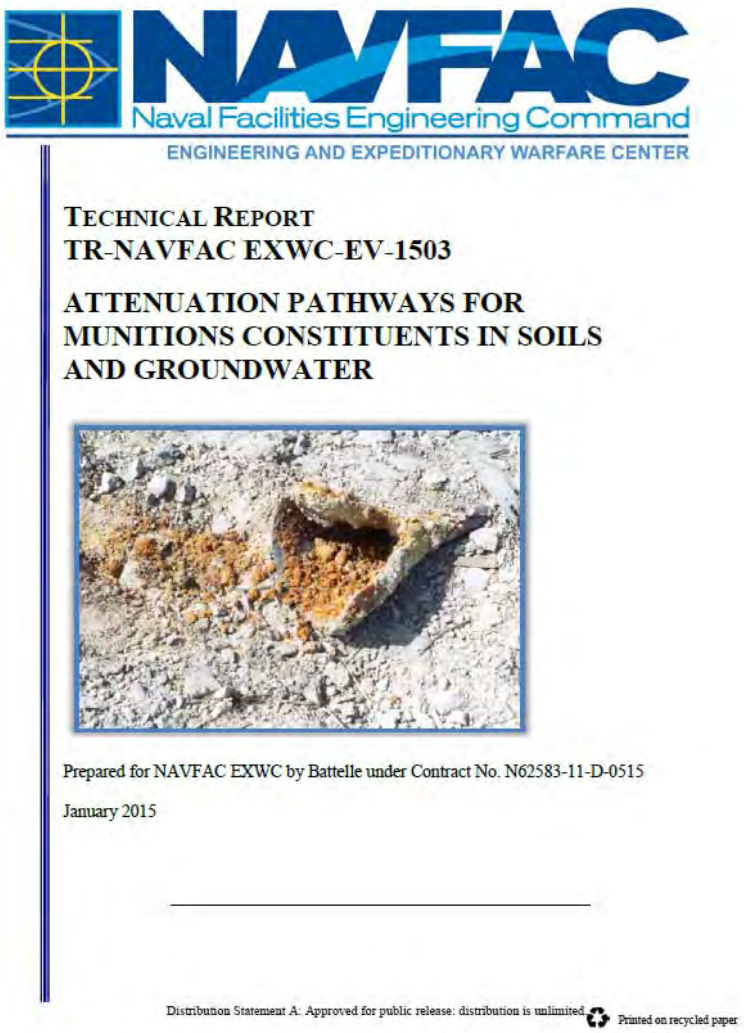
Site	Contaminant	Technology	Outcomes
Naval Base Kitsap-Bangor Site F	RDX, TNT, 2,6-DNT, 2,4-DNT	MNA and biostimulation	• RDX concentrations decreased in the microcosm study under Mn-reducing conditions • MNA was not possible to be implemented • A push-pull pilot was planned that involved the injection of a non-reactive tracer and a reactive carbon substrate
Umatilla Chemical Depot	RDX	Bioaugmentation	• Lab column tests suggest bioaugment as an effective aerobic remediation strategy for RDX-contaminated groundwater • Next steps include a series of push-pull tests to quantify rate and extent of RDX removal
Active Navy Range	RDX, HMX, and perchlorate	Passive emulsified oil biobarrier	• Perchlorate biodegraded rapidly, followed by RDX and then HMX • Emulsified oil biobarrier with pH buffering can be a viable alternative to treat perchlorate and explosives in shallow groundwater
Picatinny Arsenal Site 157	RDX, HMX, TNT, 2,4-DNT, and 2,6-DNT	Biostimulation with cheese whey	• Within 62 days after the injection, TNT concentrations declined to below analytical detection limits • Within 148 days after the initial injection of cheese whey, RDX <5 µg/L

Case Studies

Site	Contaminant	Technology	Outcomes
Pantex Plant, Amarillo, TX	RDX	Biostimulation with soybean oil and lactic acid	• RDX was reduced by 52% to 89% within 8 months in and continued to decline to 97% of the baseline concentrations in the treated wells following the second injection.
Iowa Army Ammunitions Plant	RDX	EISB	• Results of the pilot study indicate that injection of sodium lactate can decrease RDX concentrations to below the target 50 µg/L
Nebraska Ordnance Plant	RDX	Biostimulation with sodium acetate	• RDX concentrations were reduced by a range of 74% to 98% in the treatment area within 300 feet downgradient of the injection well
Pueblo Chemical Depot	RDX, HMX	Mulch permeable reactive barrier	• After 15 months of operation of the biowall, no breakthrough of RDX was observed indicating that the wall was still operating.

Conclusions

- Visit the NAVFAC ERB Web site for more information
- View the full document on attenuation pathways for MCs
- Other useful MRP technical resources available on MRP Web Page



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