**Report Title:** Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection

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**Abstract:**

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Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection

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Agenda

• Introduction
• Technology Description
• Carbon Source Comparison
• BioBarrier
• SE Hot Spot 1
• SE Hot Spot 2
• SE Hot Spot 3
• Conclusions
Introduction

- West Virginia Ordnance Works (WVOW) was a TNT manufacturing facility from 1942-1945
- The WVOW site is located on the east bank of the Ohio River, six miles north of Point Pleasant, WV
- WVOW included 12 TNT production lines
- TNT production resulted in soil and groundwater contamination
- Complete decontamination was not achieved, so portions were transferred to the state of West Virginia for use as a wildlife management reserve
- The site is now the McClintic Wildlife Management Area
WVOW TNT Manufacturing Area
EISB Study Area

LEGEND

EISB GROUNDWATER STUDY AREAS

FIGURE 1-1
SITE LOCATION MAP

THE EISB TREATABILITY STUDY
WORK PLAN
WEST VIRGINIA ORDNANCE WORKS
MASON COUNTY, WEST VIRGINIA

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Introduction (continued)

• Four study areas; Seep Area, SE Hot Spot 1, SE Hot Spot 2, and SE Hot Spot 3

• Primary chemicals of concern (COCs) include: 2,4,6-Trinitrotoluene (TNT), 2,4-Dinitrotoluene (2,4-DNT), 2,6-DNT, 2-Amino-4,6-DNT (2ADNT), and 4-Amino-2,6-DNT (4ADNT)

• Enhanced in situ bioremediation (EISB) was selected for field-scale evaluation

• Three different carbon sources are being compared for their effectiveness: SRS™ - Emulsified Vegetable Oil (Terra Systems, Inc.), HRC-X™ (Regenesis), and LactOil™ (JRW)

• The study is focused only on groundwater treatment
• Soil Retention Tests were performed to confirm adequate injection solution concentration
• Slug tests were performed to determine hydraulic conductivity and groundwater flow rate
• Baseline sampling was performed prior to injection of the carbon source in the study areas
• Nine wells and four seep locations were sampled
• Performance sampling was conducted quarterly after injection
• Sampling will continue on a quarterly basis for the first year followed by semi-annual sampling for a second year
• A comprehensive evaluation report will be prepared at the conclusion of the study
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Technology Description

• EISB is a process where a reducing environment is created for indigenous microorganisms

• A carbon source is injected into the aquifer, which provides an energy source for indigenous microorganisms

• As carbon is consumed, O₂ is depleted until the system becomes anaerobic

• After O₂ is consumed, anaerobic fermentation begins and H₂ is released into the system

• H₂ is consumed in competing reactions – reduction of electron acceptors and reduction of nitroaromatics
Carbon Source Degradation and TNT Biodegradation Pathway

- Carbon source → water → Lactic acid
- Lactic acid → fermentation → propionic and pyruvic acids
- Propionic and pyruvic acids → acetic acid → methane
- TNT → 2ADNT, 4ADNT
- 2ADNT, 4ADNT → 2,4-Diamino-6-Nitro
- 2,4-Diamino-6-Nitro → 2,6-Diamino-4-Nitro
- 2,6-Diamino-4-Nitro → TAT
- TNT → H₂
- H₂ → binding to soil
Carbon Sources Used

• SRS™, Emulsified Vegetable Oil was used for the Seep Area (BioBarrier) and SE Hot Spot 1
• HRC-X™ was used for SE Hot Spot 2
• LactOil™ was used for SE Hot Spot 3
Carbon Source – SRS

- **SRS™, Emulsified Vegetable Oil**
  - SRS is a slow release substrate comprised of a mixture of emulsified oil (50-70%) and sodium lactate (< 5%) manufactured by Terra Systems, Inc.
  - Fast-release lactate creates reducing conditions soon after injection to kick-start the bioactivity
  - Emulsified oil dissolves slowly, releasing hydrogen to maintain reducing conditions, providing a longevity of three to five years
  - Emulsified oil is immobile after adsorbing to soil particles
  - SRS has the consistency of milk and comes ready for injection
  - Applied at the Seep Area to form long lasting BioBarrier and at SE Hot Spot 1, which has a high groundwater flow velocity
Carbon Source – HRC-X

- Hydrogen Release Compound (extended release formula)
  - A proprietary polylactate ester manufactured by Regenesis Bioremediation Products, Inc.
  - A viscous material that slowly releases lactic acid
  - High viscosity at ambient temperature – needs to be heated for injection
  - Relatively immobile and does not migrate; ideal for aquifers with steep hydraulic gradients and/or high flow velocities
  - Extended release formula remains active for multiple years
  - Applied at SE Hot Spot 2, which has a high groundwater flow velocity
  - Provides a side-by-side comparison with SRS at SE Hot Spot 1
Carbon Source – LactOil

- A mixture of ethyl lactate (40%) and vegetable oil (40%) manufactured by JRW

- Ethyl lactate generates more metabolic acids per unit weight than sodium lactate. It has the potential to reduce pH, thus requiring pH buffering

- One micrometer oil droplet compared to 5-10 micrometers in common emulsified oil, moves through pore space more easily, but also has a shorter active life

- Applied at SE Hot Spot 3 where COC concentrations are lower and longevity is not as critical
TNT Concentration Trends to Date

PRE-INJECTION, Q-1, Q-2

No definitive trend

DOWNWARD TREND

DOWNWARD TREND

UPWARD TREND

UPWARD TREND
Seep Area – BioBarrier Installation

- SRS injected in a linear pattern perpendicular to groundwater flow
- Forms a long-lasting BioBarrier to intercept groundwater flow and prevent downgradient migration of COCs to the seeps
- BioBarrier consists of 72 injection points with a 10-foot spacing
- A total of 32,791 lbs of SRS was mixed with potable water to provide 20,000 gallons of solution for injection
- 197 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution (35% of available pore volume) was injected at each point
- A target injection interval of 10-18 feet below ground surface was adjusted 10 feet deeper for a few points based on lithology
- Surfacing occurred at several injection points due to local lithologic variations
Seep Area – BioBarrier Installation

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BioBarrier SRS Mixing and Injection
BioBarrier Installation and Impact at the Seep Area
BioBarrier Results – Within the Injection Array

- Water samples collected prior to injection and every three months after injection.
- TNT series compounds decreased to below detection limit of 20 ug/L three months after injection.
- ORP dropped from 326.7 to -66.4 mV, DO from 9.7 to 0.72 mg/L, sulfate from 59.9 to 1.2 mg/L, and methane increased from 1.4 to 580 mg/L.
BioBarrier Results – Within the Injection Array

- TOC increased to 4,800 mg/L, and gradually decreased to 1,600 mg/L
- Metabolic acids increased to 820 mg/L, gradually decreasing
BioBarrier Results – Downgradient Seeps

- More than 90% reduction of TNT series immediately downgradient at the seep location (WCASW-002)
- Further downgradient at seep location WCASW-003, increasing trend of degradation intermediates including 2ADNT, 4ADNT.
BioBarrier Result –
Downgradient TNTGW-055

- Increasing concentrations of nitroaromatics observed at TNTGW-055
BioBarrier Result – Downgradient TNTGW-057

- No significant impact observed in the first two quarterly sampling events at TNTGW-057
Other Surface Water Samples

TNTSW-011 -- TNT Series

Sampling Time

Concentration, ug/L

2,4,6-TNT
1,3,5-TNB
4ADNT
2ADNT
2,4-DNT
2,6-DNT

8/4/10
11/11/10
2/21/11

TNTSW-010 -- TNT Series

Concentration, ug/L

2ADNT
4ADNT
2,4,6-TNT

8/3/10
11/10/10
2/21/11

Sampling Time
SE Hot Spot 1 Area

- Located upgradient of the western portion of the BioBarrier
- High TNT concentration (156 ug/L), and relatively high groundwater flow rate (0.5 feet/day) → suitable for SRS

- A total of 17,867 lbs of SRS was mixed with potable water to provide 11,400 gallons of solution for injection at 37 points
- 107 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution was injected at each point
SE Hot Spot 1 SRS Injection

- 250-foot × 50-foot injection grid
- ~200 feet upgradient of the western portion of the BioBarrier (~ one year of groundwater travel time)
- Total of 37 injection points aligned in three parallel rows
- Target depth interval of 10-18 feet below ground surface, adjusted accordingly based on changes in elevation
SE Hot Spot 1 Injection
SE Hot Spot 1 Injection
SE Hot Spot 1 Results – Within the Injection Array

- Water samples collected prior to injection and every three months after injection
- TNT series compounds decreased to below detection limit of 20 ug/L
- ORP and sulfate decreased; methane generated (592 mg/L)
SE Hot Spot 1 Results – Within the Injection Array

- TOC have increased from 1.1 mg/L to 6,400 mg/L
- Metabolic acids have increased to 1,380 mg/L
Increase of some TNT series compounds – a slug of contaminated groundwater was likely pushed toward this monitoring well during BioBarrier injection.
SE Hot Spot 2 Area

- Located upgradient of the central portion of the BioBarrier
- High TNT concentration (156 ug/L) and relatively fast groundwater flow (0.5 feet/day)
- HRC-X selected for this area → side-by-side comparison with SRS (SE Hot Spot 1)
- A total of 810 lbs of HRC-X was injected through 24 points (~34 lbs for each point)
- HRC-X was heated to 160°F in a hot water bath to reduce viscosity prior to injection; no dilution required
SE Hot Spot 2 HRC-X Injection

- A 100-foot × 50-foot injection grid
- ~180 feet upgradient of the BioBarrier (~ one year of groundwater travel time from SE Hot Spot 2 to BioBarrier)
- Total of 24 injection points spaced on 10-foot centers, aligned in four rows based on accessibility, in a staggered configuration
- Target depth interval of 3-8 feet below ground surface at the lowest elevation points, adjusted accordingly at higher elevations
Heating HRC-X
SE Hot Spot 2 Injection
SE Hot Spot 2 Results – Downgradient Monitoring Well

- Decrease in TNT from 176 to 34.3 ug/L
- Steady decrease in ORP from 206.9 mV to -2.4 mV
- Slight decrease in sulfate in second quarterly post-injection sample
SE Hot Spot 3 Area - LactOil Injection

• Soil treatment (blending/removal) was conducted previously in this area

• Groundwater flow velocity 0.58 feet/day at nearby well TNTGW-019

• Relatively low TNT concentration (85 ug/L) – no critical requirement on carbon source longevity

• LactOil with relatively short life-span was selected as the carbon source

• A total of 5,714 lbs of LactOil was mixed with potable water to produce 3,500 gallons of solution for injection through 18 points (~200 gallons at each point)

• 34 lbs of yeast extract was added as a nutrient

• 300 lbs of NaHCO₃ added as a pH buffer
SE Hot Spot 3 LactOil Injection

- A 80-foot × 80-foot injection grid
- Sixteen injection points in four staggered rows
- Due to surfacing at some points, two points were added in the field to achieve the design injection volume
- Target depth interval of 10-15 feet below ground surface at the lowest elevation points was adjusted accordingly at the higher elevation points
SE Hot Spot 3 Injection
SE Hot Spot 3 Results – Within the Injection Array

- TNT series compounds decreased to below detection limit of 0.20 ug/L
- ORP and DO decreased; TOC and methane increased
- No metabolic acids detected to date
SE Hot Spot 3 Results – Downgradient Monitoring Well

- No downgradient impact six months after injection
Comparing Performance of SRS, HRC-X and LactOil

Both SRS and LactOil decreased TNT series compounds to below detection limits within the injection grids.

Down-gradient of HRC-X injection grids showed a steady decrease of TNT series in the first two quarterly samples.

All three substrates successfully created reductive conditions at the designed dosing rates.

LactOil generated a spike of methane and lowest ORP—short bloom of electron donors.

SRS generated two orders of magnitude higher TOC and metabolic acids—long-lasting slow release carbon source.

### Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SRS (TNTTW-010 Biobarrier)</th>
<th>TNTGW-016 SE Hot Spot 1</th>
<th>HRC-X (TNTGW-056 SE Hot Spot 2)</th>
<th>LactOil (TNTGW-052 SE Hot Spot 3)</th>
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<tr>
<td>Sulfate, mg/L</td>
<td>1.2</td>
<td>3.8</td>
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<td>0.9</td>
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<td>Methane, µg/L</td>
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<td>592</td>
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<td>ORP, mV</td>
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<td>DO, mg/L</td>
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<td>Butyric Acid, mg/L</td>
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<td>607</td>
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</tbody>
</table>
Conclusions

• EISB is shown to be effective for treatment of ground water contaminated with nitroaromatics

• Carbon source selection was based on several factors
  – Hydraulic gradient and ground water flow velocity
  – Contaminant concentrations

• The designed dosing rates of carbon sources were able to create reducing conditions within the injection zones
  – Negative ORP values
  – Decreasing DO and sulfate
  – Increasing methane and metabolic acids
  – Contaminants decreased to below detection limits

• No downward trend in concentration observed downgradient of SRS injection area in the first two quarterly sample rounds

• Downward trend in concentration observed at the seep location nearest the BioBarrier, and down gradient of the HRC-X treatment area

• Pilot-scale field application provides valuable information for carbon source selection and full-scale design parameters
Questions?