Benzene Removal by a Novel Modification of Enhanced Anaerobic Bioremediation


October 16, 2013
Outline

1. Introduction
2. Study Site
3. Methods
4. Results
Introduction

- Petroleum hydrocarbon (PHC) release into soil and groundwater occurs at every stage of oil extraction, refinement, storage, transportation, and disposal.
- Anaerobic subsurface environmental development:
  - Fast oxygen consumption rate
  - Slow oxygen supply rate
- Enhanced anaerobic bioremediation (EAB) - a practical and cost-effective PHC remediation method:
  - Electron donor: PHC
  - Electron acceptor: nitrate or sulfate
Introduction

• EAB is effective for the removal of toluene, ethylbenzene, and xylenes; however, benzene is particularly persistent.

• Phosphorus usually controls the PHC biodegradation process.

• Precipitation of inorganic phosphorus (phosphorus source for organism growth), making phosphorus unavailable to the microbes.

• Organic phosphorus is much more mobile in soil than inorganic phosphorus; however, length of time for organic phosphorus to release orthophosphate may be significant.
Introduction

• A novel EAB approach was developed, which consisted of injecting nitrate and organic phosphorus into the subsurface followed by the addition of non-activated persulfate.

• Injected persulfate would be capable of breaking down organic phosphorus into orthophosphate.

• Released orthophosphate might stimulate benzene removal through promoting nitrate reduction and/or sulfate reducing bacterial (SRB) activities.
Methods

• Stage 1 was completed in November 2009 and consisted of the injection of approximately 42,000 L of water, 1,400 kg of potassium nitrate (KNO₃), and 219 kg of triethly phosphate (TEP, (C₂H₅)₃PO₄).

• Stage 2 was completed in September and October 2010 and consisted of injecting approximately 13,100 kg of non-activated sodium persulfate (Na₂S₂O₈) mixed with approximately 49,000 L of water.
Methods

- Soil – Direct push drilling methods were used to evaluate attenuation rates of absorbed-phase hydrocarbons.
- Groundwater – Low flow sampling techniques were used to evaluate changes in groundwater conditions at dedicated performance monitoring wells RW1 to RW8. Groundwater samples were analyzed for:
  - PHC, general chemistry and metal analyses
  - Compound specific isotope analysis (CSIA)
  - Microbial quantitative polymerase chain reaction (qPCR)
  - Microbial denaturing gradient gel electrophoresis (DGGE) and 16S ribosomal RNA (16S rRNA)
Results

Benzene Removal from Groundwater

Nitrate and TEP Injection
Persulfate Injection

Benzene Concentration (mg/L)

Date

11/02/09 11/26/09 02/17/10 05/04/10 06/29/10 10/03/10 04/11/11

Criterion = 1.8 mg/L
Results

Removal from Benzene Groundwater

BH10-01
BH10-02
BH10-03
BH10-04
BH11-01
BH11-02
BH11-03
BH11-04

RE=92.8%
RE=87.7%
RE=89.2%
RE=75.9%

BH10-01
BH10-02
BH11-01
BH11-02

0.01
0.03
0.093
0.491

RE=75.9%
BH11-02
BH10-02

Benzene, mg/kg

Organic Vapour Measurement (ppm)

Depth (m)

0 2000 4000 6000 8000 10000

0 1000 2000 3000 4000 5000

0 2000 4000 6000 8000 10000
Results

Nitrate Utilization

<table>
<thead>
<tr>
<th>Date</th>
<th>RW1</th>
<th>RW3</th>
<th>RW7</th>
<th>RW8</th>
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<tbody>
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</table>

Nitrate and TEP Injection

Persulfate Injection

Nitrate Concentration (mg/L)
Results

Phosphorus Uptake

![Graph showing phosphorus uptake over time with dates and concentration levels.](image)

- **Nitrate and TEP Injection**
- **Persulfate Injection**

**Orthophosphate Concentration (mg/L)**

- **Date**
  - 11/02/09
  - 11/26/09
  - 02/17/10
  - 05/04/10
  - 06/29/10
  - 10/03/10
  - 04/11/11

**Organic Phosphorus**

- **RW1 Organic-P**
- **RW3 Organic-P**
- **RW7 Organic-P**
- **RW8 Organic-P**

**Graph Legend**

- **RW1**
- **RW3**
- **RW7**
- **RW8**

**Stantec**
Results
Sulfate Utilization

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[S²⁻] = 0.0107 mg/L
[S²⁻] = 0.0157 mg/L
[S²⁻] = 0.0266 mg/L
[S²⁻] = 0.145 mg/L
[S²⁻] = 0.0157 mg/L
[S²⁻] = 0.0107 mg/L
## qPCR Analytical Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>bssA</th>
<th>DSR</th>
<th>nirS</th>
<th>nirK</th>
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<tbody>
<tr>
<td>RW7</td>
<td>&lt;9.00E-1</td>
<td>7.00E-01</td>
<td>2.92E+03</td>
<td>1.96E+01</td>
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<td>RW8</td>
<td>1.11E+02</td>
<td>1.41E+04</td>
<td>2.22E+01</td>
<td>2.15E+04</td>
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<tr>
<td>MW08-07</td>
<td>1.80E+00</td>
<td>1.12E+03</td>
<td>5.03E+05</td>
<td>6.07E+04</td>
</tr>
</tbody>
</table>
Results

DGGE Profile

- RW7: May 2010, April 2011
- RW8: May 2010, April 2011
- MW08-07: April 2011

A (Firmicutes)
B (Algoriphagus spp.)
C (Comamonadaceae)
D (Treponema spp.)
E (Desulfovibrio spp.)
Results
Isotopic Analytical Results

\[ Y = 30.1 + 0.027X, \quad R^2 = 0.88 \]
Isotopic Analytical Results

$^{2}\text{H}_{\text{benzene}} = 3.53^{13}\text{C} + 11.13$, $R^2 = 0.93$

$^{15}\text{N}_{\text{nitrate}} = 0.7^{18}\text{O} - 2.19$, $R^2 = 0.96$

$^{34}\text{S}_{\text{sulfate}} = 0.31^{18}\text{O} + 1.25$, $R^2 = 0.77$
Results

Schematic Process of Benzene Removal

NO\textsubscript{3}^-(electron acceptor) and macronutrient

TEP ((C\textsubscript{2}H\textsubscript{6})\textsubscript{3}PO\textsubscript{4})

 Persulfate Oxidation

S\textsubscript{2}O\textsubscript{8}^2-

Persulfate Decomposition

SO\textsubscript{4}^2-(electron acceptor)

Denitrifying Bacteria

Algortiphagus Spp.
Comamonadaceae (Family)
Firmicutes (Phylum)

TEP Mineralization

PO\textsubscript{4}^3-(macronutrient)

Phosphate Uptake

Sulfate Reducing Bacteria

Algortiphagus Spp.
Treponema Spp.
Desulfovibrio Spp.

Benzene

Nitrate Reduction

NO\textsubscript{2}^-, NH\textsubscript{3}, and N\textsubscript{2}

Benzene Biodegradation

CO\textsubscript{2}+H\textsubscript{2}O

Sulfate Reduction

S\textsuperscript{2}^{-}
Conclusion

• Removal of PHC, including benzene, in the subsurface was optimized through a novel EAB approach integrating nitrate and TEP injection with the subsequent addition of non-activated persulfate.

• Injected persulfate broke down organic phosphorus into inorganic orthophosphate, thereby stimulating nitrate and sulfate reduction.

• CSIA analysis provided further direct evidence for the occurrence of PHC degradation by nitrate and sulfate reduction.

• Dominant EAB mechanism to date appears to be nitrate reduction, although sulfate reduction also appeared to play an important role on portions of the study site.
Thank you