Multi-Component Treatment Strategy for Chlorinated Ethene and Chlorinated Benzene DNAPL Source Area at Hunters Point Shipyard

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Background

• Hunters Point Naval Shipyard (HPNS) in San Francisco CA, Building 134 was historically used for machining operations and contained a degreaser and a sump for separating chlorinated solvents from sludge.

• Contaminants, primarily chlorinated benzenes and ethenes were released into the subsurface as dense non aqueous phase liquid (DNAPL).

• Conducted a treatability study (TS) to evaluate multi-component treatment strategy for the contaminant source area and dissolved phase plume.
HPNS Treatability Study Area

Former degreaser/sump

Building 134
Problem: Complex Mix of Contaminants in Groundwater and Low-Permeability Soils

Building 134 source area containing DNAPL.

Volatile Organic Contaminants (VOCs):
- 1,2 Dichlorobenzene (DCB),
- 1,3 DCB,
- 1,4 DCB,
- Chlorobenzene (CB),
- Trichloroethene (TCE),
- Tetrachloroethene (PCE),
- cis-Dichloroethene (DCE)
- Vinyl chloride (VC).
Complex Geology/Hydrology

- **A-E Aquifer**
  - Bedrock
  - Bay Mud
  - **B-Aquifer k** = 0.014 - 0.078 ft/d
  - **A-Aquifer k** = 0.8 - 4.2 ft/d

- **Bedrock**
  - k = 0.36 - 1.04 ft/d
Treatability Study Objectives

Groundwater Treatment Technology: Hydraulic Fracturing to emplace EHC®

- Destruction of contaminants to achieve an 80% reduction of chlorinated VOCs in groundwater.
- Polish remaining VOCs post-TCH to meet very stringent cleanup criteria (generally less than 5 ppb).

Soil/DNAPL Treatment Technology: Thermal Conduction Heating (TCH)

- Thermally-Enhanced Extraction of DNAPL.
- Destruction of contaminants to achieve a 90% reduction in chlorinated VOCs in soil.

Achieve Objectives in Stringent 18 month Timeframe
Pre-Remediation: DNAPL/Soil Mass Estimate

Estimate ~300 lb of VOCs present in the source area.

### Total (lbs)

<table>
<thead>
<tr>
<th></th>
<th>1,2-DCB</th>
<th>1,2-DCA</th>
<th>1,3-DCB</th>
<th>1,4-DCB</th>
<th>PCE</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Rem</td>
<td>136</td>
<td>2.8</td>
<td>2.8</td>
<td>48</td>
<td>101</td>
<td>291</td>
</tr>
<tr>
<td>Remediation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pre-Remediation: Groundwater Contaminant Plume

<table>
<thead>
<tr>
<th>Total (lbs)</th>
<th>1,2-DCB</th>
<th>1,2-DCA</th>
<th>1,3-DCB</th>
<th>1,4-DCB</th>
<th>PCE</th>
<th>benzene</th>
<th>CB</th>
<th>Cis-DCE</th>
<th>TCE</th>
<th>VC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Remediation:</td>
<td>4.7</td>
<td>0.7</td>
<td>0.01</td>
<td>1.5</td>
<td>0.6</td>
<td>0.03</td>
<td>0.2</td>
<td>2.1</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**Total Mass in Groundwater: 10.6 lbs**
Technology 1 Implementation: Hydraulic Fracturing/EHC® Emplacement

- Advanced 6 source fracture wells (SFW) and 6 plume fracture wells (PFW).
- Radius of amendment distribution 15-20 feet from fracture location.
- Emplaced 13,419 lbs in SFWs and 17,126 lbs of amendment EHC® in PFWs.
In Situ Attenuation Pathways

Chloroethene Degradation Pathway

- Tetrachloroethene (PCE)
  - reductive dechlorination
- Trichloroethene (TCE)
  - reductive dechlorination
- Dichloroethene (trans-1,2-DCE) (1,1-DCE)
  - reductive dechlorination
- Vinyl Chloride (VC)
  - reductive dechlorination
- Ethene
- Ethane

Chlorobenzene Degradation Pathway

- 1,2,4-trichlorobenzene (1,2,4-TCB)
- Dichlorobenzene (1,2-DCB, 1,4-DCB)
- Chlorobenzene
- Benzene

Reductive B-elimination

Manganese-reducing conditions
Anaerobic oxidation

Acetate
Sulfate-reducing/iron reductin conditions/anaerobic oxidation

Sulfate-reducing conditions

Biological reaction
Abiotic reaction

CO₂
CH₄
Evaluate Fracture Propagation: Tiltmeter Geophysics

- Analyzed tiltmeter data for 60 of 87 fracs.
- Modeled fracs for every borehole except PFW6 (near IR26MW16A).

Tiltmeters estimate:
1) Frac extent,
2) How fracs are centered to the borehole, and
3) How fracs propagate.
Results of Fracking: Amendment Distribution

- Established treatment 18-23 feet from the fracture boreholes.
- Geochemical conditions conducive to reductive dechlorination, i.e. methane-producing redox and pH > 5.5.
- Heterogeneous distribution of amendments.
- Evaluated Technology for 4 months.
Technology 2 Implementation: Thermal Conduction Heating

- Installed 18 heater wells, soil vapor extraction system and above ground treatment.
- Operated system for 4 months.
Organic Removal in Extracted Vapors During TCH

Mass Removal

- Influent Vapor Rate (based on PID) [lbs/day]
- Effluent Vapor Rate (based on PID) [lbs/day]
- Average TTZ temp [°F]

Graph showing the mass extraction rate and average temperature over time.
Contaminant Removal in Extracted Vapors During TCH
Contaminant Mass Before and After-Treatment in Soil

Pre-TCH Soil total VOCs | Post-TCH Soil total VOCs

<table>
<thead>
<tr>
<th>Total (lbs)</th>
<th>12DCB</th>
<th>12DCA</th>
<th>13DCB</th>
<th>14DCB</th>
<th>PCE</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Remediation:</td>
<td>136</td>
<td>2.80</td>
<td>2.80</td>
<td>48.00</td>
<td>101.00</td>
<td>291</td>
</tr>
<tr>
<td>After Remediation:</td>
<td>19.1</td>
<td>0.01</td>
<td>0.08</td>
<td>2.60</td>
<td>0.01</td>
<td>22</td>
</tr>
<tr>
<td>% Reduction</td>
<td>86%</td>
<td>99.8%</td>
<td>97.2%</td>
<td>94.6%</td>
<td>99.9%</td>
<td>92.5%</td>
</tr>
</tbody>
</table>
Contaminant Mass Before and After-Treatment in Groundwater

<table>
<thead>
<tr>
<th>Parent Compounds</th>
<th>Reductive Daughter Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,2-DCB</td>
</tr>
<tr>
<td>Before Remediation:</td>
<td>4.7</td>
</tr>
<tr>
<td>After Remediation:</td>
<td>2.7</td>
</tr>
<tr>
<td>% Reduction</td>
<td>44%</td>
</tr>
</tbody>
</table>

Total CoC Mass In Groundwater Pre-Treatment- 10.6 lbs
Total CoC Mass In Groundwater Post-Treatment- 4.1 lbs
Chlorinated Benzenes: IR25MW63A
Chlorinated Ethenes: IR25MW63A

Fracturing TCH

VOCs (ug/L)

TETRACHLOROETHENE
TRICHLOROETHENE
1,2-DICHLOROETHANE
CIS-1,2-DICHLOROETHENE
VINYL CHLORIDE
ETHENE
ETHANE
Fracturing and Injection

cis-1,2-DCE PAL = 6 ug/L,
TCE PAL = 2.9 ug/L,
PCE, 1,2-DCA, and
VC PAL = 0.5 ug/L
Chlorinated Benzenes: IR25MW64A

IR25MW64A

Fracturing → TCH

1,3-DCB, 1,4-DCB, CB, and Benzene (ug/L)

1,2-DCB PAL = 600 ug/L
1,3-DCB PAL = 183 ug/L
CB PAL = 70 ug/L
Benzene PAL = 0.5 ug/L
1,4-DCB PAL = 2.1 ug/L
Chlorinated Ethenes: IR25MW64A

- Fracturing
- TCH

**Graph Details:**
- Y-axis: VOCs (ug/L)
- Lines represent different VOCs:
  - Tetrachloroethene
  - Trichloroethene
  - 1,2-Dichloroethane
  - cis-1,2-Dichloroethene
  - Vinyl Chloride
  - Ethene
  - Ethane
  - Fracturing and Injection

**Legend:**
- TCE PAL = 2.9 ug/l
- PCE, 1,2-DCA, and VC PAL = 0.5 ug/l
- cis-1,2-DCE PAL = 6 ug/l

**Sites:**
- IR25MW62A
- IR25MW63A
- IR25MW64A
- IR25MW65B
Long-term Results - Dichlorobenzenes

Graph showing the concentration of different dichlorobenzenes over time, with levels dropping significantly during thermal treatment.
Long-term Results - Chloroethenes
Conclusions: HPNS Treatability Study

- Tiltmeter data: frac extent ranged from 2.5 to 89 ft, with an average extent from the borehole of 18-23 feet in the source area and 13-24 feet in the dissolved phase plume.

- Based on tiltmeter and geochemical changes the radius of influence > 20 ft. EHC® was emplaced as discrete “sheets” with diffusion of amendments to groundwater effective at creating reducing within the source area and dissolved plume treatment areas.

- Fracturing/EHC® - a 24-99.9% reduction in PCE and 1,2-DCA achieved and a 5-57% reduction in 1,2-, 1,3- and 1,4-DCB within four months.

- PCE reduced to ethene through cis-DCE and VC, and the dichlorobenzenes predominantly reduced to chlorobenzene with little benzene four months after injection.
Conclusions: Impact of Thermal Treatment

- Little/no reductive dechlorination observed at temperatures >70°C.

- Removed >90% of total VOC mass in soil, with lowest removal observed for 1,2-DCB (86%) and highest for PCE (99.9%).

- Initially, parent compound groundwater concentrations reduced 50-93% for 1,2-DCB, 1,3-DCB, 1,4-DCB, except in IR25MW63A, and >94-100% for PCE and 1,2-DCA.

- Reductive daughter product concentrations reduced 61-99% for chlorobenzene/benzene except IR25MW62A and IR25MW63A which increased (due to post-TCH attenuation).

- Thermally-enhanced ISB, post-ISTR, has increased treatment rates by a factor of two compared to ISB alone, resulting in 90-99.99 % reductions in contaminants in groundwater.