Enhanced In-Situ Bioremediation Using Emulsified Edible Soybean Oil

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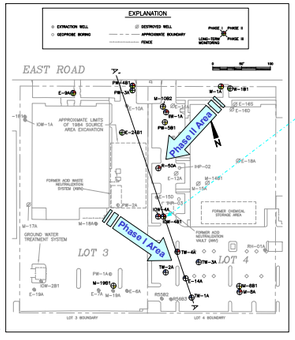
ABSTRACT

Soil and ground water at an industrial site in Mountain View, California have been affected by unintended releases of chlorinated and aromatic volatile organic compounds (VOCs) since 1965. Contaminants consist primarily of trichloroethene (TCE), degradation products cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride, and ethene, as well as ethylbenzene, xylenes and toluene. High dissolved-phase concentrations of VOCs have been detected mainly in two water-bearing zones, the A-and B-zone, separated by a clayey A/B aquitard. Between 1982 and 2005, approximately 79,100,000 gallons (gal) of ground water and 1,986 pounds of VOCs were removed by a conventional ground water extraction and treatment system. In 2004, a feasibility study concluded that *in-situ* bioremediation and bioaugmentation had a reasonable chance of hastening progress towards cleanup standards. This poster describes the two phases of the remediation work.

Phase I of the project, which targeted a high-concentration area (1,400 µg/L TCE, 960 µg/L cis-1,2-DCE) in the shallowest water-bearing zone in the upgradient portion of the site, was initiated in August 2005. Approximately 26,000 gallons of 2% emulsified oil were simultaneously injected through nine temporary 2-inch diameter injection wells. Performance monitoring after 27 months of treatment showed that TCE concentrations throughout the treatment area had been reduced between 56 and 99%, with ongoing reduction of cis-1,2-DCE to vinyl chloride; however, little ethene or ethane concentrations were observed.

Phase II, initiated in July 2006, addressed a larger downgradient hot spot (430 µg/L TCE, 6,400 µg/L cis-1,2-DCE, 6,000 µg/L vinyl chloride, 20,000 µg/L xylenes, and 5,800 µg/L ethylbenzene) in the shallowest water-bearing zone. Forty temporary injection points were installed over a 11,400 square foot area, and approximately 91,000 gal of 2% oil emulsion were injected into the subsurface. Additionally, based on the results of Phase I, 20 of the injection points were bioaugmented with *Dehalococcoides ethenogenes* culture KB-1™ to reduce the likelihood of partial dechlorination and increase the rate of reductive dechlorination. Ground water monitoring one month after implementation indicated rapid degradation of TCE, and production of cis-1,2-DCE and vinyl chloride in, and downgradient of, the injection zone. Furthermore, polymerase chain reaction analysis of ground water samples collected after three months confirmed the presence of dechlorinating organism *Dehalococcoides ethenogenes* 30 feet downgradient of the injection zone. Sampling at four months indicated that TCE concentrations throughout most of the treatment area have been reduced by more than 99%, with ongoing reduction of cis-1,2-DCE and vinyl chloride to ethene.

SITE HISTORY



- VOCs first detected in 1981 (Lots 3 and 4).
- Sources of VOCs (TCE, cis-1,2-DCE, vinyl chloride, ethylbenzene, xylenes, toluene): soil in the vicinity of acid waste neutralization system (Lot 3), acid neutralization vault) and chemical storage area (Lot 4).
- Majority of VOCs present in A-zone (15 to 40 feet below ground surface [ft bgs]); lesser extent in B1-zone (40 to 80 ft bgs).
- Ground water extraction system installed in 1982 removed ~ 80 million gal and ~2000 lbs of VOCs between 1982 – 2005.
- Source remediation in 1984: removal and onsite treatment of 4,000 cubic yards of soil.
- Treatment system shutdown on August 28, 2005 as part of the enhanced *in-situ* bioremediation pilot test.
  - **Phase I Emulsified Oil Injection: August 29 – September 2, 2005**
  - **Phase II Emulsified Oil Injection: July 17 – 26, 2006**

OBJECTIVES

The primary objectives for this enhanced *in-situ* bioremediation project are to

- (1) Reduce hot spot VOC concentrations without operating the pump-and-treat system,
- (2) Achieve these concentration reductions within a relatively short (four-year) time frame.

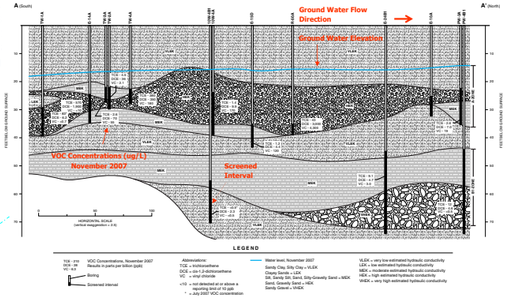
SITE GEOLOGY & HYDROGEOLOGY

- **Alluvial deposits:** Heterogeneous mixture of sand and gravel (stream channel deposits with high to very high relative permeability) interbedded with silt and clay; highly stratified, greater horizontal than vertical hydraulic conductivity.
- **Upper aquifer zone:** Subdivided into two aquifer units, the A aquifer (or A-zone) and the B aquifer (or B-zone), which are separated by the A/B aquitard; vertical hydraulic conductivity range of 3 x 10^{-8} to 1.5 x 10^{-6} cm/sec .

	A-Zone (15-40 ft bgs)	B1-Zone (40-80 ft bgs)
Hydraulic conductivity	3.0x10^{-3} cm/sec	3.6x10^{-3} cm/sec
Horizontal gradient	0.004 ft/ft	0.003 ft/ft
Average ground water velocity	63 ft/yr	52 ft/yr
Max. TCE conc. (prior to pilot test)*	1,400 µg/L	46 µg/L
Max. TCE conc. (after Phase I)*	570 µg/L	59 µg/L
Max. TCE conc. (after Phase II)*	43 µg/L	46 µg/L

* = The pilot test targeted only the A-zone, no emulsified oil was injected into the B1-zone

Geological cross-section: Cross-section A-A' traverses the site from the southeast corner of Lot 3 (PW-3A) to the southwest corner of Lot 4 (TW-1A). [see map to the left]



EMULSIFIED OIL SUBSTRATE

- Newman Zone soybean oil (175 electron equivalents/kg) injected as ~2% oil emulsion during Phase I and II.
- The concentrated oil-in-water emulsion (50% soybean oil by volume) was diluted onsite with untreated ground water extracted from the site; electron donor formulation was therefore representative of site geochemical conditions.
- Newman Zone is augmented with lactate (4% by weight) & micronutrients to stimulate rapid microbial response.
- Sparingly soluble vegetable oil is retained on soil surfaces and pore spaces, slowly fermenting to volatile fatty acids and molecular hydrogen.
- Molecular hydrogen is consumed in competing reactions – reduction of electron acceptors and reduction of VOCs.

REMEDIAL DESIGN PHASE I

Phase I Emulsified Oil Injections (August - September 2005)

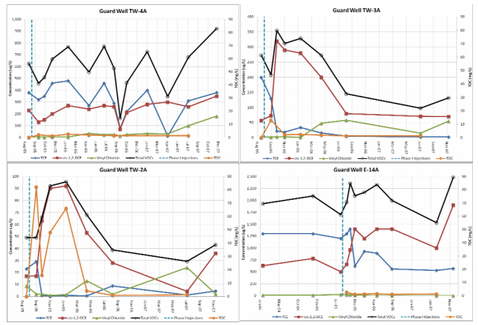
In-situ reactive barrier design: A "bioreactive zone" forms downgradient of injection points placed in line perpendicular to ground water flow; natural ground water flow helps disperse emulsified oil until emulsification breaks down and oil adsorbs to aquifer matrix.

- 25,800 gal of 2% oil emulsion injected into 9 direct-push locations;
- 2,800 gal injected at each location;
- make-up water consists of extracted untreated ground water (stored onsite in 2 tanks);
- Average injection rate: 3 gal/min;
- Injection depth: 35 ft bgs; Injection interval: 15 ft;
- Newman Zone distribution system allows for simultaneous injection into 10 points.

Emulsified Oil Totes | *Emulsified Oil Distribution Array* | *Bioaugmentation with KB-1 culture*

PHASE I MONITORING RESULTS

- Oil injection induced highly reducing conditions in area surrounding guard wells TW-2A and TW-3A → nitrate depleted, sulfate reduction, high methane concentrations (16 mg/L) → in-situ fermentation
- TCE concentrations decreased and daughter products cis-1,2-DCE and vinyl chloride increased in all four guard wells (TW-2A, TW-3A, TW-4A, E-14A); ethene concentrations very low (max. 5.3 ug/L).
- Cis-1,2-DCE concentrations in TW-2A and TW-3A greater than those of the parent TCE compound, indicating the dissolution of TCE from the sorbed phase.
- Guard well E-14A appears to have "stalled" at cis-1,2-DCE, suggesting *Dehalococcoides ethenogenes* not present.
- Low levels of total organic carbon (TOC) suggests emulsified oil substrate not effectively distributed in Phase I.



REMEDIAL DESIGN PHASE II

Design Recommendations based on Phase I

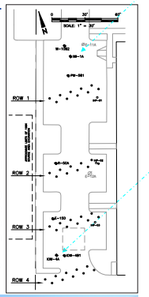
- Based on sulfate depletion, methane and cis-1,2-DCE concentration increase, ground water velocity is faster (~100-200 ft/yr) than previously estimated (~60 ft/yr).
- Injection row spacing equivalent to distance ground water migrates in ½ year.
- Low concentrations of vinyl chloride and ethene indicates sufficient population of *dehalococcoides* bacteria is not present or population is slow to respond → therefore bioaugment Phase II
- Bioaugmentation with *dehalococcoides ethenogenes* culture KB-1™ to reduce likelihood of partial dechlorination and increase rate of reductive dechlorination.

Phase II Emulsified Oil Injections (July 2006)

- 91,000 gallons of 2% oil emulsion injected into 40 direct-push locations (four rows)
- 2,300 gallons injected at each location
- Average injection rate: 4 gal/min
- Injection depth: 35 ft bgs; Injection interval: 15 ft

Bioaugmentation of Rows 1 & 2

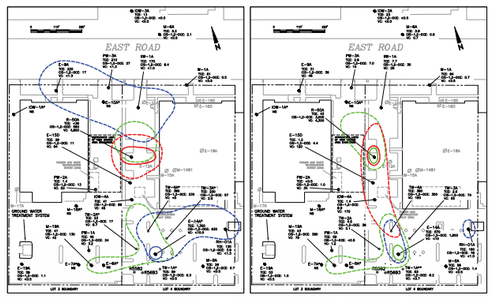
- Bioaugmentation with *dehalococcoides* culture KB-1™ and indigenous microorganisms at 20 direct-push points (rows 1 & 2)
- Anaerobic chase water (ORP= -211mV; DO= <0.2mg/L) prepared from onsite well R-50A, where 2,200 µg/L of ethene indicated active *dehalococcoides ethenogenes* population prior to electron donor addition (co-location with existing hydrocarbon contamination).
- 1.1 L of KB-1™ culture injected at each point, followed by anaerobic chase water.



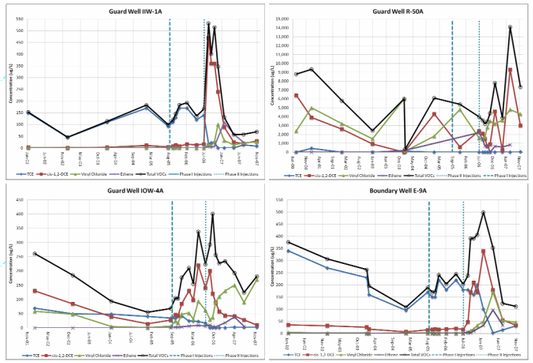
Argon Purge prior to KB-1 Injection | *Ten Channel Injection Manifold* | *Ground Water Storage Tanks*

PHASE II MONITORING RESULTS

Comparison of the VOC distribution in the A water-bearing zone



PHASE II MONITORING RESULTS (cont.)



RESULTS AND CONCLUSIONS

- Geochemical parameters in guard wells IIW-1A, IOW-4A, and R-50A, downgradient of the emulsified oil barriers, demonstrated favorable anaerobic reducing conditions 30 days after oil emplacement (DO = 0.6 mg/L, ORP= -280 mV, 23 mg/L methane, 4.3 mg/L sulfide, 34 mg/L ferrous iron).
- Sampling at six and nine months: TCE concentrations near or below the analytical reporting limits and more than 99% of the TCE converted to cis-1,2-DCE, vinyl chloride and ethene.
- *Dehalococcoides* Gene-Trac assay (SIREM, Guelph, Canada) collected 100 days after bioaugmentation, revealed 7x10^4 gene copies per liter in well IIW-1A indicating moderate concentrations of *Dehalococcoides ethenogenes*, and 3x10^7 gene copies per liter in well R-50A are indicative of high numbers of *Dehalococcoides ethenogenes*.
- Rate of reductive dechlorination in the treatment area increased dramatically following the emulsified oil injections as indicated by decrease in TCE, increase and subsequent decrease of cis-1,2-DCE and vinyl chloride (wells E-9A, IIW-1A and IOW-4A), and increase in ethene (wells IIW-1A, and IOW-4A).
- Cis-1,2-DCE in Phase II guard wells IIW-1A, IOW-4A, R-50A, and boundary well E-9A, reached concentrations greater than those of the parent TCE compound, indicating the dissolution of TCE from the sorbed phase.
- Vicinity of well R-50A has often shown high (mg/L range), but variable concentrations of cis-1,2-DCE, vinyl chloride, ethylbenzene, and xylenes, and lower or non-detectable TCE. Based on this, a saturated zone non-aqueous phase liquid (NAPL) source consisting of a mixture of TCE, ethylbenzene and xylenes is suspected near this well.
- Even before the enhanced bioremediation pilot test, the presence of aromatic hydrocarbons apparently fostered an active bacterial reductive dechlorination population and very effective degradation of TCE to cis-1,2-DCE kept pace with dissolution of TCE into ground water (baseline ethene concentration = 2,200 µg/L).
- Enhanced *in-situ* bioremediation appears to be at least as effective as pump-and-treat at containing VOCs, as indicated by decreased concentrations in downgradient A-zone and B-zone site boundary wells.
- TCE concentrations have been significantly reduced in all monitored wells within the enhanced bioremediation zones, generally at rates significantly exceeding reductions under pump-and-treat. The site-wide reductive dechlorination has been shown to rapidly and effectively reduce TCE to very low or non-detectable levels.
- Enhanced *in-situ* bioremediation appears to have increased the dissolution and desorption of VOCs from the soil matrix at a more rapid rate than pump-and-treat.

Next Steps:

Additional injections and bioaugmentation may be considered (Phase I area) to reduce VOCs further.

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