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Enhanced Bioremediation for Accelerated Site Closure at a Fire-Training Site

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ABSTRACT: A pump-and treat-system has been used for remediation of a fire-training site with petroleum and solvent contamination in groundwater at Brooks City-Base, formerly Brooks Air Force Base (San Antonio, Texas). After more than a decade of operation, the solvent plume has shrunk to where only the on-base portion continues to exceed groundwater criteria. However, the plume concentrations in this portion have been only slowly declining, The Air Force chose to optimize the system to more quickly attain site closure. The 900-foot long groundwater plume contains trichloroethene (TCE) as the original contaminant, with daughter products cis-1,2-dichloroethene (DCE) and vinyl chloride (VC) also present. Emulsified vegetable oil (EVO) was chosen as the electron donor to stimulate anaerobic reductive dechlorination, since it provides both a quick start carbon source (lactate) and a long-lasting carbon source in the vegetable oil. The EVO injection involved four barrier injection rows perpendicular to the plume axis. The injection approach also included a grid injection area in the plume source area (historic fire-training area) and a second grid injection in one DCE hot spot area. The injection point spacing was chosen as 10 feet in all areas. The lithology targeted for injection is a relatively thin (< 5 feet thick) clayey gravel overlain by a silty and sandy clay. Ten to fifteen gallons of EVO was delivered at each injection point, followed by a water chase of several hundred gallons. To date (6 months post-injection), several areas are exhibiting excellent response to the EVO injection, including some areas of TCE reduction and daughter product appearance.

INTRODUCTION

Site Descriptions. The FPTA2 site at Brooks City-Base (formerly Brooks Air Force Base) is a former fire-training area that was used for airplane crash fire training exercises from 1945 to 1960. Investigation activities determined that a solvent TCE plume extends from the source area towards the southwest. The TCE plume was originally 2,200 feet long. A pump-and-treat system was installed in 1995 and continues in operation today, and as a result the plume has shrunk in size to a length of 900 feet. The shallow subsurface at FPTA2 consists of three lithologic units: a recent-aged terrace (alluvium) deposit comprised of silty clay grading to clayey sand (30 feet thick); the Leona Formation, the primary water-bearing formation at the site, comprised of silty sand to clayey gravel (2 to 10 feet thick); and the Midway Group, comprised of a silty clay and representing the lower confining unit for shallow groundwater at the site(typically encountered at 20 to 25 ft below grade surface (bgs)).

Background for Accelerated Site Closure. A *Remedial System Optimization Evaluation* was completed in 2006 which included a detailed review and evaluation of historic

groundwater recovery system performance data (USAF 2006). This review was spurred in part by annual natural attenuation assessments that indicated TCE decline in groundwater concentrations was not occurring at a rate conducive to attainment of closure within the next 5 years (see Figures 1 and 2). As a result of a field investigation effort associated with the optimization evaluation, it was determined that rebound occurs in the source area when recovery wells are shut off, which suggests groundwater pumping would have to continue for some time after contaminant concentrations fall below the maximum contaminant levels (MCLs) before complete groundwater recovery system shutdown could occur. Additionally, an aquifer test completed in the wells at a cis-1,2-DCE hot spot plume did not lead to a pumping rate or well location conducive to quick reduction of the high cis-1,2-DCE groundwater concentrations there. Therefore, biostimulation with minor groundwater recovery was recommended as the preferred optimization action for at least the source and MW-28/MW-36 areas of groundwater contamination (USAF 2006).

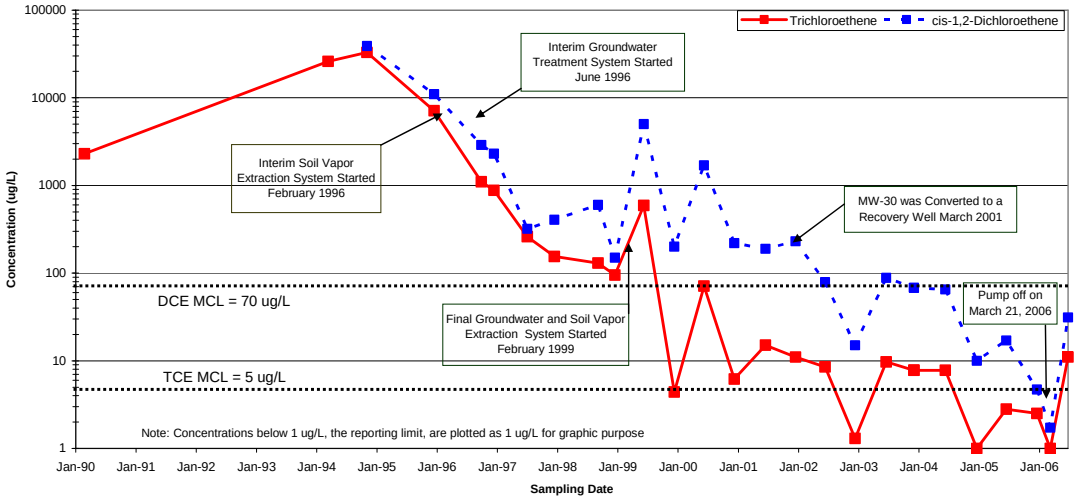

FIGURE 1. RW-30 source area well.

MATERIALS AND METHODS

Emulsified Vegetable Oil Injection Locations. The areas where carbon source injection was performed include the northern burn pit source area, plume areas around MW-28 and MW-36, and the base boundary (see Figure 3). Table 1 presents pertinent characteristics for each of the areas (USAF 2008). The injection areas for the source and MW-28 were limited to the immediate vicinity of those landmarks. At these areas, remaining solvent concentrations (both cis-1,2-DCE and TCE at the source and only cis-1,2-DCE at MW-28) have a tendency to temporarily increase with heavy precipitation events, suggesting the presence of some residual source contamination above the water table. The injection area for MW-36 was represented by the large core of the downgradient TCE plume that extends from the vicinity of RW-08 southwest to MW-36. The base boundary plume area was split into two separate entities due to the two separate "fingers" of TCE contamination (referred to as east and west) that are present at the base boundary. These areas also have been decreasing in TCE concentration over time, with the east

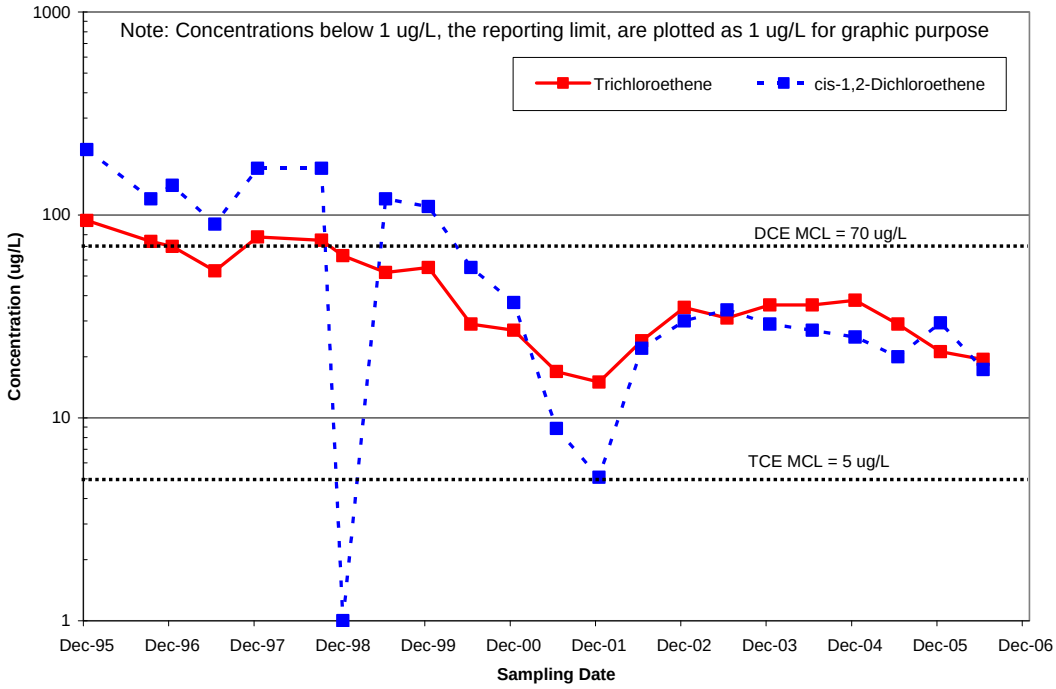

FIGURE 2. MW-36 flow path well.

finger having concentrations below the MCL in some sampling events. The reason these two areas were included in this action was to quickly "kill" the plume leading edges so that further release of contaminant mass above MCLs to off-base areas does not occur. At the source and MW-28 areas, injection was performed across the entire thickness of the saturated zone as well as into the capillary fringe to address any possible residual source present in the capillary zone. At the other areas (MW-36 and base boundary), injection was necessary only across the saturated zone thickness, because the contamination is expected to be present only in that zone. The specific locations where carbon source material was injected are summarized in Table 2 and presented in detail in Figure 3. A grid approach to locating injection points was used for the northern burn pit source area, while barrier lines were used at all other locations.

Material. For this project, commercially available EVO was chosen as the preferred carbon source because it contains emulsified vegetable oils (45 to 60 percent soybean oil) with a small amount of lactic acid (4 percent) added to provide quick initial stimulation of microbial activity to drive the aquifer to an anaerobic condition. The soybean oil serves as a long-term carbon source by virtue of its slow breakdown by bacteria into several different fatty acid molecules. Hollow-stem auger drilling was used to place temporary drill rods and screen at each injection location. A grout pump was used to pressure inject the EVO and water solution at each location.

TABLE 1. Biostimulation injection area characteristics.

Injection Area	Groundwater Contaminants and Maximum Concentration† (ppb)	Ratio of Contaminant Maximum Exceedance to Respective MCL	Media of Concern	Width of Proposed Injection Barrier (ft)
A: Source (north burn pit) plume	TCE: 5.43 DCE: 49.3 VC: 1.4	TCE: 1.09 DCE: NE VC: NE	Groundwater + residual source	Grid
B and C: MW-28 plume	TCE: 1.9 DCE: 186	TCE: NE DCE: 2.7	Groundwater + residual source	50 to 70
D, E, and F: MW-36 plume	TCE: 16.4	TCE: 3.3	Groundwater	70 to 120
G: Base boundary, west finger plume	TCE: 4.45	TCE: NE	Groundwater	120
H: Base boundary, east finger plume	TCE: 3.65	TCE: NE	Groundwater	20

† The maximum exceedance is taken from the December 2007 groundwater sampling data

1,2-DCE cis-1,2-dichloroethylene
ft feet
MCL maximum contaminant level
MW monitor well
ppb parts per billion
RW recovery well
TCE Trichloroethylene
VE vapor extraction
VC vinyl chloride
NE no exceedance

TABLE 2. Summary of biostimulation injection details.

Injection Area	Number of Injection Locations	Injection Point Spacing (ft)	Average Injection Zone Thickness (ft)	EVO Loading (gals/point)	Water Mix (gals/point)
Area A—Source	19	10	25.0	23	900
Area B—MW 28	8	10	16.1	23.5	600
Area C—MW 28	7	8	16.0	13.4	400
Area D	8	10	13.3	14	10
Area E	10	10	13.3	14	500
Area F	13	10	11.6	12	400
Area G--Base boundary	13	10	9.7	10	370
Area H--Base boundary	3	10	9.4	10	400

ft feet
MW monitor well
gals Gallons
EVO emulsified vegetable oil

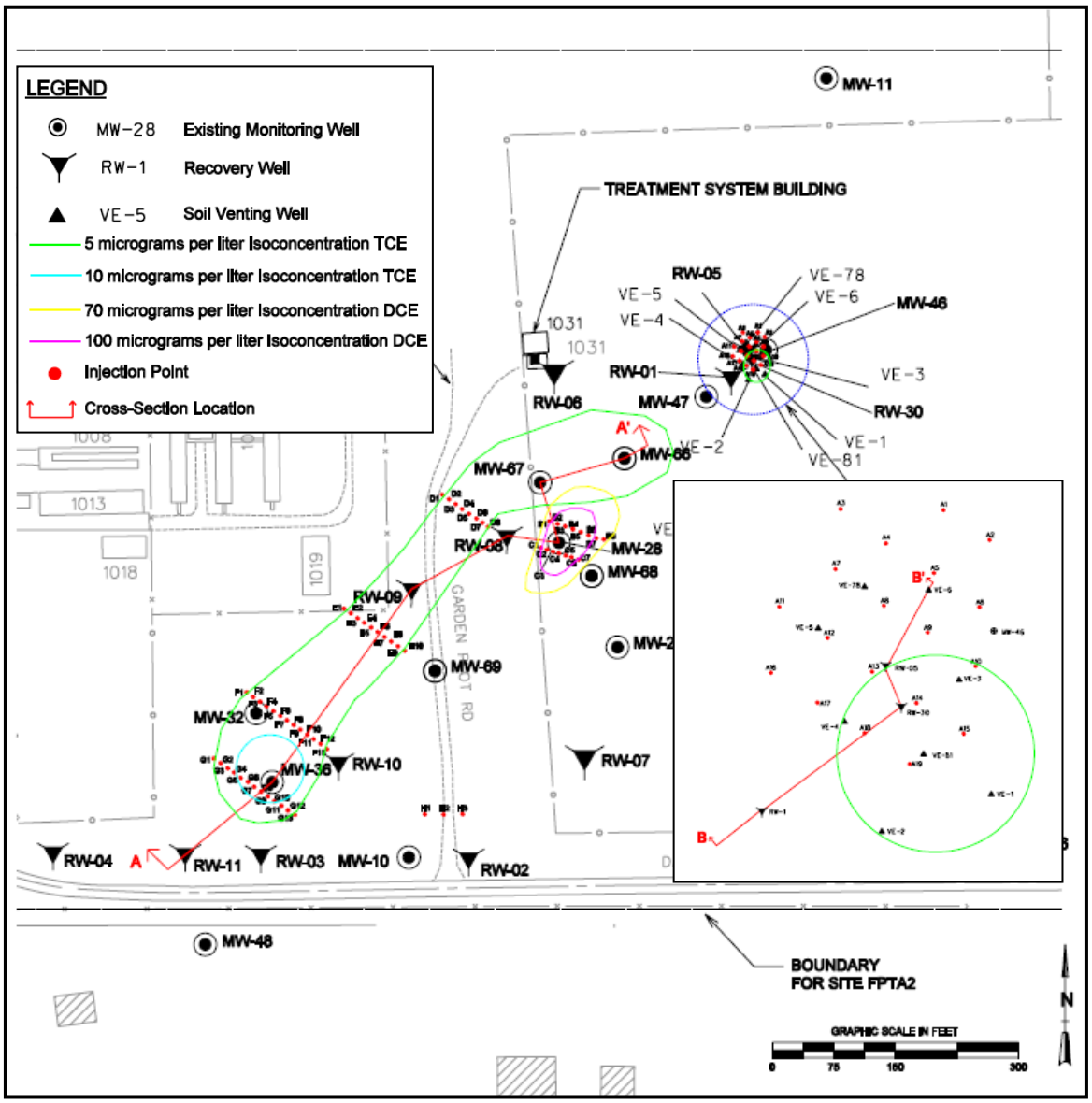

FIGURE 3. EVO injection areas at FPTA2.

Monitoring Locations and Methods. On-base flow path wells (MW-10, MW-28, MW-32, MW-36, MW-67, MW-69, RW-08, and RW-09) and source area wells (MW-46, MW-47, RW-01, RW-05, and RW-30) are being used to monitor the effectiveness of the biostimulation injection through quarterly sampling for volatile organic compounds (VOC) and monitored natural attenuation (MNA) parameters. Also, field parameters (dissolved oxygen, oxidation reduction potential, pH, temperature, specific conductivity) and water levels have been measured in these wells monthly for the first six months after injection.

RESULTS

Biostimulation Process. The biostimulation process involved injecting a carbon source into the surficial aquifer to enhance the process of anaerobic reductive dechlorination that results in destruction of chlorinated ethenes. When a carbon source such as the EVO is injected into the subsurface for biostimulation, the following processes occur in a fairly sequential fashion, as the oxidation reduction potential (ORP) steadily declines:

a. Appearance of total organic carbon (TOC) at levels higher than background, as lactate and fatty acids are transported from the injection area;
b. Reduction of nitrate, typically at ORP levels above 0 mV;
c. Reduction of ferric iron to ferrous iron, at ORP levels around -50 mV or lower;
d. Reduction of sulfate, at ORP levels around -220 mV or lower;
e. appearance of methane as a result of methanogenesis at ORP levels around -240 mV.

The favorable ORP range for reductive dechlorination of chlorinated ethenes is approximately -150 mV and lower. Therefore, reduction of sulfate and appearance of methane usually occurs at the same time as chlorinated ethene reduction.

Monitoring Evidence of Emulsified Vegetable Oil Injection. Specific VOC and MNA (including field parameters) data collected before and since the EVO injection has been evaluated in light of the biostimulation related processes described above. Besides the chlorinated ethene data, the parameters which so far provide the best evidence for anaerobic reductive dechlorination at the site are methane, nitrate, sulfate, ferrous iron, TOC, and ORP. The results of this evaluation can best be described using three general categories for monitoring locations reviewed. These three categories are:

a. Category 1: monitoring locations where there is evidence of chlorinated ethene destruction, with corroboration of conditions suitable to anaerobic reductive dechlorination by other MNA parameters;
b. Category 2: monitoring locations where there is evidence of low (below 0 mV) ORP and partial progression through the sequence of nitrate reduction-ferrous iron generation-sulfate reduction-methane generation that generally precedes anaerobic reduction dechlorination;
c. Category 3: monitoring locations where there is some evidence of the EVO injection, however no strong indication yet of the groundwater undergoing the changes

that represent the sequence of events proceeding to conditions conducive to anaerobic reductive dechlorination.

Table 3 lists categorization for the monitoring locations reviewed in regards to biostimulation evidence.

TABLE 3. Biostimulation evidence categories for monitoring locations.

	Evidence Category		
	1	**2**	**3**
Wells in Category	MW-32, RW-05, RW-30	MW-28, MW-46, MW-69, RW-01	MW-36, MW-47, MW-67, RW-08, RW-09

The monitoring locations included in category 1 provide evidence of chlorinated ethene reductive dechlorination, which includes declining levels of TCE, and increasing levels of cis-1,2-DCE and or VC. As well, the MNA parameters indicate a low ORP, with sulfate reduction and methane generation, which is consistent with the evidence of reductive dechlorination. Not surprisingly, each of these locations is directly in or very close downgradient to an EVO injection area.

The monitoring locations included in category 2 provide evidence of progress in the sequence of redox reactions for nitrate-ferrous iron-sulfate-methane, but there is only partial progress in the sequence. Typically, these locations indicate nitrate reduction but no sulfate reduction. Since the ORP is not sufficiently low, there is also no evidence of current reductive dechlorination of the solvent compounds. These locations are typically in or immediately adjacent to an EVO injection area, or are somewhat downgradient from an injection area. The lesser extent of progress towards anaerobic reductive dechlorination conditions for these locations as compared to category 1 locations can be attributed to factors such as distance from the EVO injection area, or less than ideal injection volumes due to low permeability. Monitoring location MW-28 is probably a good example of the latter circumstance.

The monitoring locations included in category 3 provide only limited evidence of the EVO injection, with very little evidence of progress through the sequence of redox reactions necessary before anaerobic reductive dechlorination conditions are attained. Not surprisingly, these monitoring locations are farther removed or up gradient of injection areas.

DISCUSSION

The level of the surficial aquifer at the site is currently low because of an extended drought in the San Antonio area. The water table rose in the source area over the June to December 2008 time interval, which is attributable to turning off recovery wells RW-05 and RW-30 and injecting approximately 900 gallons of water and EVO solution at each of 19 injection locations at the source. Otherwise, throughout the rest of the site, the surficial aquifer thickness decreased by 2 to 4 feet between June and December 2008, with the thickness in injection areas ranging from approximately 4 to 10 ft. This decreased aquifer thickness will likely correspond to a decreased level of anaerobic reductive dechlorination, since the target vertical injection interval of 15 feet is not covered by the current aquifer thickness. That is, some vegetable oil material will be

present above the current water table, where it will not be actively releasing fatty acids into the water, because the water table thickness is low.

The monitoring location data collected since the biostimulation injection was completed indicates good initial activity, especially given the drought conditions. In the near future, continued progress towards low ORP conditions conducive to the anaerobic reductive dechlorination process is expected in those areas relatively close to the original injection locations (category 2 monitoring locations). In these locations, degradation of TCE and other chlorinated ethenes can be expected to arise when evidence of sulfate reduction and strong methane generation appears. A longer time is expected to reach ORP conditions conducive to the anaerobic reductive dechlorination process in areas further downgradient of the injection areas (category 3 monitoring locations), especially given the drought conditions. Some areas may also be hampered by low permeability conditions. For those locations which are currently exhibiting chlorinated solvent degradation, this activity is expected to continue, and will likely include increases in concentrations of daughter products cis-1,2-DCE and VC as TCE is degraded.

CONCLUSIONS

Natural attenuation is continuously playing a role in reducing the contaminant levels and containing the plume at this site, but it is not effective in reaching the remedial goals in a reasonable period of time. Biostimulation noticeably enhanced the biodegradation in the source zones. TCE has been reduced to levels below reporting limit, but daughter products are experiencing a build-up. Since the residual sources of contamination are in the tight clay and in the smear zone (an area of historical high water table and current water table), TCE release from the matrix and accumulation of daughter products are expected to continue for some time. If the carbon source material from the EVO injection can out last the matrix release, we should expect continued solvent reduction. Cis-1,2 DCE and VC are currently at concentrations close to MCL and exceed it in some locations. If TCE rebound is observed after some extended period of time, it may mean carbon source levels in groundwater have returned to pre-biostimulation levels and additional injection may be needed. The effect of biostimulation in remaining portions of the plume is not apparent yet in regards to reduction of indicator species prior to evidence of reductive dechlorination. However, it has created low ORP conditions, conducive to reductive dechlorination, in significant portions of the plume, and we should expect measurable biodegradation results in the future sampling events.

ACKNOWLEDGMENTS

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Overview

- Objective
- Background for FPTA-2 Site
- Electron Donor Injections
- Post-Injection Groundwater Monitoring Results
- Conclusions

Objective

to accelerate attainment of site closure at Brooks City-Base Site FPTA-2 by biostimulation of groundwater solvent contaminants after more than a decade of contaminant removal by groundwater pump and treat

Objective

Brooks City-Base to close in 2011

Prior to remedial system optimization, contaminant fate assessment indicated 15 more years to closure of on-base groundwater using only existing pump and treat operation

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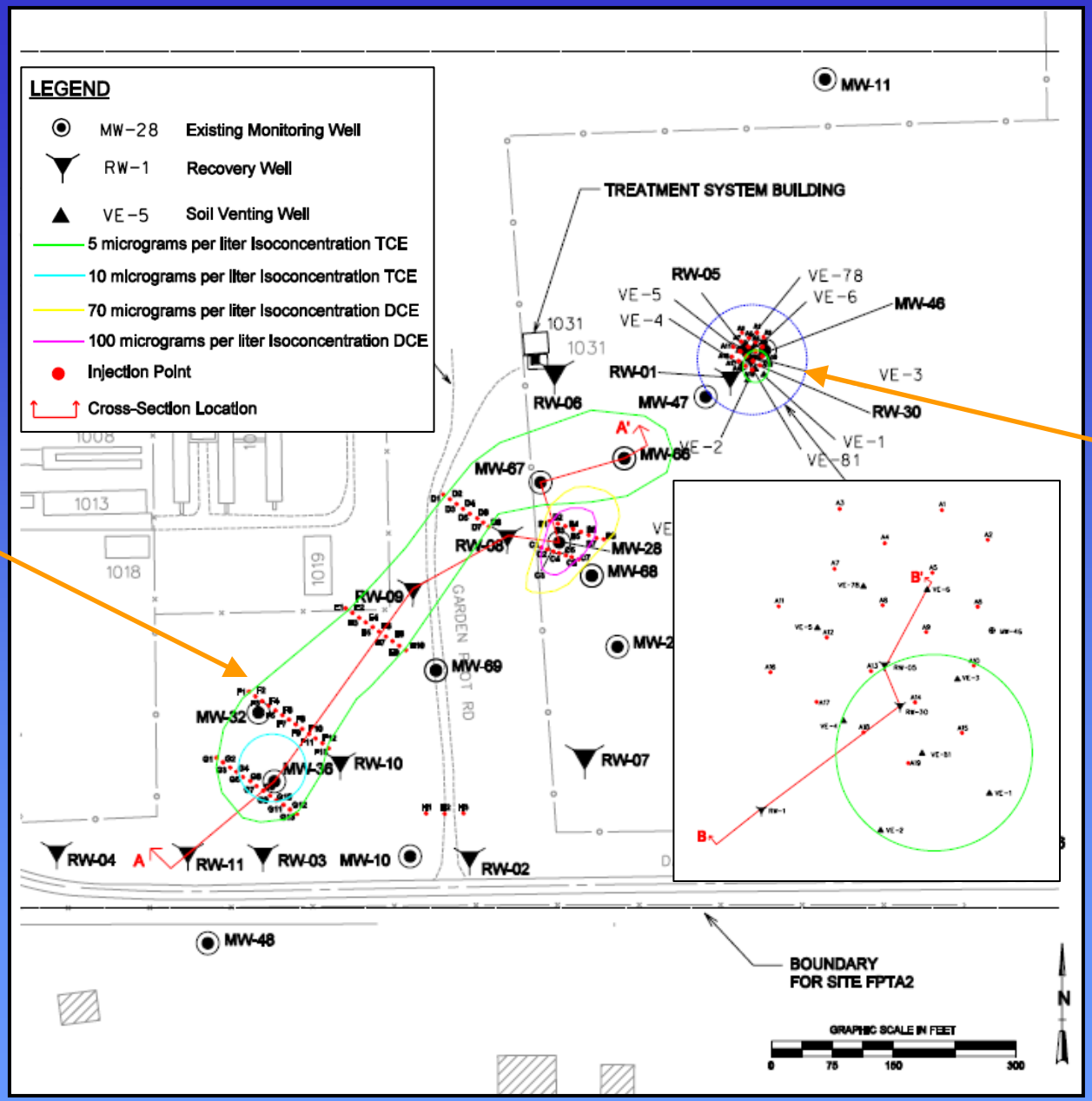
Site Map



On-base Plume

FPTA-2 Source Area

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Site Background – FPTA-2

- Contamination at site from release of petroleum and solvent compounds during historic fire training exercises
- Original TCE plume extended 2,200 feet to southwest, including off-base areas
- Primary contaminant TCE, with cis-1,2-DCE present in some areas, and sporadic detects of VC

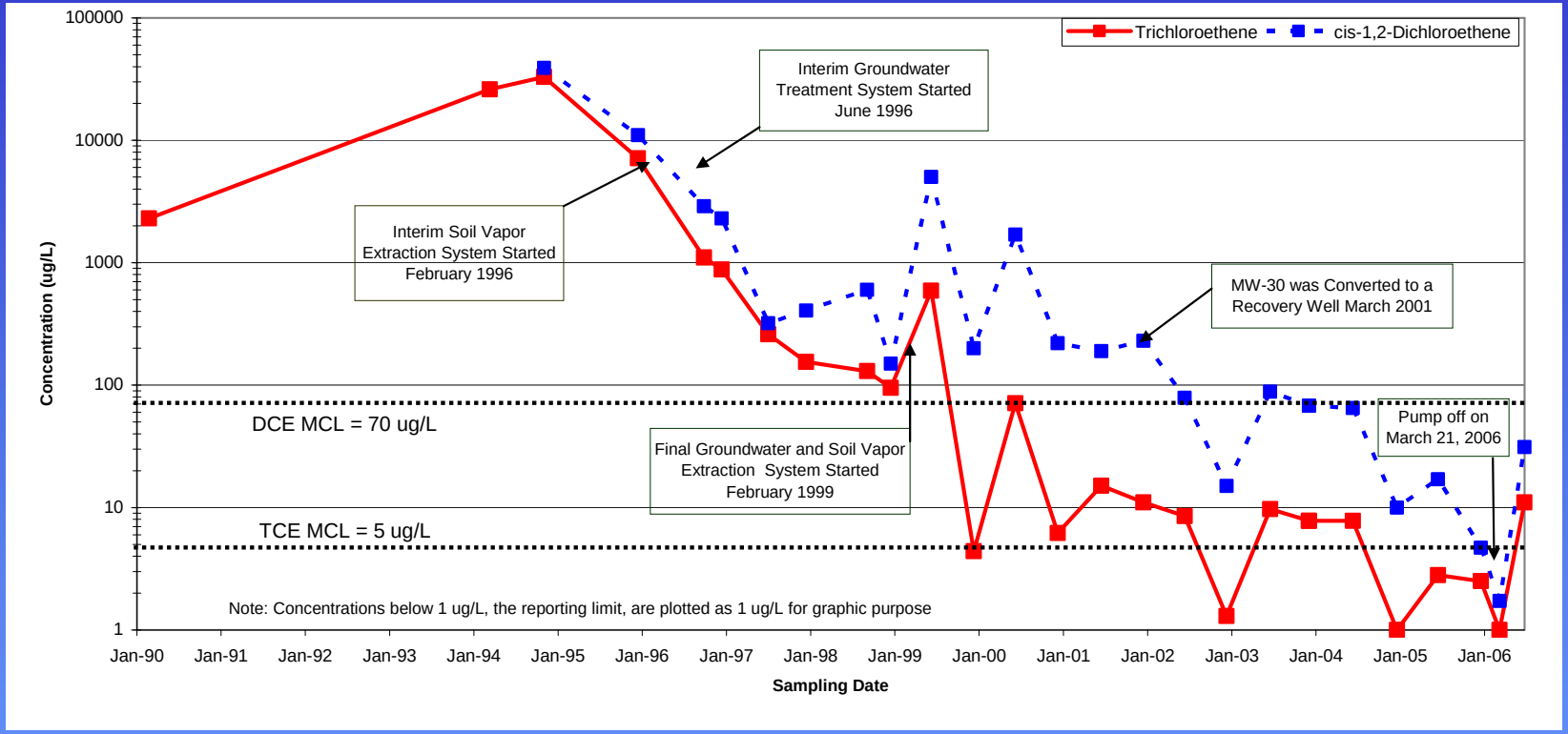
Site Hydrogeology – FPTA-2

- Upper soils (alluvium)--silty clay and clayey sand— 0–20 ft
- Surficial water bearing formation (Leona Formation) -- silty sand and clayey gravel– 20-30 ft—INJECTION TARGET ZONE
- Lower confining unit (Midway Group)-- silty clay 30 ft

Remedial System at FPTA-2

- SVE and groundwater pump and treat system installed in 1996, and optimized in 1999 for on-base source/plume treatment; MNA for off-base areas (very low concentrations)
- Contaminant mass removal rates have declined over time
- After almost 10 years P&T operation, plume is now restricted to on-base areas only (900 feet long)

Single Well Contaminant Trend



MW-30 Source Area Well

Rebound occurs in source area when recovery wells shutdown or with heavy precipitation

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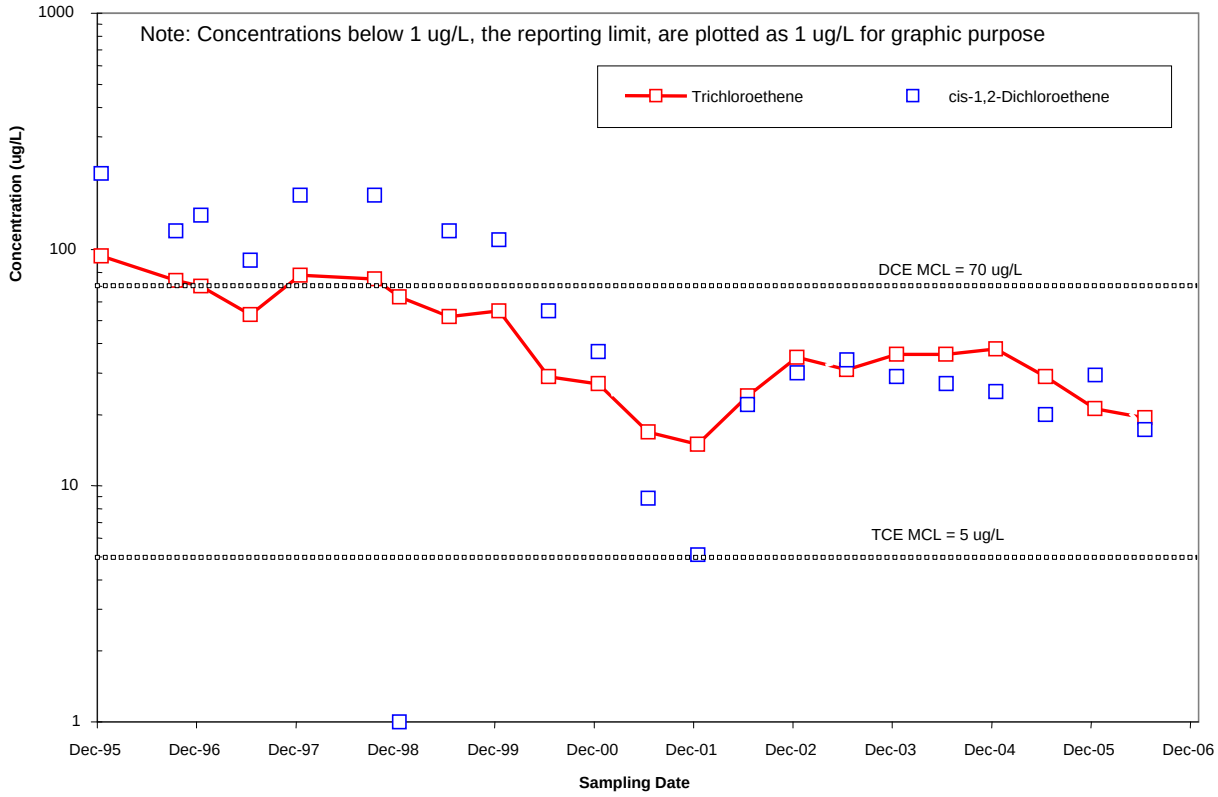
Single Well Contaminant Trend

Figure 4-2
TCE and cis-1,2-DCE Concentrations at MW-36 (Flow Path Well)
FPTA2 at Brooks City-Base, Texas



MW-36 Plume Flow Path Well
Contaminant declining rate is too slow

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Remedial System Optimization Evaluation

Objective—attain closure of groundwater operable unit earlier than 10-15 years in future

Optimization Action

- **Veg oil injection selected as technology for accelerating residual contaminant reduction**
- **Limited groundwater pumping to continue at wells located at the base boundary**
- **Closure of soils operable unit at source area**

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Injection of Emulsified Veg Oil

- Hollow-stem auger used to install temporary casing/wells for injection
- Injection performed in rows of wells, grid in source and hot spot
- Emulsified veg oil (EVO): ~45% veg oil and 4% lactate
- Approximately 10-15 gal. EVO followed by 400 gal. injection water per well—targeted for 50% pore volume
- Injection performed July-August 2008

Injection of Emulsified Veg Oil

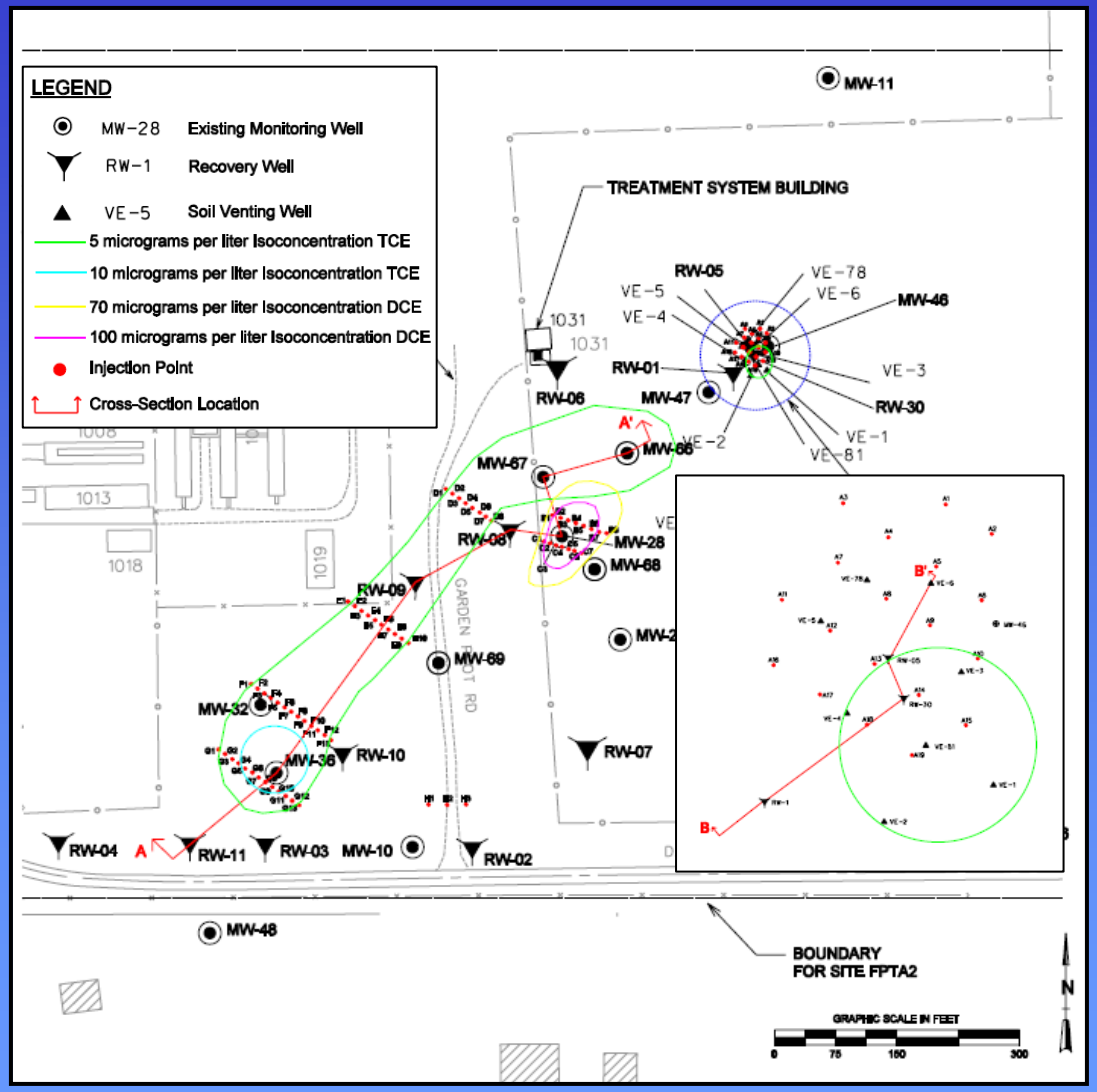
- Highest contaminant concentrations in injection areas
  - 50 µg/L DCE in source area
  - 186 µg/L DCE in hot spot area @ MW-28
  - 15 µg/L TCE in main plume

Veg Oil Injection Details

Injection area	Number of Locations	Spacing (ft)	Target Thickness	EVO Loading (gal/point)	Water Mix (gals/point)
A—source	19	10	25	23	900
B—DCE hot spot	8	10	16.1	23.5	600
C—DCE hot spot	7	8	16	13.4	400
D	8	10	13.3	14	10
E	10	10	13.3	14	500
F	13	10	11.6	12	400
G—base boundary	13	10	9.7	10	370
H—base boundary	3	10	9.4	10	400

Total of 81 injection points

Injection Locations at FPTA-2



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Veg Oil Injection at FPTA-2

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Site Monitoring for Biostimulation

- **Groundwater samples collected at**
  - **On-base flow path wells**
    - MW-10, MW-28, MW-32, MW-36, MW-67, RW-08, RW-09
  - **Source area wells**
    - MW-46, MW-47, RW-01, RW-05, RW-30
- **Samples analyzed for VOCs, ferrous Fe, nitrate, sulfate, TOC, methane/ethane/ethene, and field parameters of pH, O_2, conductivity and ORP**
- **Sampling frequency:**
  - **Pre-injection semi-annual system sampling—June 2008**
  - **Quarterly sampling started in October 2008 for 1 year**
  - **Monthly field parameter analysis**

Classification of Post-injection Results by Monitoring Well

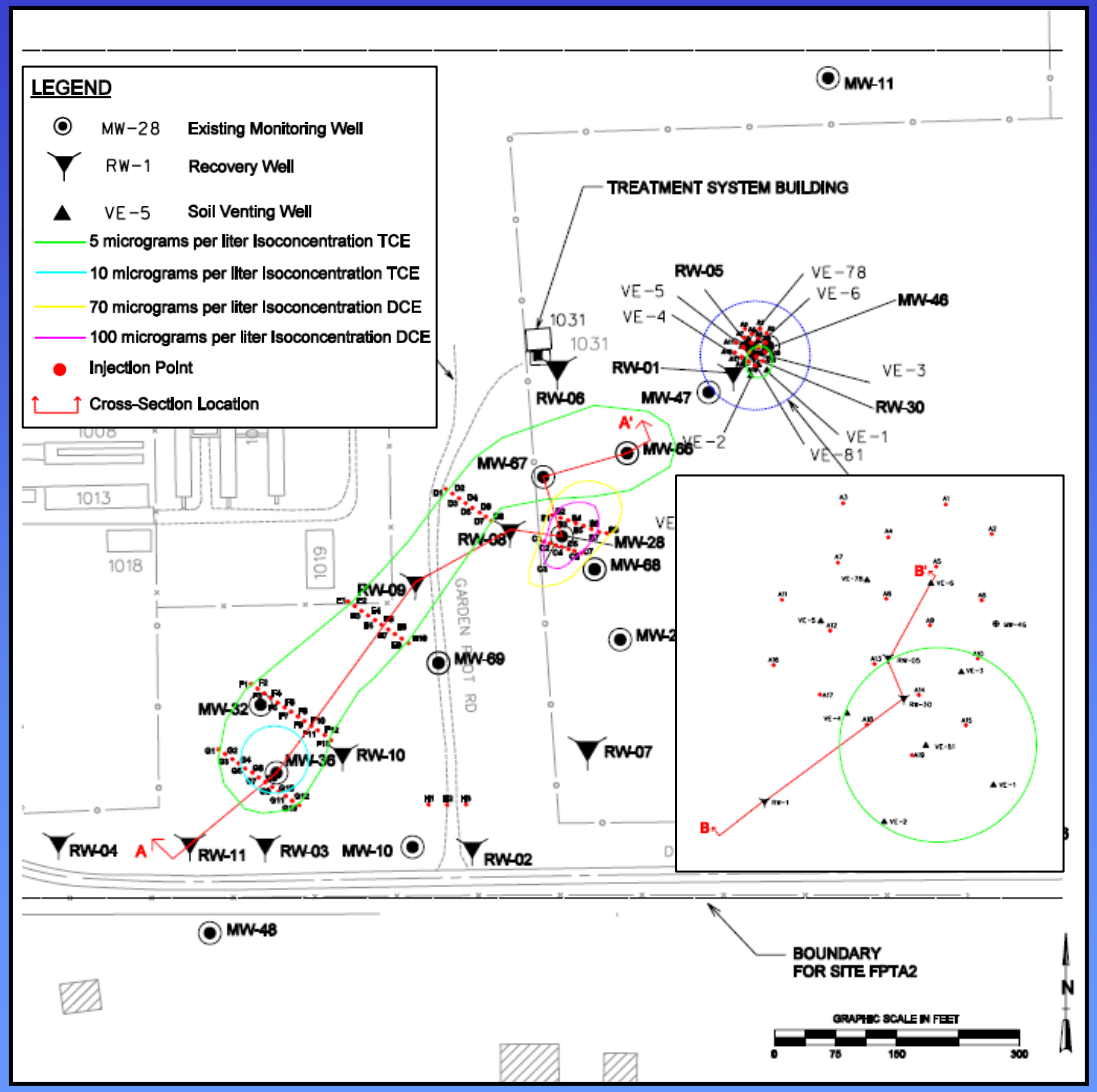
	Category 1	Category 2	Category 3
Evidence of EVO injection by TOC increase	**Y**	**Y**	**Y**
Progression through reduction of electron acceptors	**Y**	**Y**	**N**
Conditions suitable to an-aerobic reductive dechlorination	**Y**	**Y**	**N**
CAH degradation	**Y**	**N**	**N**

Classification of Monitoring Results

	Category 1	Category 2	Category 3
Source Area	RW-05, RW-30, MW-46	RW-01	MW-47
Plume	MW-32	MW-28, MW-69	MW-36, MW-67, RW-08, RW-09

- **Category 1 wells within or immediately downgradient of an injection area**
- **Category 2 wells close to injection areas, but less influence to date because of less than ideal injection conditions (low volume injected)**
- **Category 3 wells farther from injection influence, or up gradient**

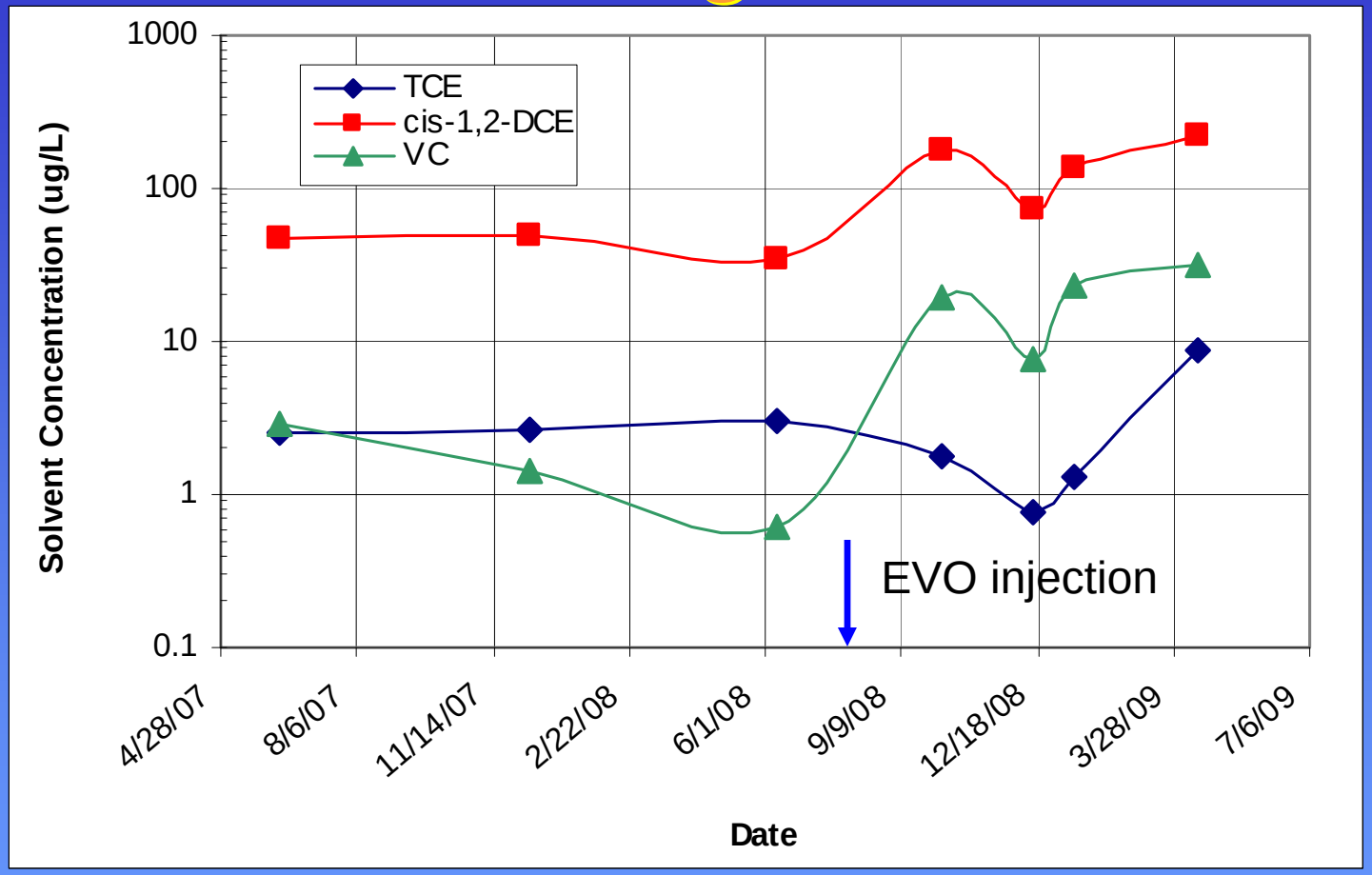
Injection Locations at FPTA-2



Monitoring Results

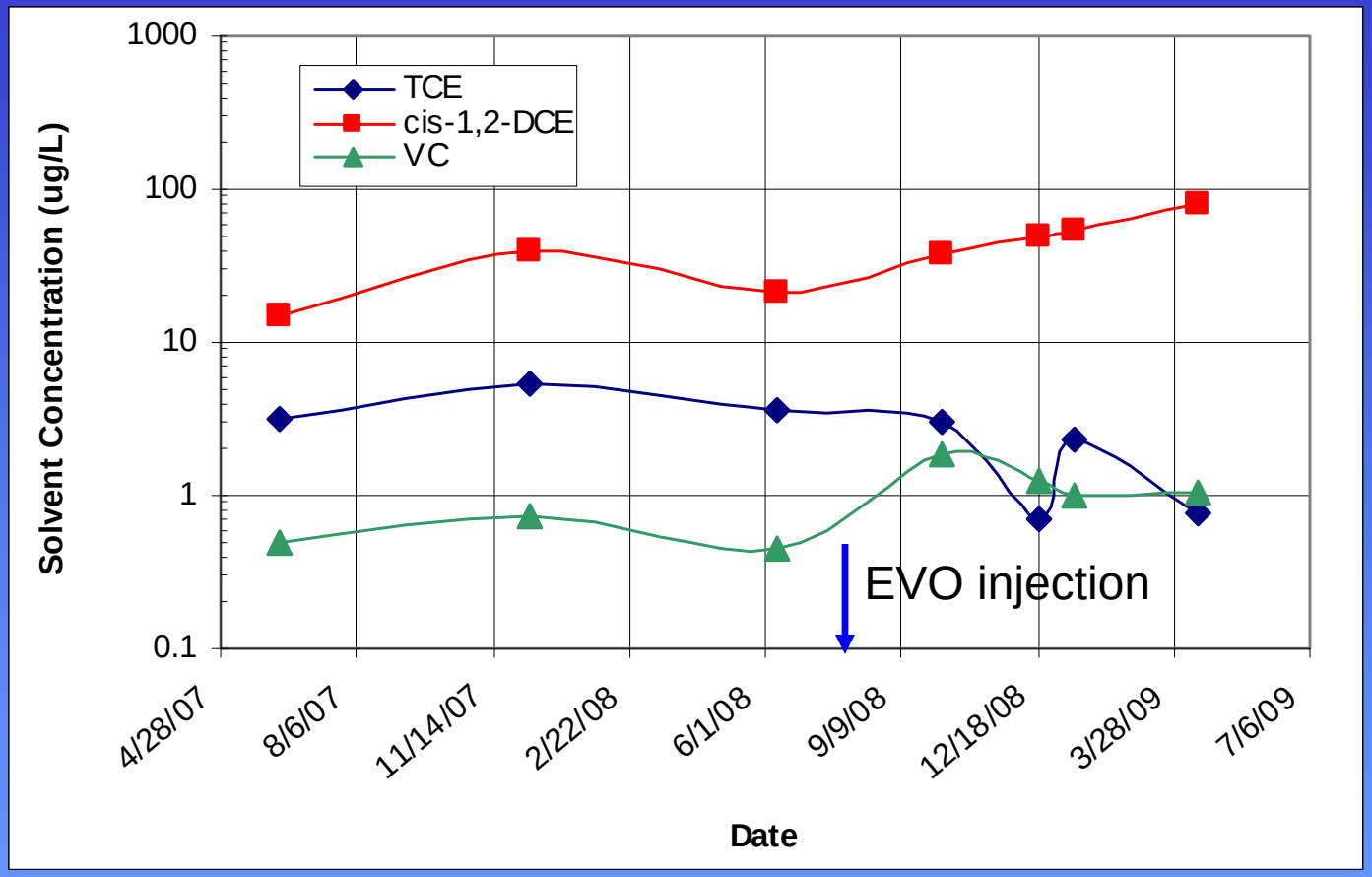
- **Wells indicating solvent degradation show 3 to 10 times decrease in TCE, and increases in VC and DCE**
- **Majority of wells are indicating increased TOC—initially from lactate spike and then from breakdown of the veg oil (monitoring data through Apr 2009).**

Monitoring Results



RW-05 Source Area Well—Increase in daughter products, TCE spike from source area desorption

Monitoring Results



RW-30 Source Area Well — Increase in daughter products

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Biostimulation at FPTA-2

- Water level in surficial aquifer is several feet low due to drought—lower level of solvent degradation expected
- EVO injected over a greater thickness than current water table thickness in source and hot spot areas, to address residual contaminants in capillary zone
- Expect greater activity to occur when precipitation leads to infiltration and replenishes the surficial aquifer

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