Use of Innovative In-Situ Remediation Strategies to Achieve Cleanup of a Complex Site

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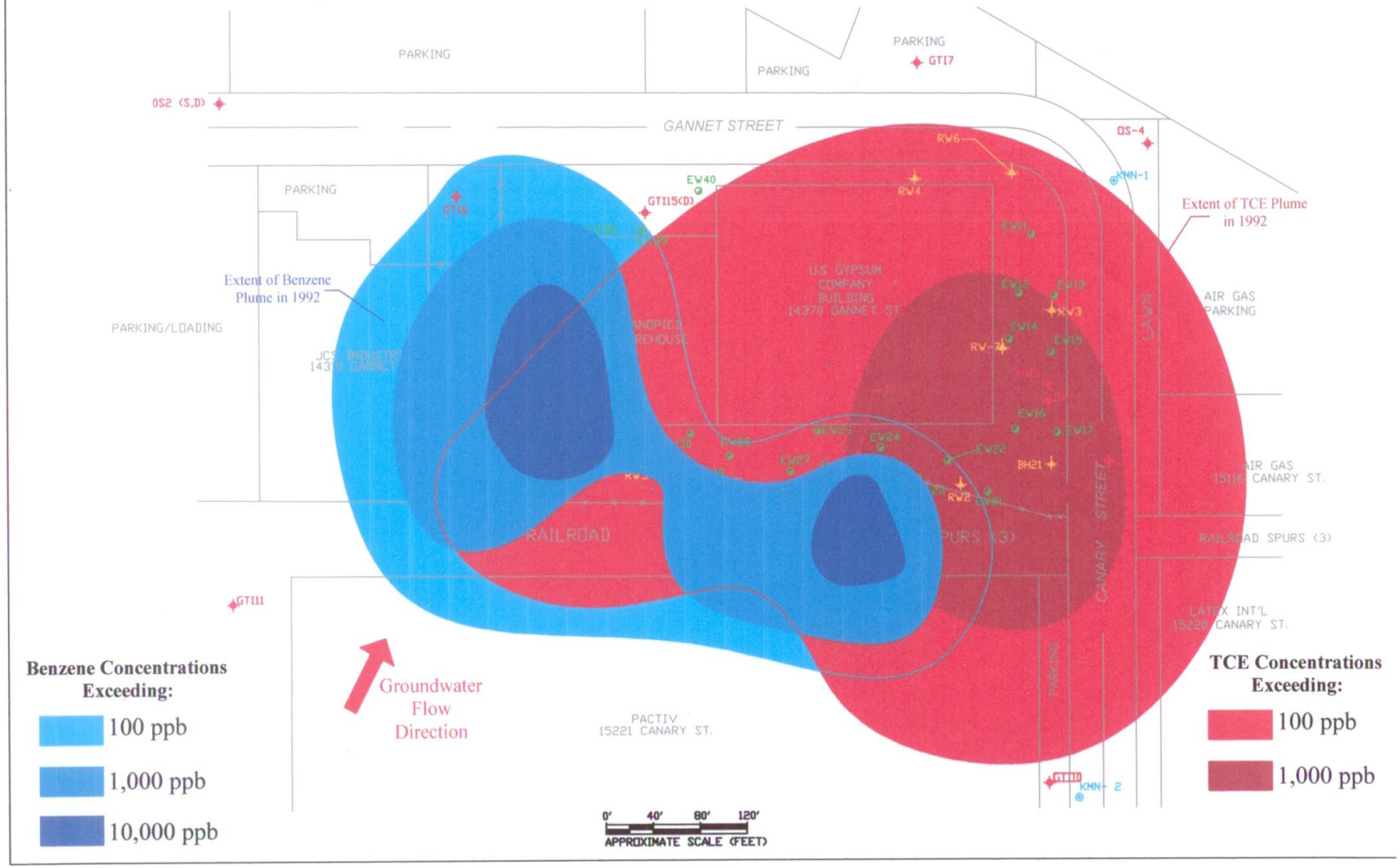
Overview of Presentation

- Over past 20 years, many advances in in-situ remediation technology
  - ISCO (multiple oxidants and activation methods)
  - Bioremediation
  - Direct Push Technology
- This Case Study illustrates application of these technology advances to a Complex project site with a long history of remediation (25 years)
- Availability of advances allowed for timely remediation at lower cost

Site Description and Complexities

- Job site is an active industrial site in Los Angeles County, CA
- 12 USTs removed from East Tank Farm in 1990.
- 10 USTs removed from South Tank Farm in 1994
- Approximately 3 acres in size with over 85 wells installed across site
- Sites Complexities:
  - Extreme depth to groundwater (80 ft) (increases drilling/well costs)
  - Two distinct but overlapping groundwater contaminant plumes
    - Benzene plume (on-site)
    - Larger more diffuse TCE, 1,1-DCE, and 1,4-Dioxane plume migrating off-site
  - Groundwater plume impacted by two neighboring properties (same suite of VOCs)
  - Subject to Los Angeles RWQCB cleanup requirements (extremely conservative)

Figure 2 - Lateral Extent of Contaminant Plumes in 1992



Chronology of Remediation Technologies

Year	Technology Implemented
1995	Groundwater pump & treat – 10 years
1995	Soil vapor extraction (thermal oxidizer) – 11 years
2002	ISCO using Permanganate (chlorinated plume) – 1st Pilot Scale ISCO in LARWQCB
2006	ISCO using Persulfate and Peroxide (benzene plume) – Peroxide Activation
2007	Second ISCO using Persulfate (benzene plume) – Iron Activation
2008	Started using direct push technology (borings)
2008	Full Scale ISCO using Permanganate (chlorinated plume)
2009	Second Full Scale ISCO using Permanganate (chlorinated plume)
2014	Used hybrid drilling for Persulfate injections
2014	ISCO using Persulfate and ORC (benzene plume) – High pH activation
2015	Aerobic biodegradation identified – Cometabolism by Methane Oxidizing Bacteria
2019	Continuing with Monitored Natural Attenuation

Groundwater Pump and Treat System

- 11 groundwater extraction wells (ave. 9 gpm)
- Six carbon canisters (1,000 lb each)
- Disposal of treated water by NPDES permit
- Removed 409 lbs VOCs over 10 years

Potassium Permanganate Injections

- Permanganate used for treatment of TCE plume
- Mixing of 1,500 gallon batches (24 batches total)
- Use of eductor feed system for mixing
- Injection into existing monitoring wells wherever possible

- Permanganate is easily detected by pink/purple color

Peroxide and Persulfate Injections

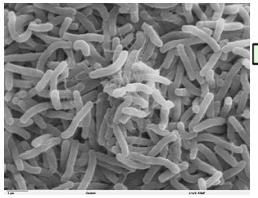
- **Stronger oxidants used for treatment of benzene plume**
- **Two 3,000 gal tanks of Hydrogen Peroxide**
- **Sodium Persulfate bags stored on Pallets**
- **Injection into injection wells (1st event) or direct push borings (later events)**

Use of Molecular Biological Tools (MBTs)

- Many advances in MBTs have occurred in last 10 years
- Microbial testing now routinely used to identify anaerobic and aerobic processes responsible for biodegradation of VOCs
- Microbial sampling started in 2014 and identified robust populations of aerobic methane oxidizing bacteria (MOB)
- Confirmed presence of methane mono-oxygenase (MMO) and propane mono-oxygenase (PPO) functional genes which are responsible for co-oxidation of TCE, 1,1-DCE, and 1,4-dioxane.
- Over the past 8 years, an average VOC attenuation rate between 8% to 12% per year has been maintained for TCE, 1,1-DCE, and 1,4-Dioxane.

TCE Biodegradation Pathways (Aerobic)

Two co-metabolic pathways, one involving methane and one involving propane, have been confirmed. Both pathways provide complete mineralization of TCE.



Methylosinus trichosporium

Mycobacterium vaccae

(MMO) Methane Mono-Oxygenase

(PPO) Propane Mono-Oxygenase

(methane) CH4 → (methanol) CH_3OH → (carboxylate) CHOOH → (carbon dioxide) CO_2 + (water) H_2O

(TCE) C_2HCL_3 → (TCE epoxide) C_2HCL_3O → (dichloro-acetic acid) $C_2H_2CL_2O_2$ → (carbon dioxide) CO_2 + (chloride) Cl_2 + (water) H_2O

(propane) C_3H_8 → 2-propanol C_3H_8O → (methanol) CH_3OH → (carbon dioxide) CO_2 + (water) H_2O

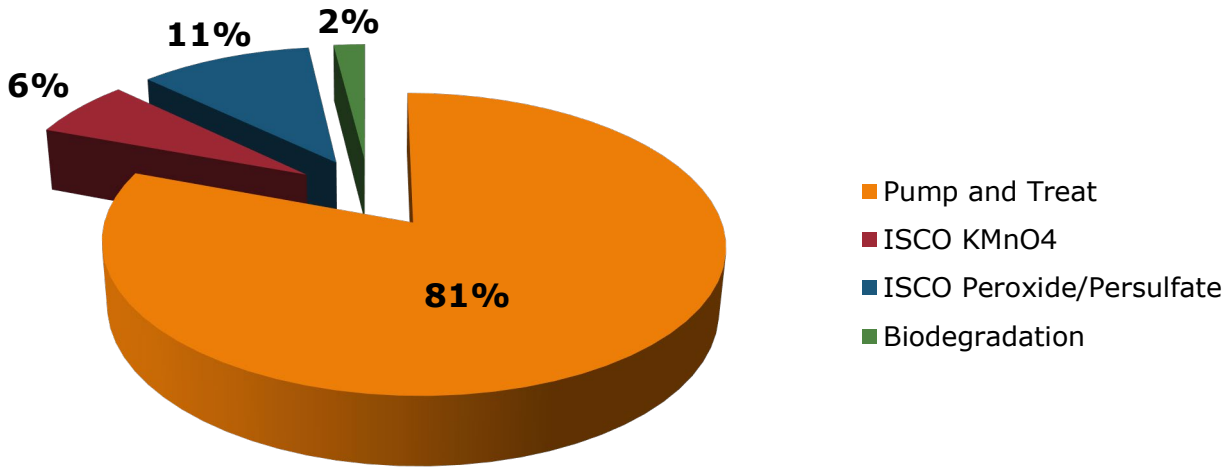
References: Kotani et al, 2003 and Vangnai et al, 2002.

Reduction of VOCs by Technology

Years	Technology Implemented	VOC Reductions
1995 to 2005	Groundwater pump & treat	Reduction of benzene from 90,000 to 5,000 ug/L
1995 to 2005	Groundwater pump & treat	Reduction of TCE from 2,700 to 550 ug/L
2002, 2007, 2008	Potassium permanganate injections	Reduction of TCE from 550 to 250 ug/L
2006, 2007, 2014	Peroxide and persulfate injections	Reduction of benzene from 5,500 to 4 ug/L (20 wells ND)
2015 to 2019	Aerobic Biodegradation	Attenuation of TCE from 250 to 30 ug/L
2015 to 2019	Aerobic Biodegradation	Attenuation of 1,1-DCE from 150 to 40 ug/L
2015 to 2019	Aerobic Biodegradation	Attenuation of 1,4-Dioxane from 100 to 40 ug/L

- **As observed at many sites, the cleanup of chlorinated constituents typically takes considerable longer than petroleum hydrocarbons**
- **Benzene cleanup achieved– 19 years (nearly ND)**
- **TCE, 1,1-DCE, and 1,4-dioxane cleanup – 25+ years (ongoing)**

Mass Removal by Technology



Technology	Mass Removed (lbs)	Percentage of Total
Pump and Treat (10 yrs)	409	80.67%
ISCO Permanganate	33	6.51%
ISCO Peroxide/Persulfate	55	10.85%
Aerobic Biodegradation	10	1.97%
Total Mass	**507**	**100.00%**

Use of Direct Push Technology

- Direct push technology used for shallow drilling (50 to 60 ft depth) starting in 2007
- For deeper depths, developed hybrid drilling plan
- Drill first 55 feet with hollow stem, then switch to direct push to advance remaining 20 ft and use injection tooling.

- Angle boring injection used to inject persulfate and magnesium peroxide (ORC) under property line

Advances in Direct Push Injection Tooling

- Specialized Injection tool (5 foot long) with adjustable screen length
- Inject at successive 2 foot to 5 foot depth intervals
- Used in lieu of dedicated injection wells

Groundwater Closure Issues

- Natural biodegradation processes are continuing to cleanup the TCE plume
- Levels of TCE, 1,1-DCE, and 1,4-dioxane now below 10 times the MCL level
- Complications from off-site VOC contaminant sources
- Benzene plume virtually eliminated

Soil Closure Issues

- SVE removed 99.9% of VOCs in vadose zone over 11 years

- However, a few isolated benzene “hot spots” exist in clayey soils in lower vadose zone (at 60 to 65 ft)

- V-Leach modeling has determined that benzene leachate will not significantly increase the groundwater level (less than 5 ug/L)

Technology Cost Savings

- ISCO injections saved an estimated $500,000 versus continuing with pump & treat

- Direct push technology saved an estimated $200,000 in drilling, direct injection tooling, and soil disposal costs

- Natural biodegradation of VOCs will save an estimated $300,000 over active remediation

- Total Savings using Innovative Technologies: **Over $1 million**