Long Term Performance Assessment at a Highly Characterized and Instrumented DNAPL Source Area following Bioaugmentation

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Motivation

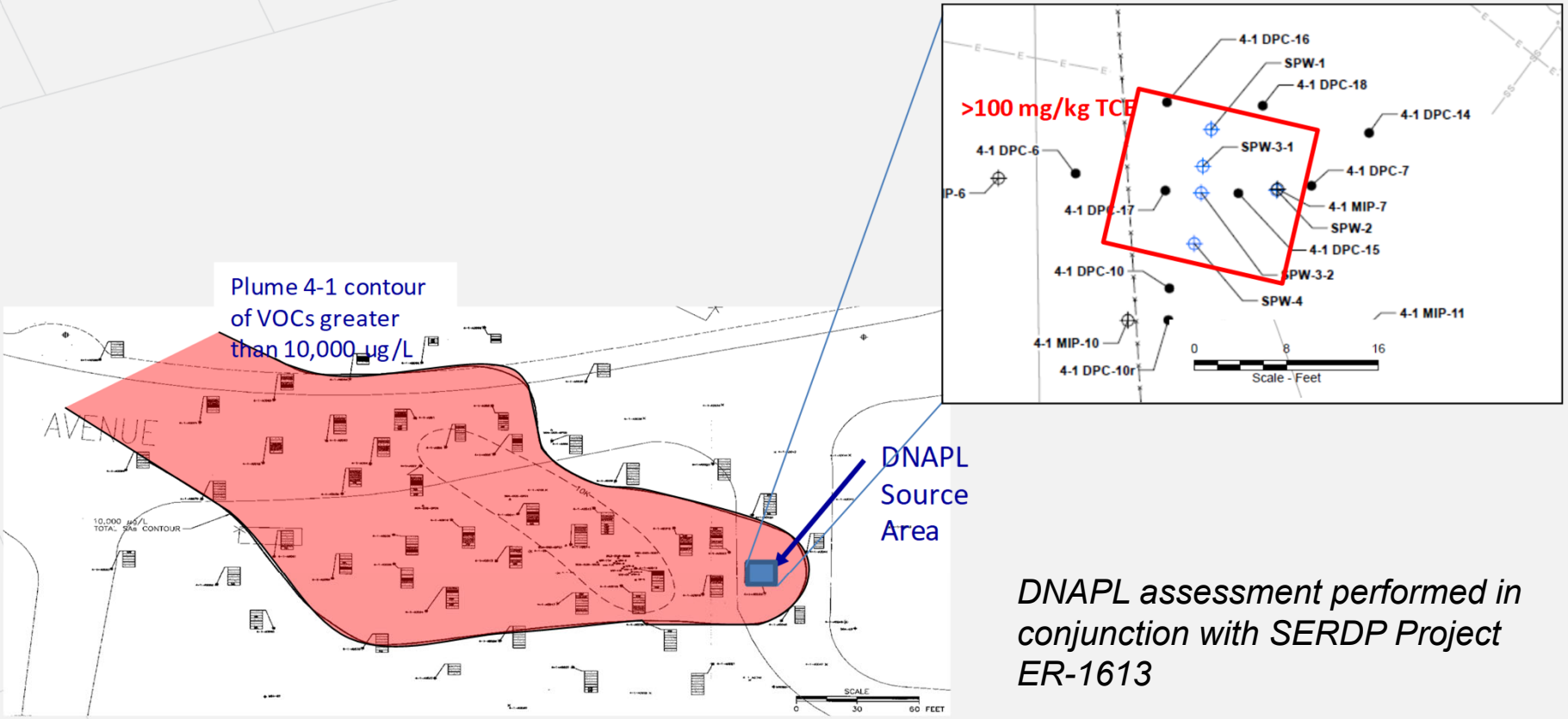
- Bioremediation/bioaugmentation for chlorinated ethenes has been widely and effectively applied

- Questions remain regarding long-term impacts after active treatment phase is completed
  - *Heterogeneous flow field*
  - *Residual DNAPL*

- How long will dechlorination persist after cessation of active treatment, and what type of dechlorination rates can be expected?

Can this be incorporated into site management to save resources?

Alameda Point, CA (former Alameda NAS)

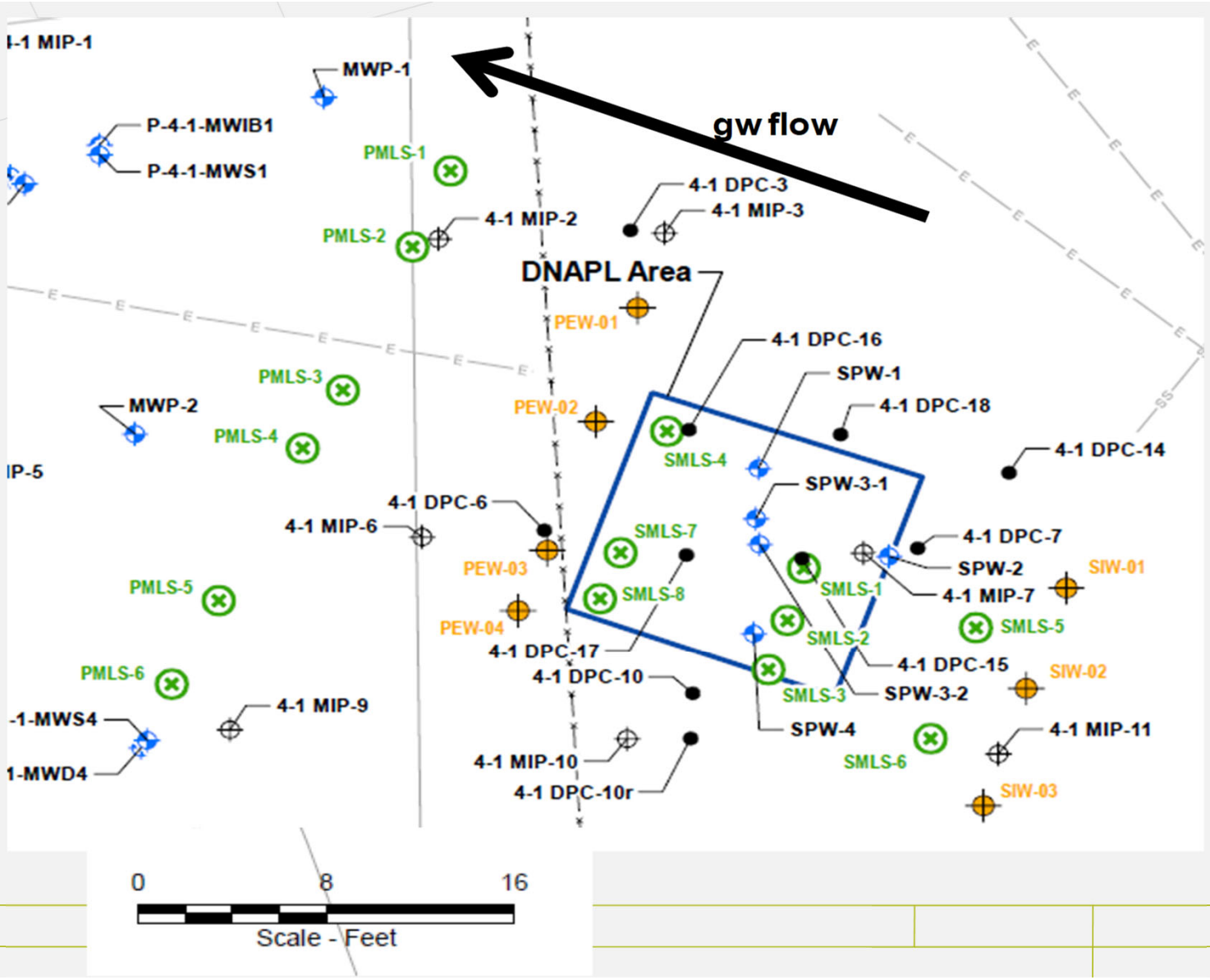


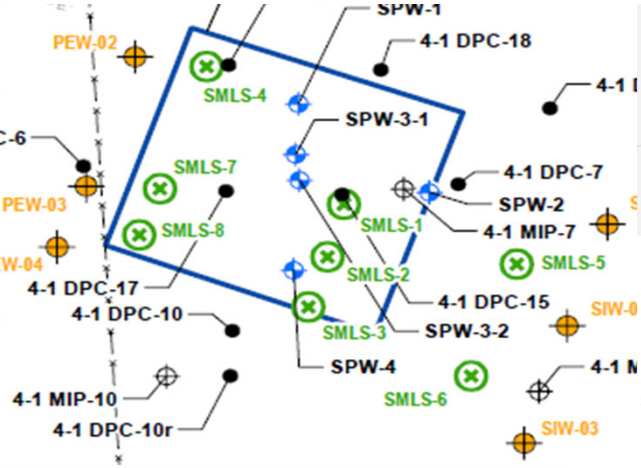
DNAPL assessment performed in conjunction with SERDP Project ER-1613

Source: Plume outline and figure from Data *Transmittal of Design Investigation (Phase III) for Plume 4-1 at IR Site 4, Alameda Point, Alameda, California*, Figure 7B: Groundwater VOC Screening Analyte Data for Plume 4-1 (IT Corporation, August 21, 2002)

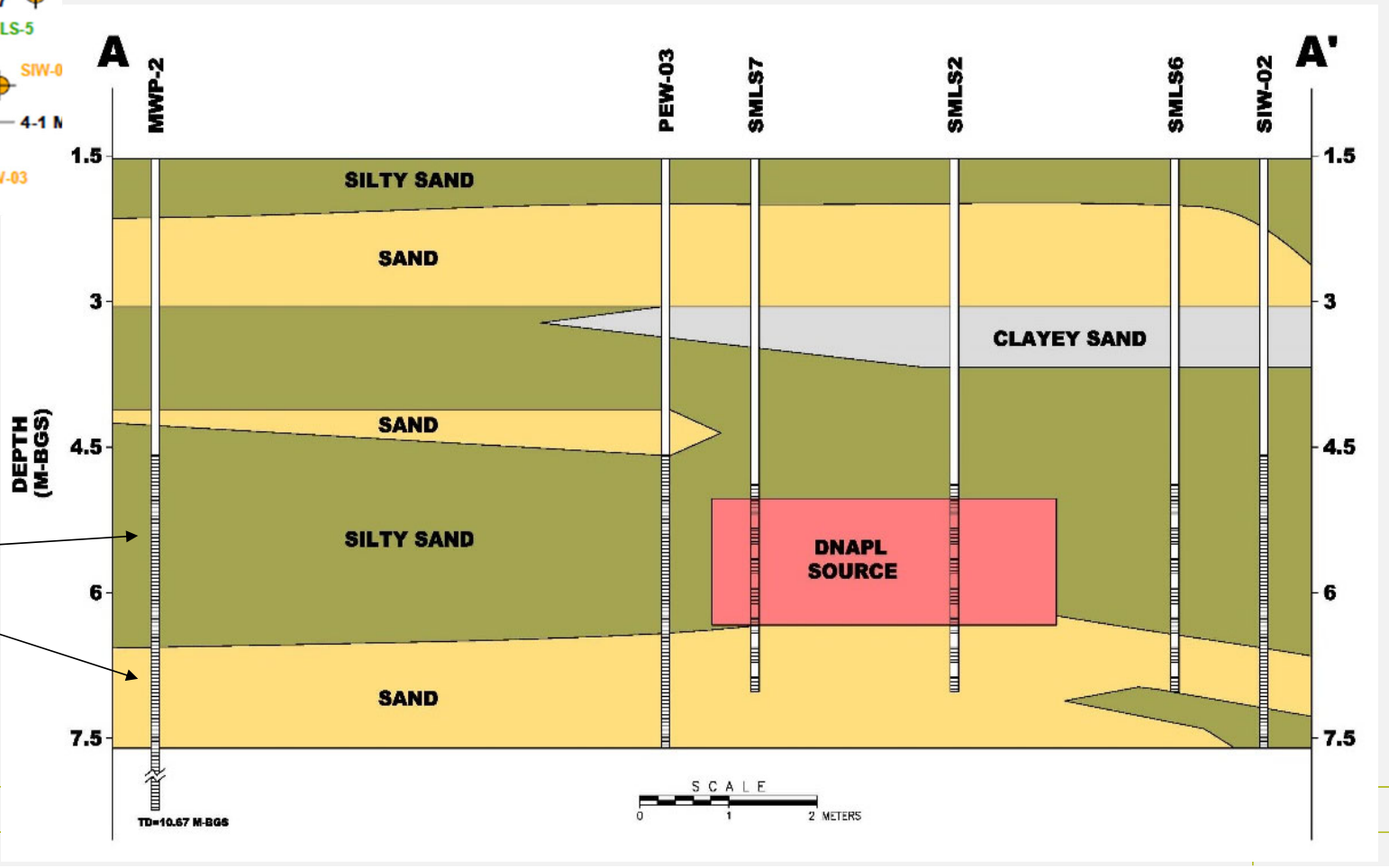
Source Area Activities (2011-2013)

- Soil & MIP investigations
- PFMs
- PTT
- Dissolution
- Bioaugmentation *with 9 weeks gw recirculation and lactate addition*





GW flow direction



V_L ~ 0.01 ft/day

V_H ~ 0.04 ft/day

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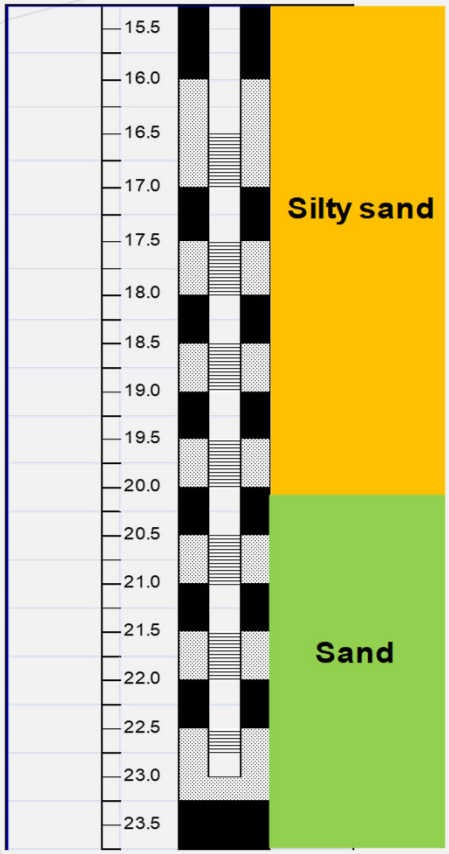
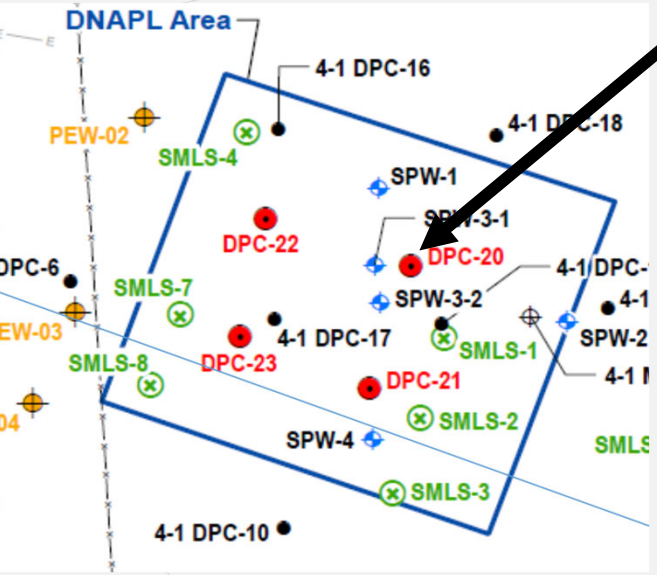
MLS Wells (Solinst)

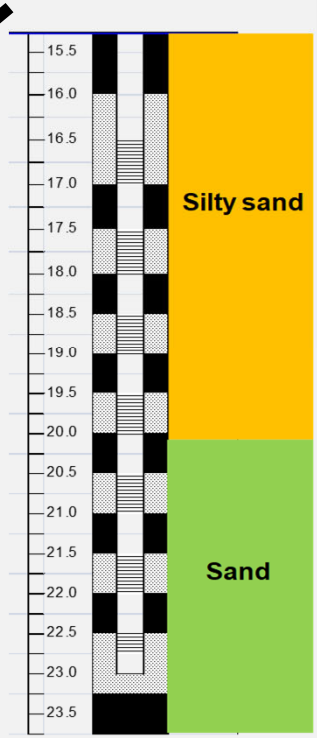


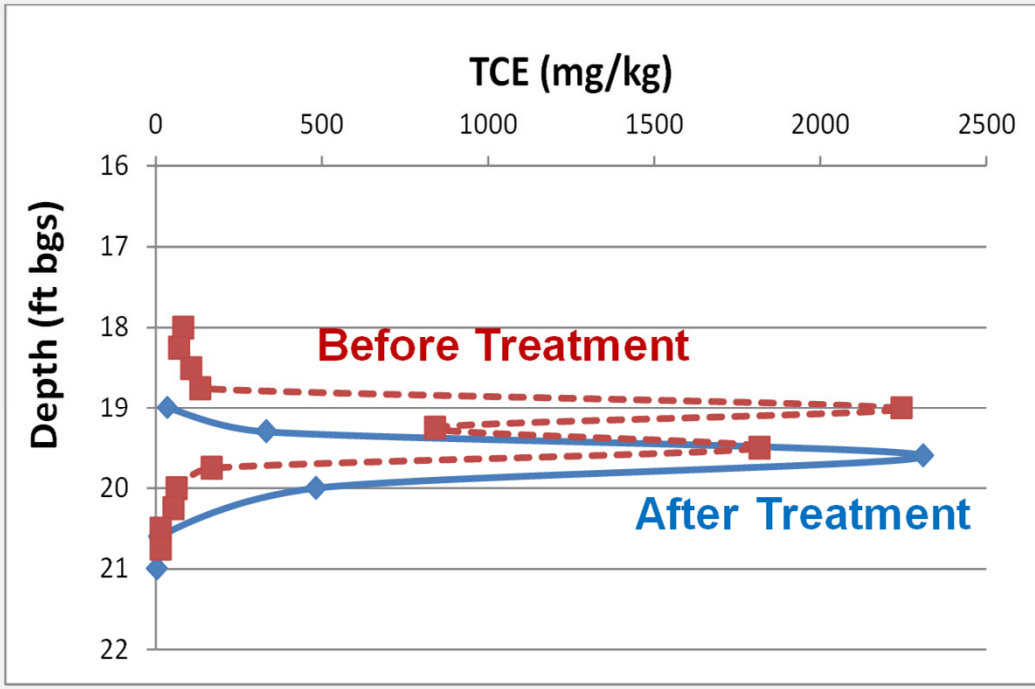
Post Treatment Monitoring

- 3 rounds of gw sampling performed 2 to 4 years following end of active bioremediation
  - VOCs, reduced gases, anions, hydrogen
  - *Dehalococcoides* sp. and functional genes
- Soil sampling to assess DNAPL persistence
- CSIA (carbon)

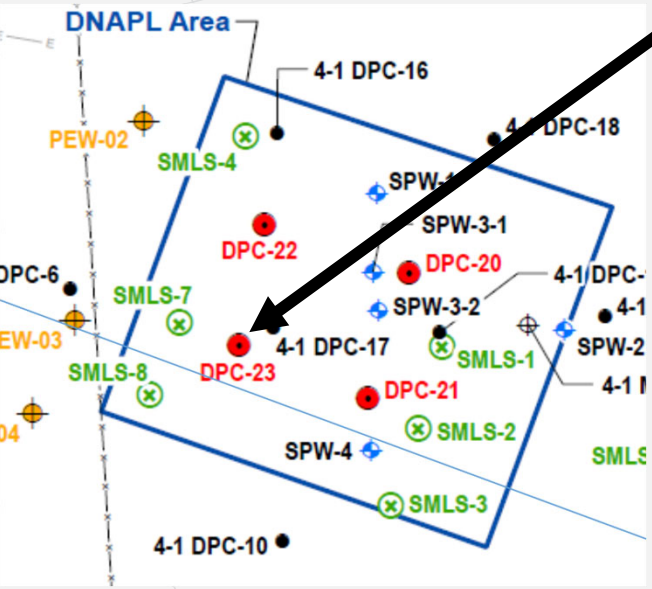
Soil Results – DNAPL Persistence

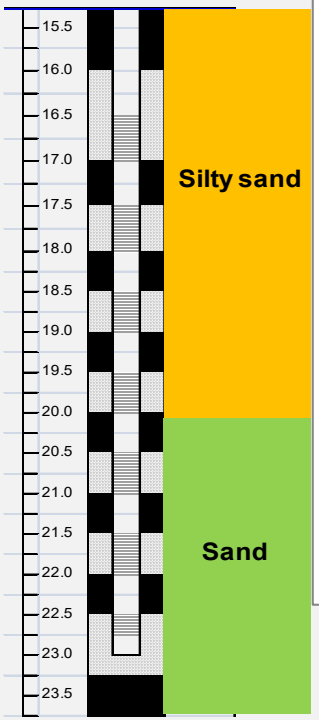


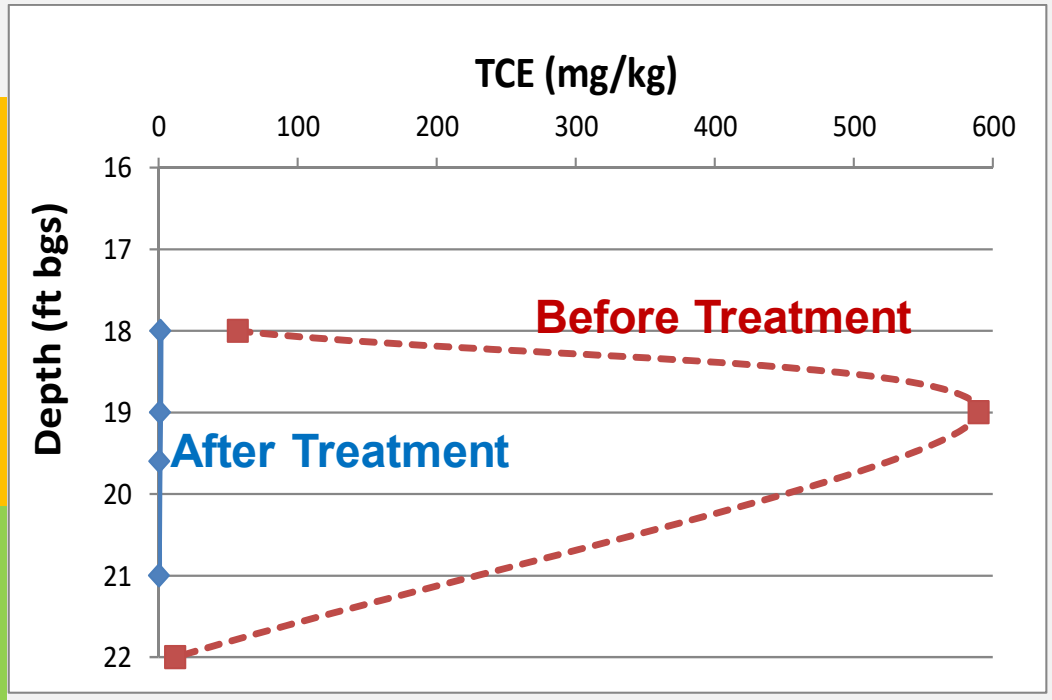




Soil Results – DNAPL Removed







Ratios [4 year post bioremediation : Pre-bioremediation]

- ***No VFAs***
- ***Anaerobic (background)***
- ***Background TOC 1 to 30 mg/L***

Data suggest conditions for enhanced biotic reductive dechlorination still persist

Well Identification	Methane Ratio	Sulfate Ratio	DHC Ratio
Low Permeability			
SMLS 1-1	46	0.48	NA
SMLS 1-2	40	0.50	4700
SMLS 1-3	48	0.46	1100
SMLS 4-2	23	0.68	1700
SMLS 4-3	124	0.48	2000
SMLS 7-1	15	0.34	73000
SMLS 7-2	48	0.23	830
SMLS 7-3	19	0.23	140
High Permeability			
SMLS 1-4	22	0.56	438
PEW-02	4.4	0.64	NA
PEW-03	8.6	0.80	NA

Molar Fraction of Ethene to Chlorinated Ethenes

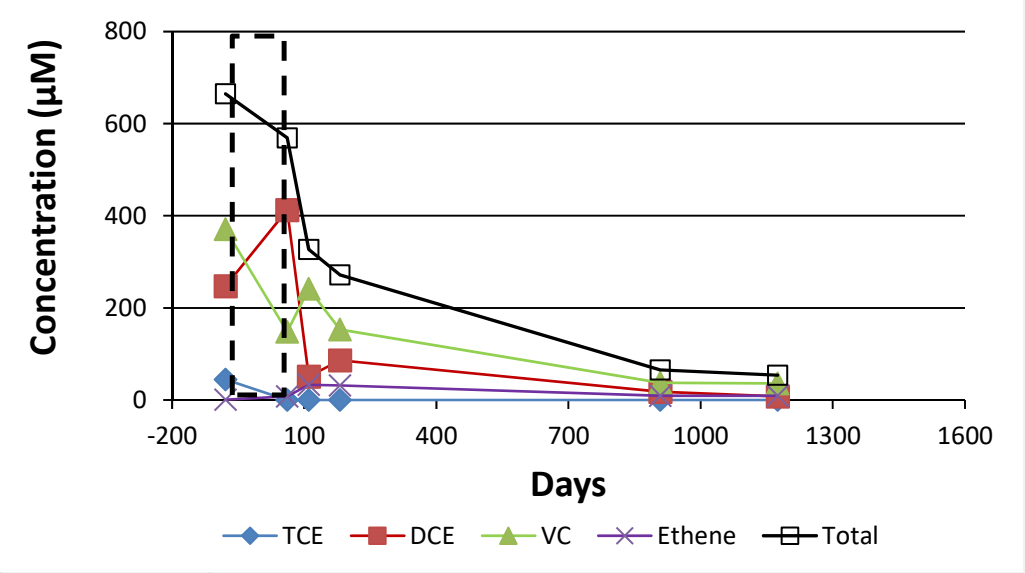
Well Identification	Prior to Bioaugmentation	Final Rebound Sampling
Low Permeability		
SMLS 1-1	0.013	1.7
SMLS 1-2	0.0035	0.088
SMLS 1-3	0.0026	0.052
SMLS 4-2	0.16	0.021
SMLS 4-3	0.042	0.28*
SMLS 7-1	0.0020	0.031
SMLS 7-2	0.0018	0.22
SMLS 7-3	0.0024	0.038
High Permeability		
SMLS 1-4	0.0099	0.093
PEW-02	0.017	0.069
PEW-03	0.23	0.097

Downgradient of existing DNAPL

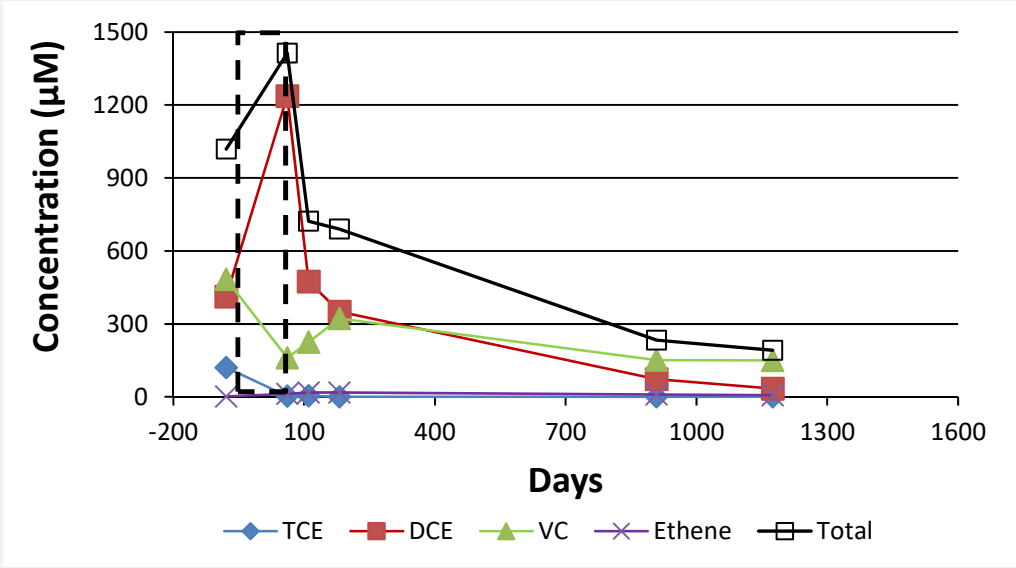
Chlorinated Ethenes & Ethene – Low Flow Zone

Zone where DNAPL was Treated

SMLS 7-2



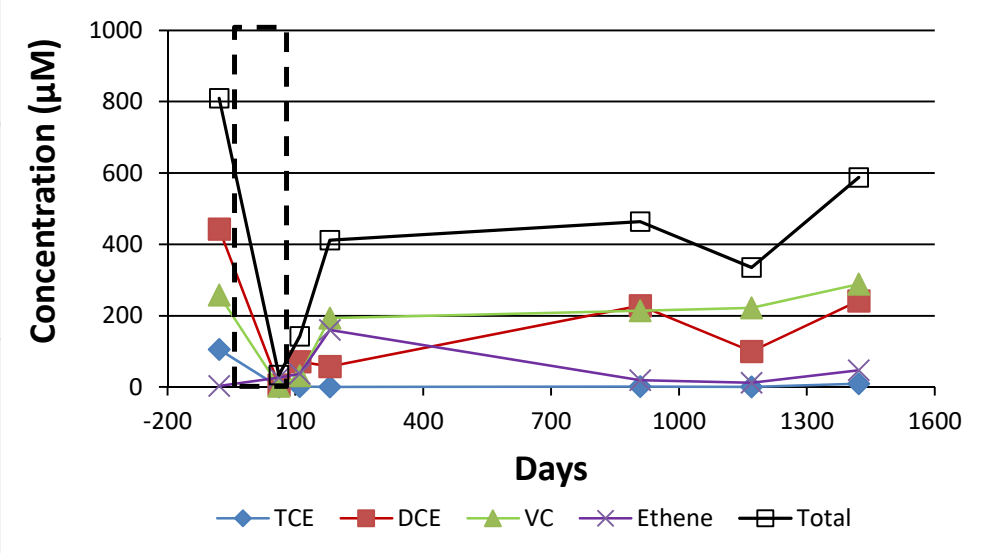
SMLS 7-3



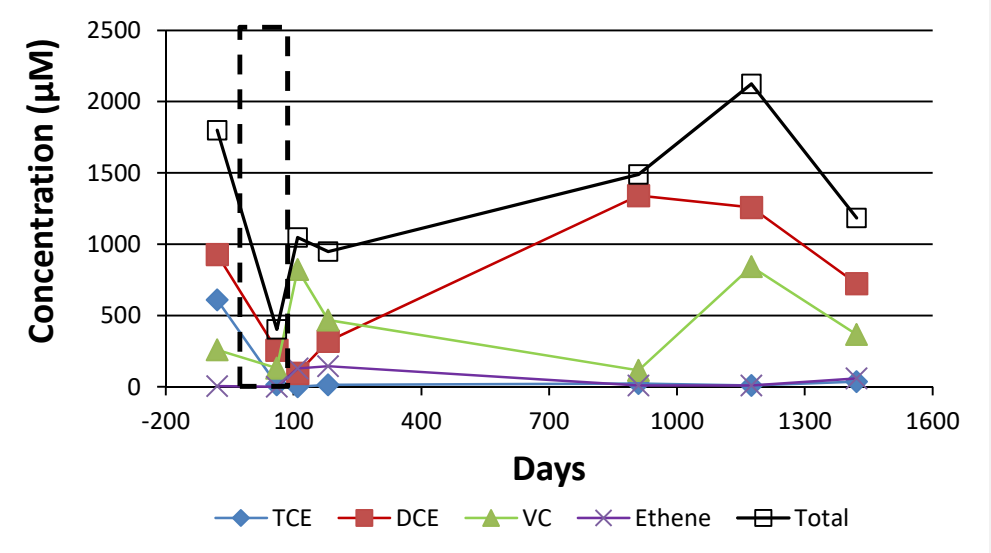
Chlorinated Ethenes & Ethene – Low Flow Zone

Zone where DNAPL was Remaining

SMLS 1-2

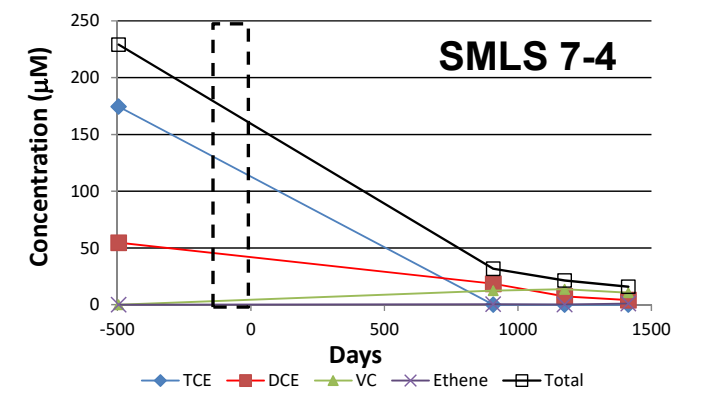


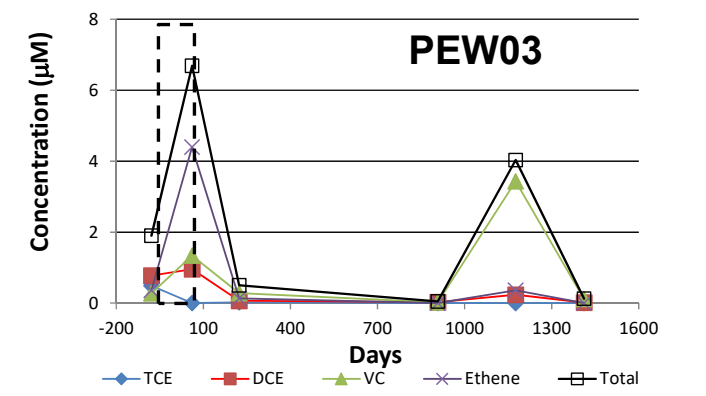
SMLS 1-3



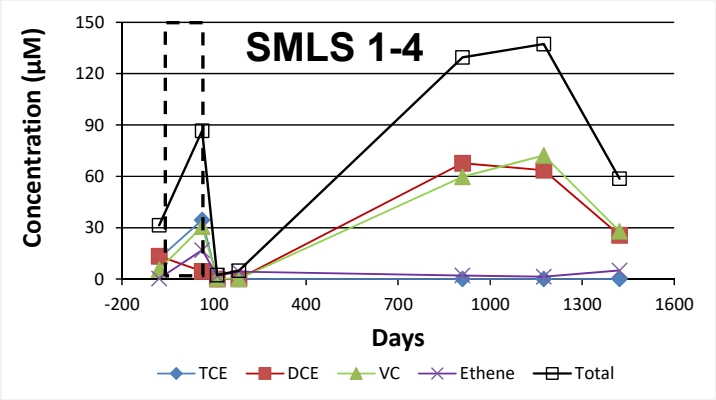
Chlorinated Ethenes & Ethene – High Flow Zone

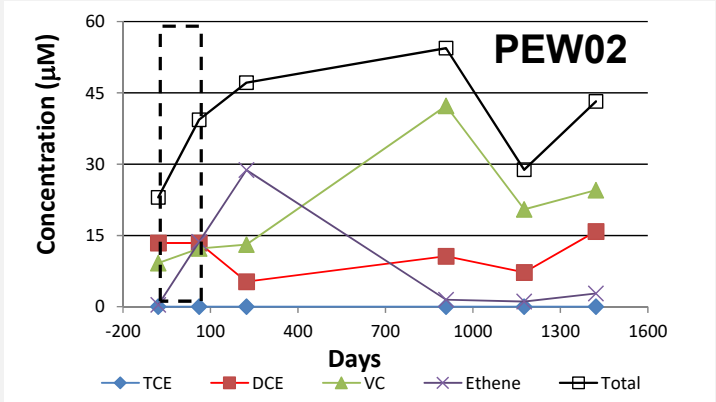
DNAPL Removed





DNAPL Remaining



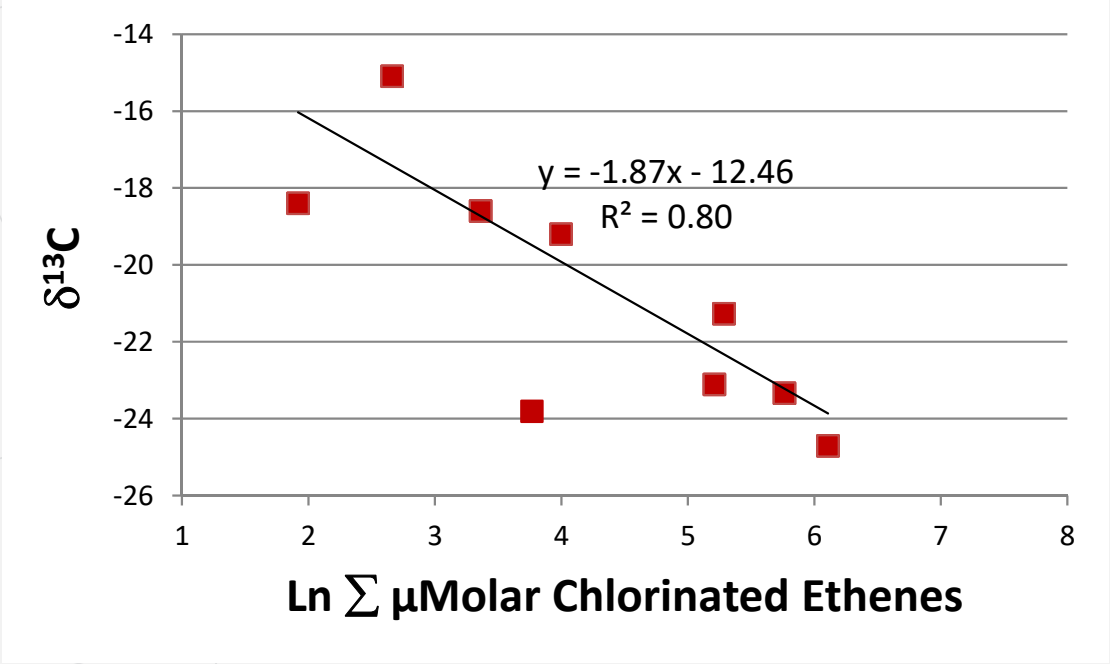


Quantification of Complete Dechlorination

CSIA (carbon) molar balance on chlorinated ethenes

$$\delta^{13}C = (\underbrace{\chi_{TCE}}_{\text{mole fraction}} \underbrace{\delta^{13}C_{TCE}}_{^{13}\text{C isotopic level } ‰} + \chi_{DCE}\,\delta^{13}C_{DCE} + \chi_{VC}\,\delta^{13}C_{VC})$$

Isotopic Enrichment along Flowpath Emanating from DNAPL Sources (High Flow Zone)



Enrichment Factor (ε) = -1.87

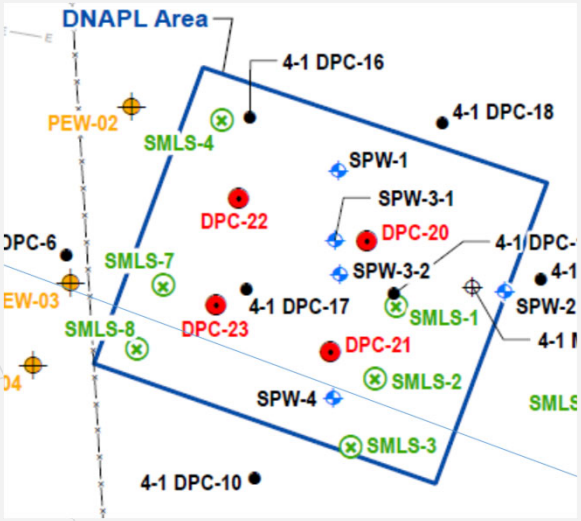
- Apparent contradiction of ethene data (ethene < 10% of chlorinated ethenes)
- Less negative than the range typically observed for biotic reductive dechlorination

Possible oxidation of VC or ethene

Ongoing Dechlorination

$$k = \frac{v\left(\delta^{13}C_0 - \delta^{13}C_{PMLS}\right)}{\varepsilon d}$$

K = 3.6 yr^{-1} (half life = 0.19 yr)



Assuming this rate remains unchanged, remaining DNAPL mass removed in 12 to 15 years

Summary

- Enhanced reductive dechlorination can occur several years after cessation of active bioremediation, even when using a rapidly depleted electron donor (e.g., lactate)
- CSIA can be an effective tool for estimating dechlorination rates, while reliance on ethene generation alone can be misleading
- Consideration of long-term dechlorination rates may justify shorter active treatment duration

Research Funding