Where is the Vinyl Chloride?

Alternative Natural and Enhanced Degradation Pathways for Chlorinated Solvents

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Battelle 6th International Symposium on Bioremediation and Sustainable Environmental Technologies

Abstract #407

Session: D9. Tools for Site Assessment and Bioremediation Monitoring

May 11, 2023

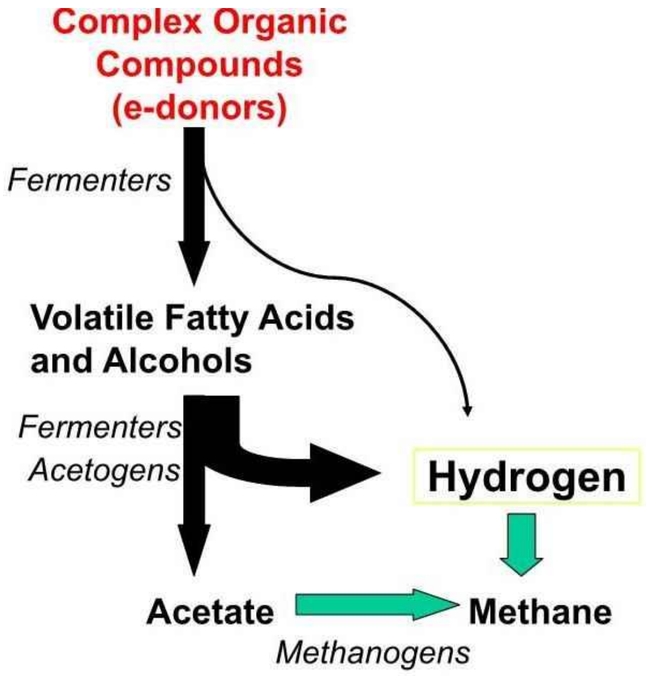
Outline

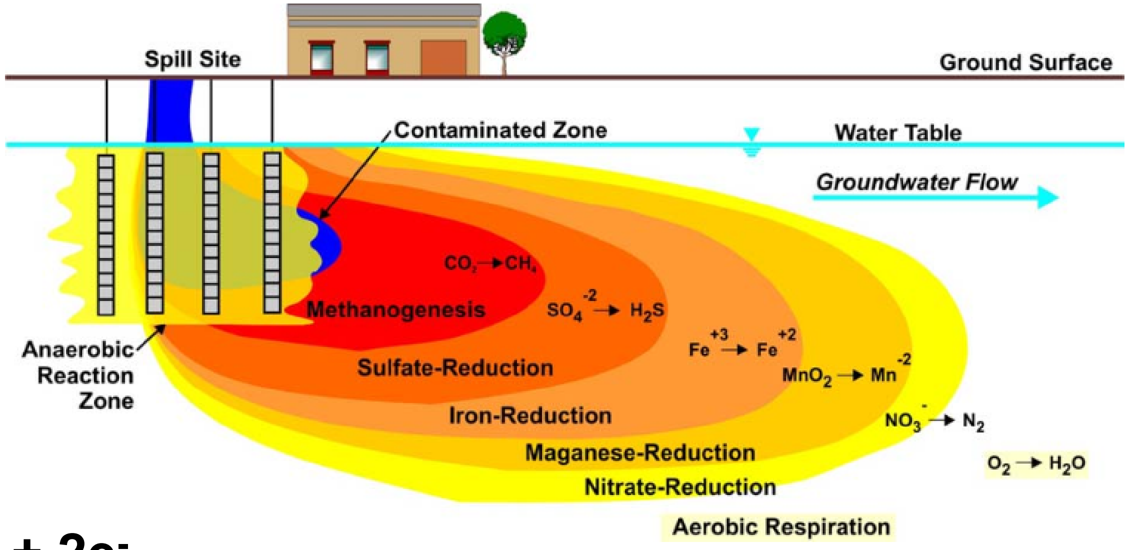
- Overview of Chlorinated Solvent Degradation Pathways
- Where is the vinyl chloride?
  - Active Manufacturing Site – Central Kansas – Alluvial Aquifer
  - Former Manufacturing Site – Southern California – Colluvial Aquifer
- Conclusions / Lessons Learned
- Questions

Overview of Chlorinated Solvent Degradation Pathways

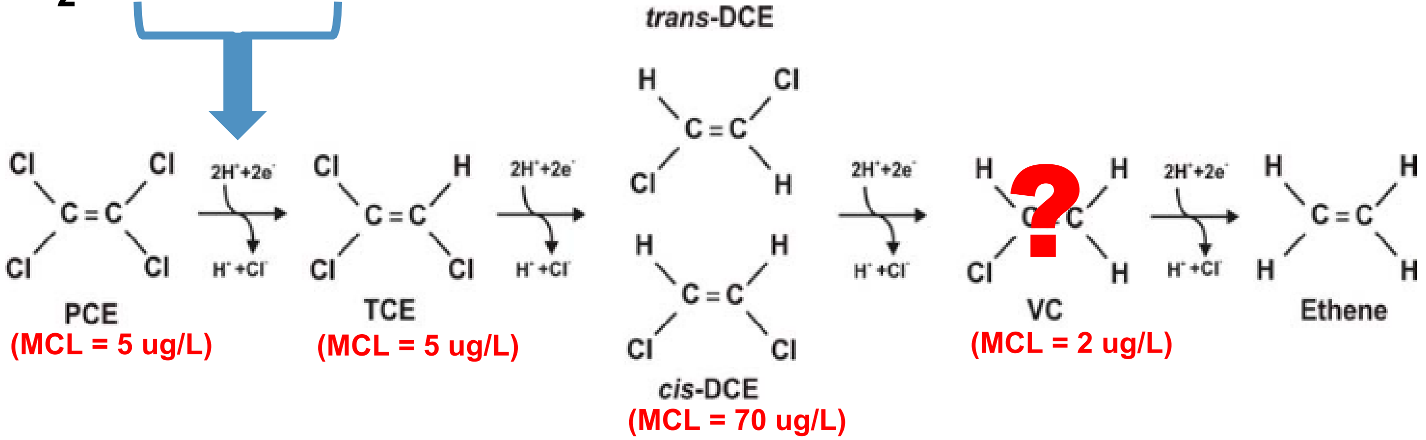
Common & Less Common Pathways

Anaerobic Reductive Dechlorination (Hydrogenolyis)



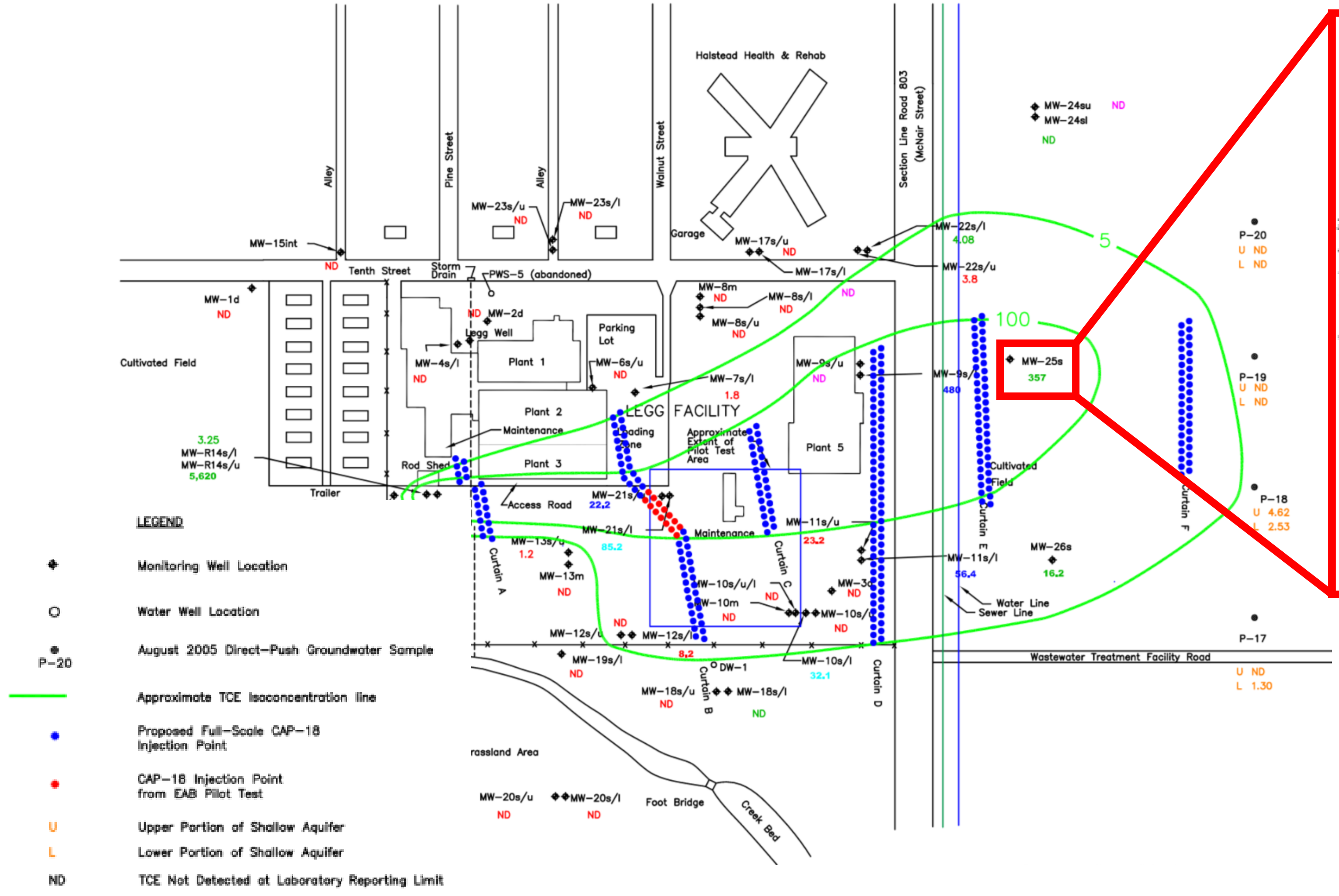


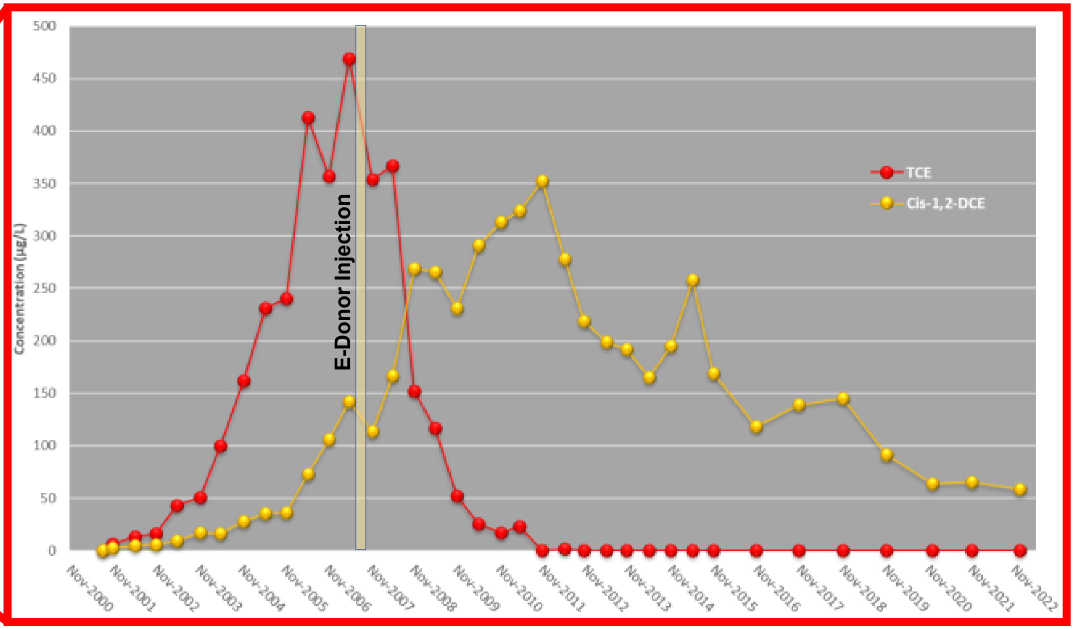
$$H_2 \rightarrow 2H^+ + 2e^-$$



Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents (Parsons, 2004)

Where is the Vinyl Chloride?
Active Manufacturing Site – Central Kansas





- Aerobic alluvial aquifer
- 60-acre dilute plume
- Marked increase in cis-1,2-DCE (cDCE) following EISB; followed by gradual cDCE decrease
- No vinyl chloride detections for over 20 years of monitoring

Alternative Pathways

- Abiotic dichloroelimination (β-elimination)
- Aerobic cometabolism
- Direct oxidation

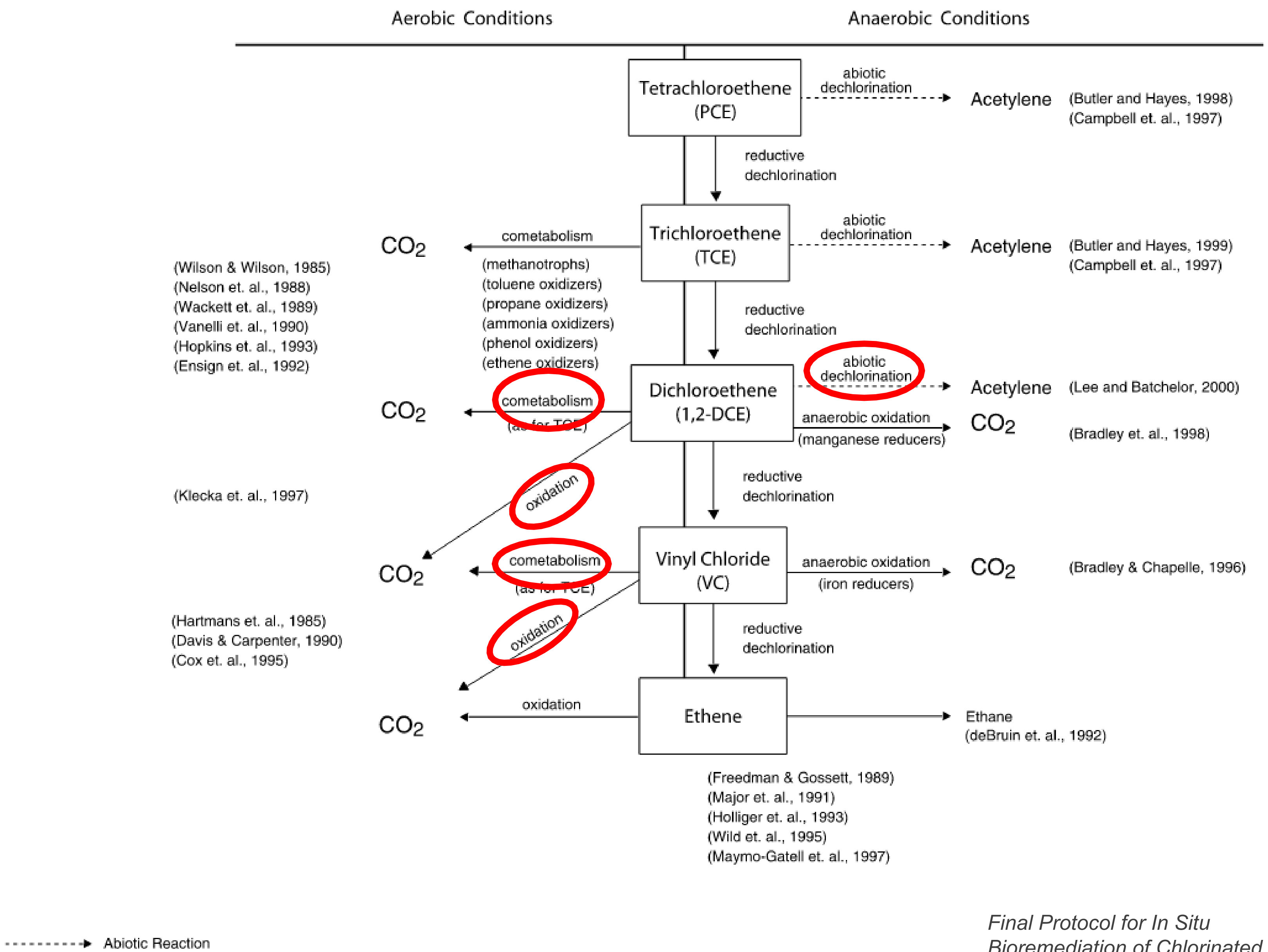


Figure 1.2: Pathways for the Degradation of Chlorinated Ethenes

Final Protocol for In Situ Bioremediation of Chlorinated Solvents using Edible Oil (AFCEE, 2007)

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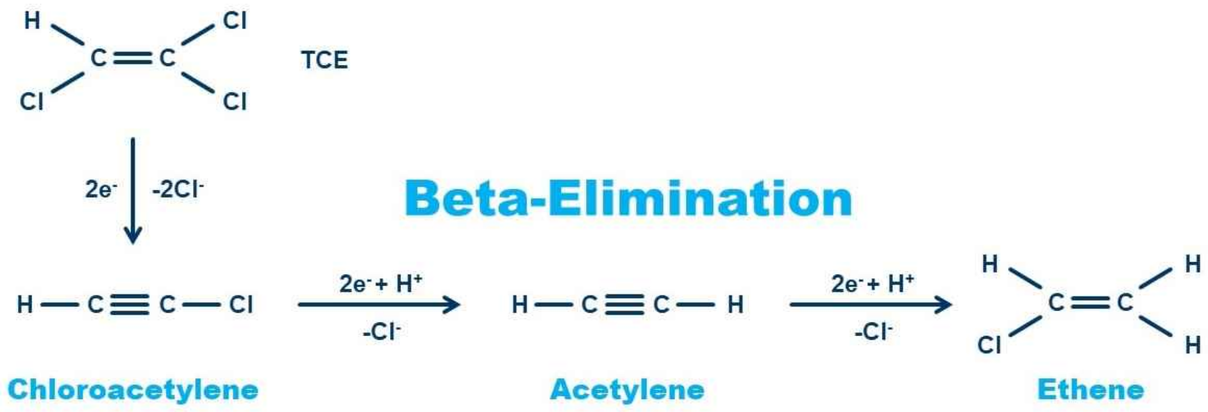
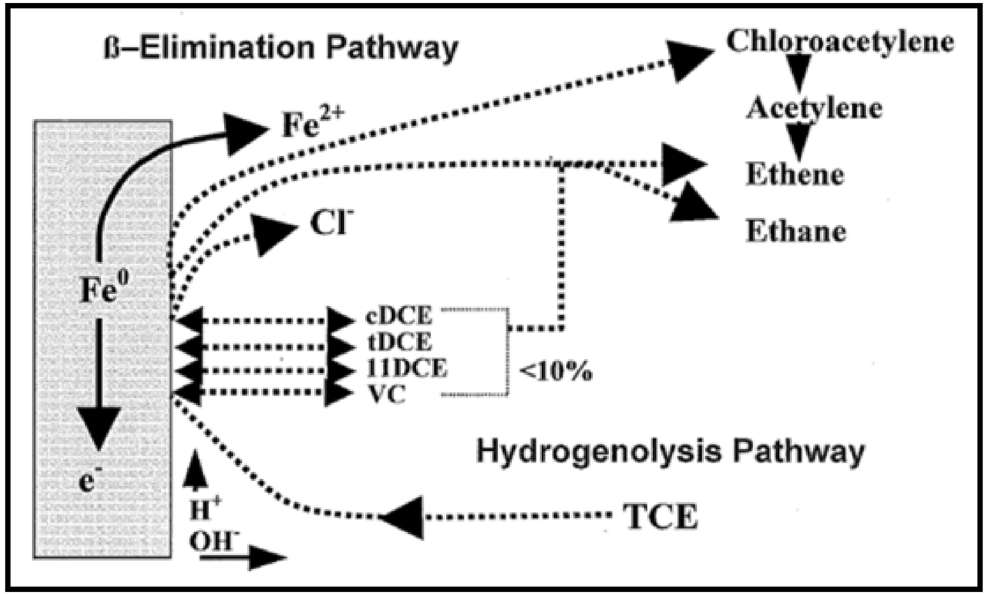
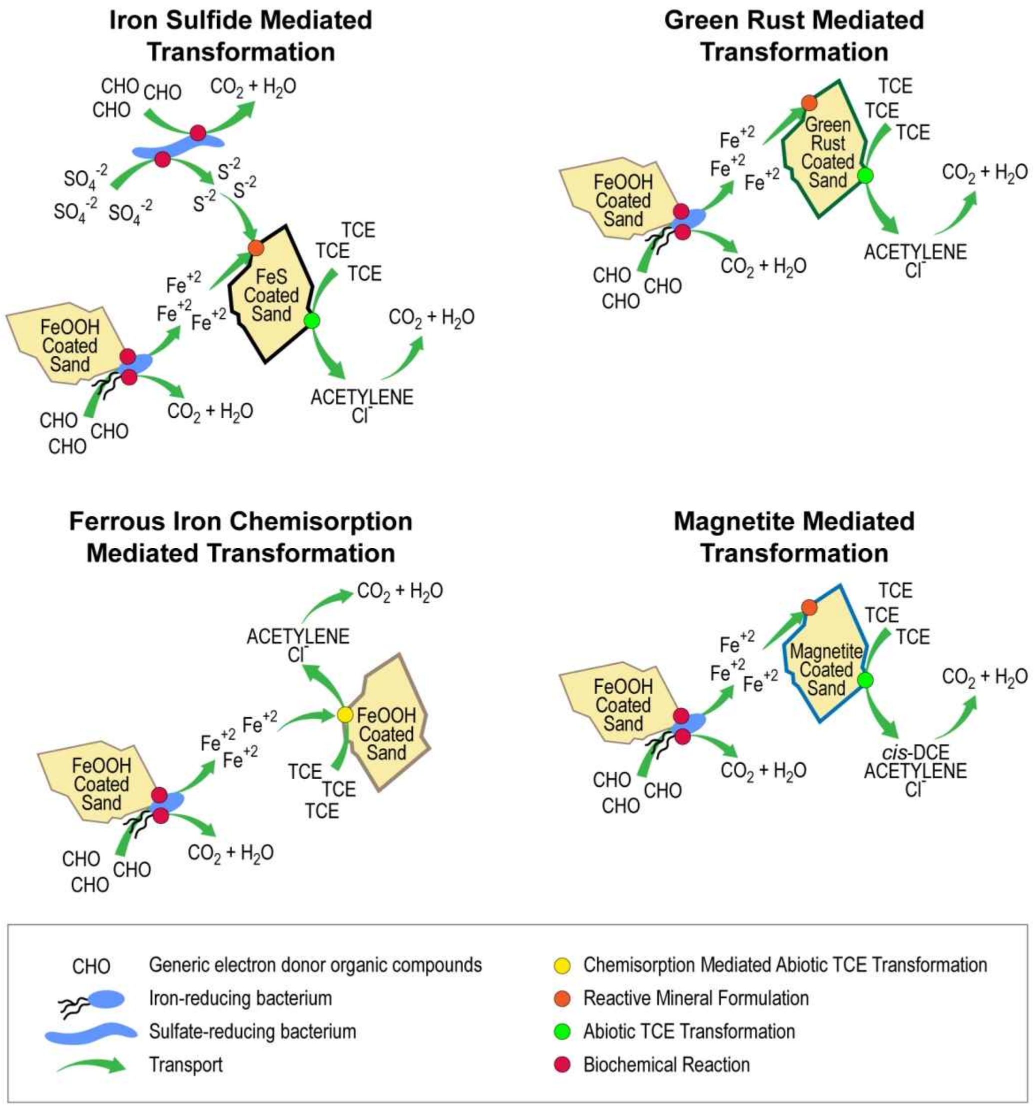
Abiotic β-elimination



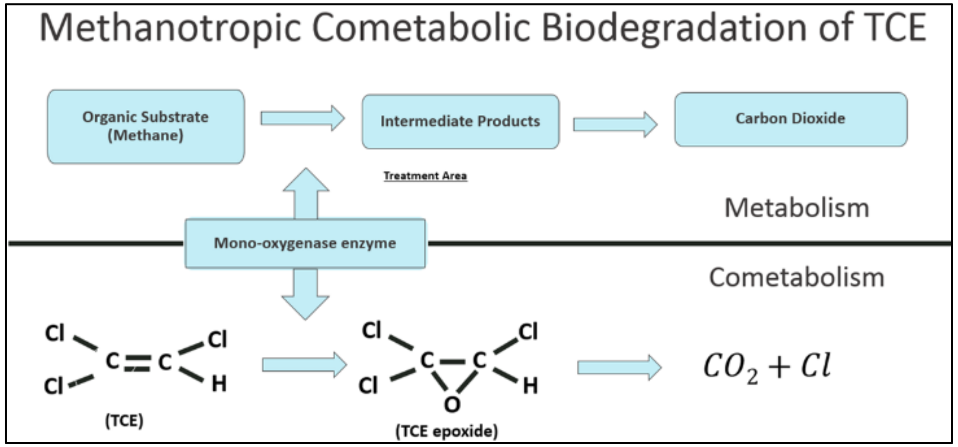




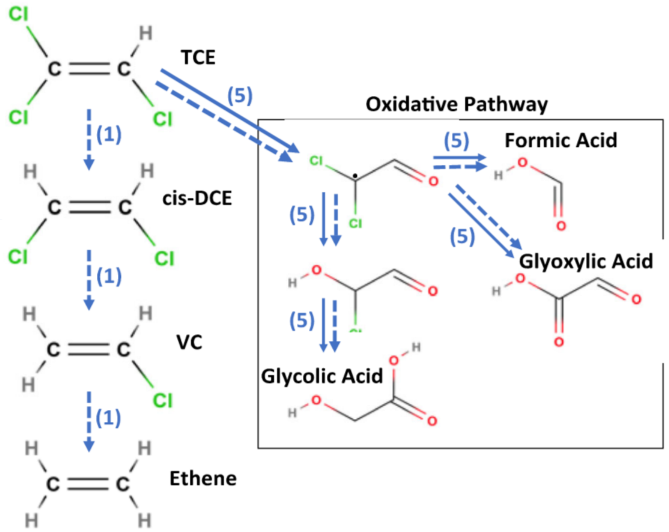
Stroo, H.F., Ward, C.H., 2010. Future Directions and Research Needs for Chlorinated Solvent Plumes. *In Situ Remediation of Chlorinated Solvent Plumes*, Springer, New York. pgs. 699-725.

Aerobic Cometabolism & Direct Oxidation

- **Cometabolism**
  - COC oxidized by enzyme produced during primary reaction
  - Oxygen is the electron acceptor
  - Methane, toluene, propane, phenol, etc. are electron donors
- **Direct Oxidation**
  - Hydroxyl radicals may be produced when ferrous iron minerals react with oxygen (DO)



Cometabolic Methanotrophic Enhanced Natural Attenuation at a TCE Superfund Site
(T. Cornuet et. al, Battelle Bioremediation Symposium, 2019)



Werth, C., et al. (2020). Final Report – Biogeochemical Processes that Control Natural Attenuation of Trichloroethylene in Low Permeability Zones – SERDP Project ER-2530. SERDP. Alexandria, VA.

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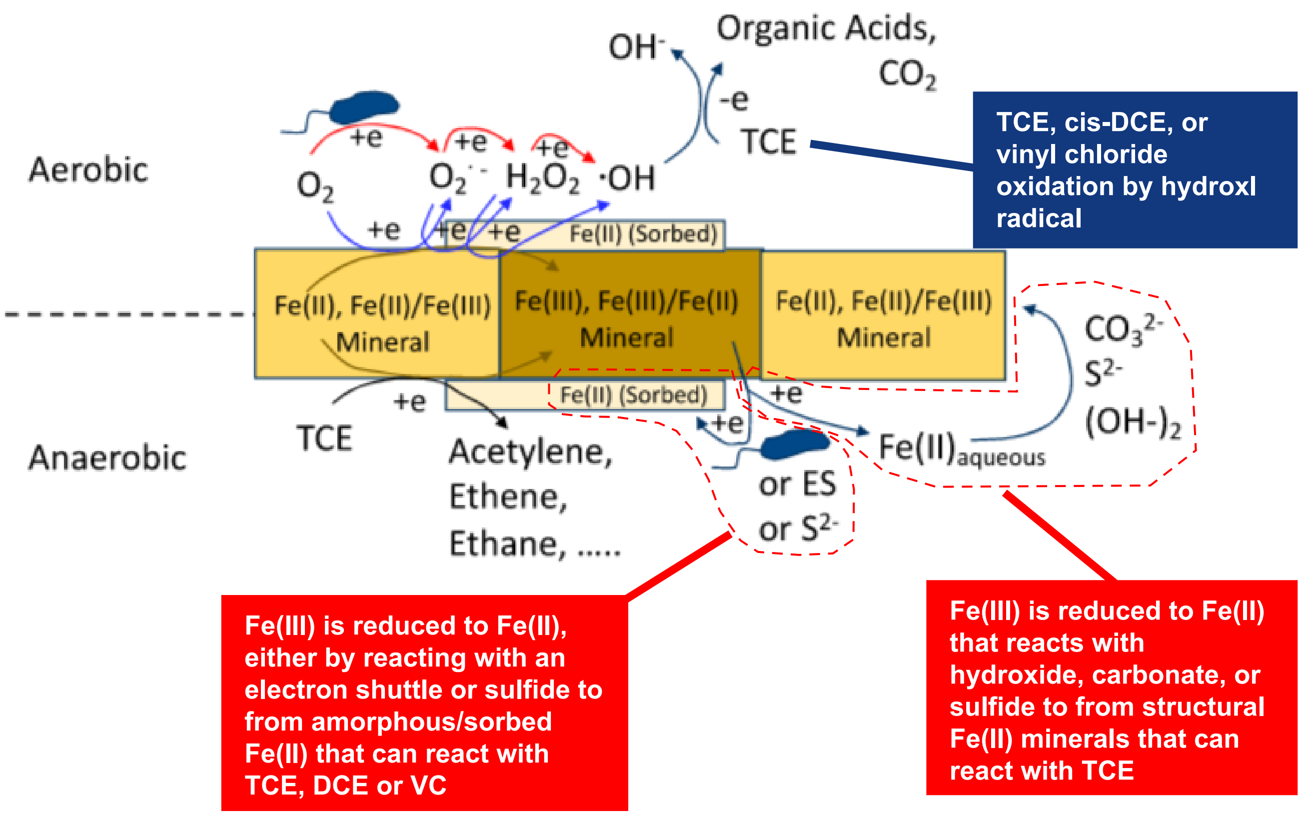
Synergistic Mechanisms at Boundaries

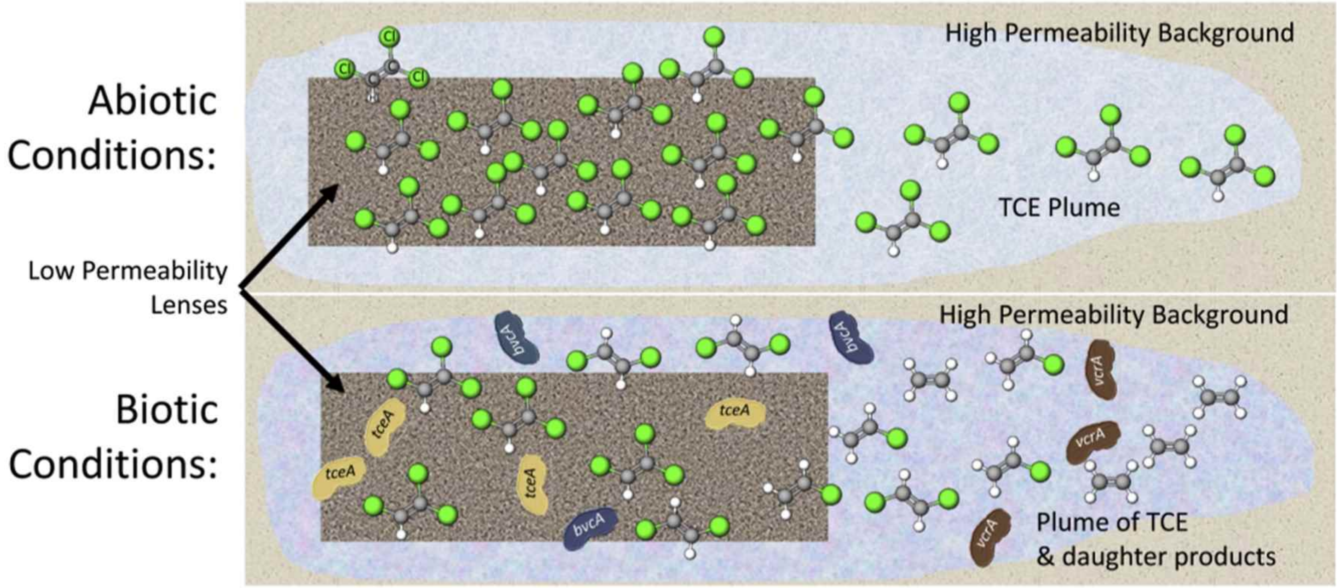
- Potential for multiple, synergistic mechanisms at subsurface boundaries
  - Aerobic / Anaerobic
  - Low / High Permeability



Conceptual model of TCE abiotic reactions under aerobic and anaerobic conditions.
Werth, C., et al. (2020). Final Report – Biogeochemical Processes that Control Natural Attenuation of Trichloroethylene in Low Permeability Zones – SERDP Project ER-2530. SERDP. Alexandria, VA.

Importance of the Conceptual Site Model

- Conditions vary with geology, geochemistry & permeability
- Low-k zones within aerobic aquifers often:
  - Harbor high concentrations of VOCs due to matrix diffusion
  - Contain organic carbon and reactive minerals species
  - Can support biotic/abiotic reductive dichlorination
- These zones may be leveraged or created as part of EISB or MNA strategies



Abriola, Capiro, Hnatko, Pennell, Yan, 2020. *Bioenhanced Back Diffusion and Population Dynamics of Dehalococcoides Mccartyi Strains in Heterogeneous Porous Media*, Chemosphere, Volume 254, 2020, 126842, ISSN 0045-6535, https://doi.org/10.1016/j.chemosphere.2020.126842.

Where is the Vinyl Chloride?

Active Manufacturing Site – Central Kansas – Alluvial Aquifer

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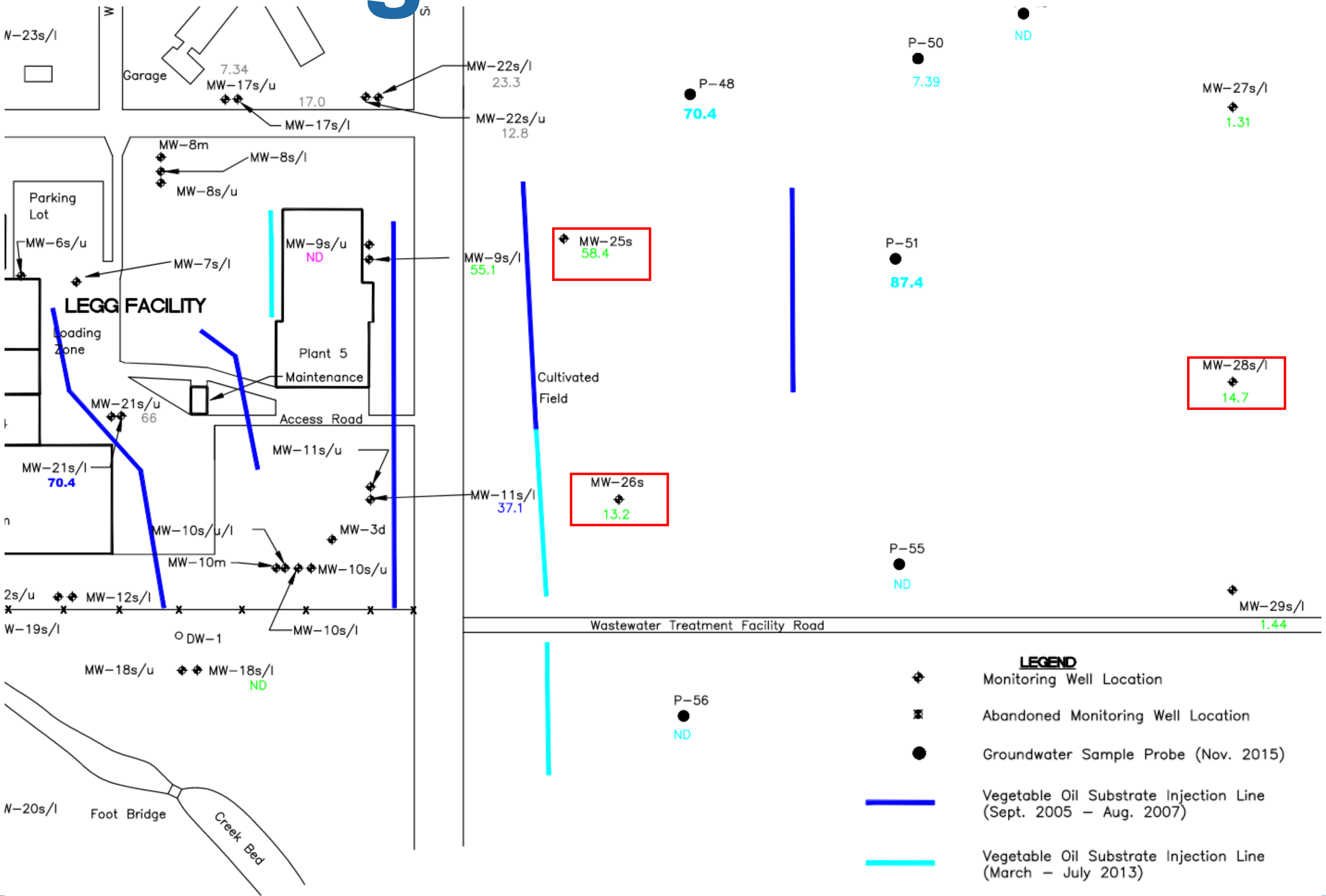
Lines of Evidence Evaluation for Biodegradation



- Geochemical Results
  - DO: varies with infiltration rates (typ. 2 – 4 mg/L)
  - ORP: also variable (typ. -50 to +100 mV)
  - Methane: 1,000 – 5,000 ug/L
  - Mn (dissolved): 500 – 800 ug/L
  - Fe(II): <100 – 300 ug/L
  - Sulfate: variable (typ. 20 – 200 mg/L)
- Potential cDCE degradation pathways
  - Hydrogenolysis – May be occurring, with VC not accumulating in detectable quantities?
  - Cometabolism – DO and methane are present
  - Abiotic Oxidation – DO and reactive Fe minerals may be present
  - β-elimination – May be occurring in anaerobic zones?

Lines of Evidence Evaluation for Biodegradation

- MBT results
  - Low DHC levels detected in all wells
  - VC reductase genes generally not detected
  - Other dechlorinators (DHBt, DHG, DSM)
    - Notable detections in MW-25s, indicating diverse microbial community
  - Sulfate reducers
    - Significant populations – potential for DHC competition and reactive mineral formation
  - Methanogens present

Microorganism / Functional Gene / Enzyme	Relevant Targeted Compounds	MW-25s		MW-26s		MW-28s/I	
		cells/mL	Percentile	cells/mL	Percentile	cells/mL	Percentile
Reductive Dechlorination							
Dehalococcoides (DHC)	PCE, TCE, DCE, VC	3.30E+01	38%	6.49E+01	44%	1.12E+01	27%
tceA Reductase (TCE)	TCE	<5.00E-01		<5.00E-01		<5.00E-01	
BAV1 Vinyl Chloride Reductase	PCE, TCE, DCE, VC	<5.00E-01		<5.00E-01		<5.00E-01	
Vinyl Chloride Reductase (VCR)	PCE, TCE, DCE, VC	<5.00E-01		2.00E-01 (J)	<8%	<5.00E-01	
Dehalobacter spp. (DHBt)	TCE	2.29E+03	67%	<4.70E+00		<4.80E+00	
Dehalogenimonas spp. (DHG)	PCE, TCE, DCE, VC	1.68E+03	28%	1.29E+03	26%	<4.80E+00	
Desulfitobacterium spp. (DSB)	TCE	3.12E+02	37%	<4.70E+00		<4.80E+00	
Dehalobium chlorocoercia (DECO)		5.99E+02		6.89E+02		8.29E+02	
Desulfuromonas spp. (DSM)	TCE	2.50E+00 (J)	<5%	<4.70E+00		6.66E+01	14%
Aerobic (Co)Metabolic							
Soluble Methane Monooxygenase	PCE, TCE, DCE, VC	2.50E+00 (J)	<1%	<4.70E+00		3.10E+00 (J)	<1%
Toluene Dioxygenase (TOD)	PCE, TCE, DCE, VC	<4.80E+00		<4.70E+00		<4.80E+00	
Phenol Hydroxylase (PHE)	PCE, TCE, DCE, VC	1.50E+02	33%	5.09E+01	21%	1.47E+02	33%
Toluene Monooxygenase 2 (RDEG)	PCE, TCE, DCE, VC	3.14E+02	41%	<4.70E+00		1.19E+02	27%
Toluene Monooxygenase (RMO)	PCE, TCE, DCE, VC	8.00E-01 (J)	<6%	3.10E+00 (J)	<6%	5.09E+02	54%
Ethene Monooxygenase (EtnC)	VC	9.20E+00	<13%	<4.70E+00		<4.80E+00	
Epoxyalkane Transferase (EtnE)	VC	<4.80E+00		3.74E+01	14%	7.07E+01	21%
Other							
Total Eubacteria (EBAC)		2.57E+06	75%	1.89E+06	70%	1.67E+06	68%
Sulfate Reducing Bacteria (APS)		5.28E+04	63%	3.35E+04	59%	3.54E+04	59%
Methanogens (MGN)		4.83E+02	49%	4.07E+01	24%	<4.80E+00	

Lines of Evidence Evaluation for Biodegradation

- MBT results (continued)
  - Low to ND SMMO levels
  - Notable PHE levels in all wells
    - Phenolic compounds abound in plants
    - Wells located in agricultural fields; may supply phenol to support PHE production.
  - Low to moderate RDEG/RMO levels in MW-25s and MW-28s/I
    - Both wells d/g of historical petroleum release
  - Low levels of EtnC and EtnE suggest some capacity for VC degradation
  - Mod. high total microbial populations (EBAC)

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Lines of Evidence Evaluation for Biodegradation

- Conclusions
  - Diverse community capable of degrading COCs via multiple pathways, albeit at slow rates.
  - cDCE and/or VC likely degrading by other mechanism(s):
    - Cometabolism – DO levels supportive at low rates
    - Abiotic Oxidation – rate influenced by DO concentration
  - VC "wave" very unlikely

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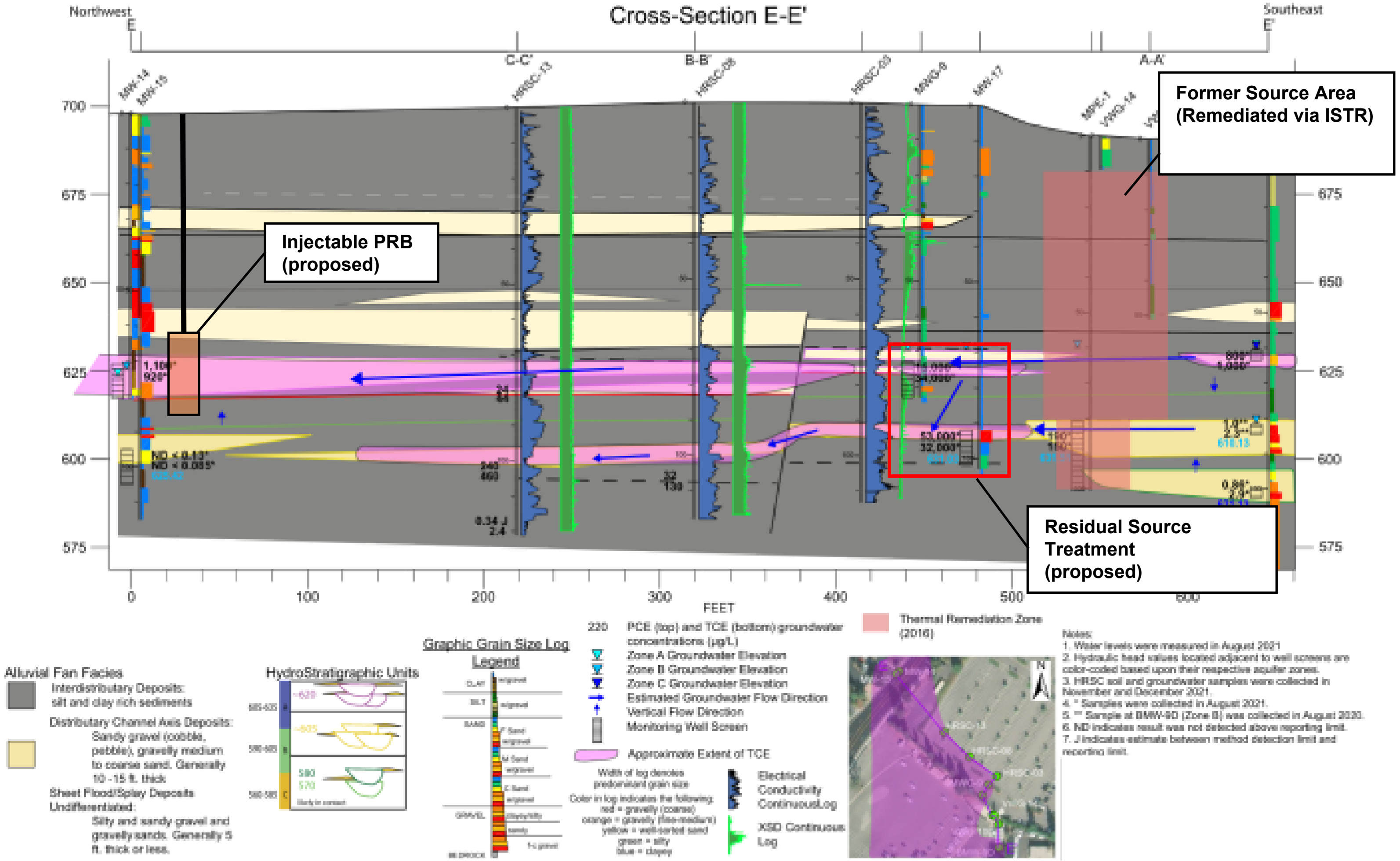
Where is the Vinyl Chloride?

Former Manufacturing Site – Southern California – Fluvial Aquifer

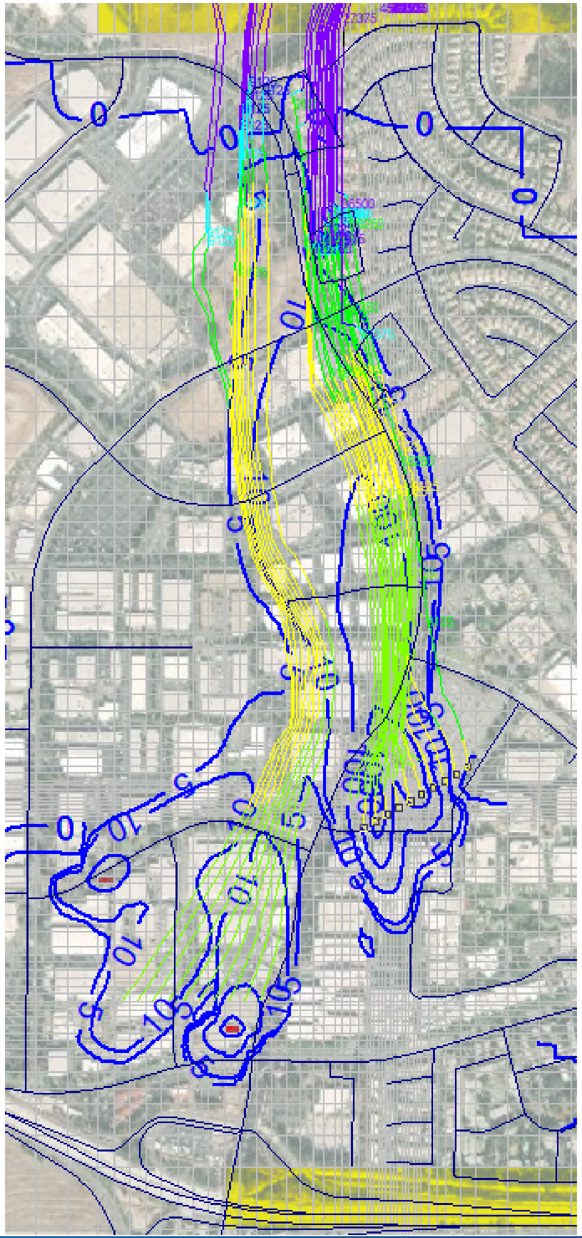
Overview

- PCE & TCE concentrations ranging from 10’s ppm (source) to 10’s ppb (off-site plume)
- Conditions generally aerobic/oxidative
- cis-1,2-DCE and 1,1-DCE detections at some wells
- No vinyl chloride detections in over 20 years of monitoring
- Heterogenous colluvial aquifer
- HSUs comprised of interconnected sand channels within low-permeability deposits
- In situ remediation technology needed for plume cut-off and source control

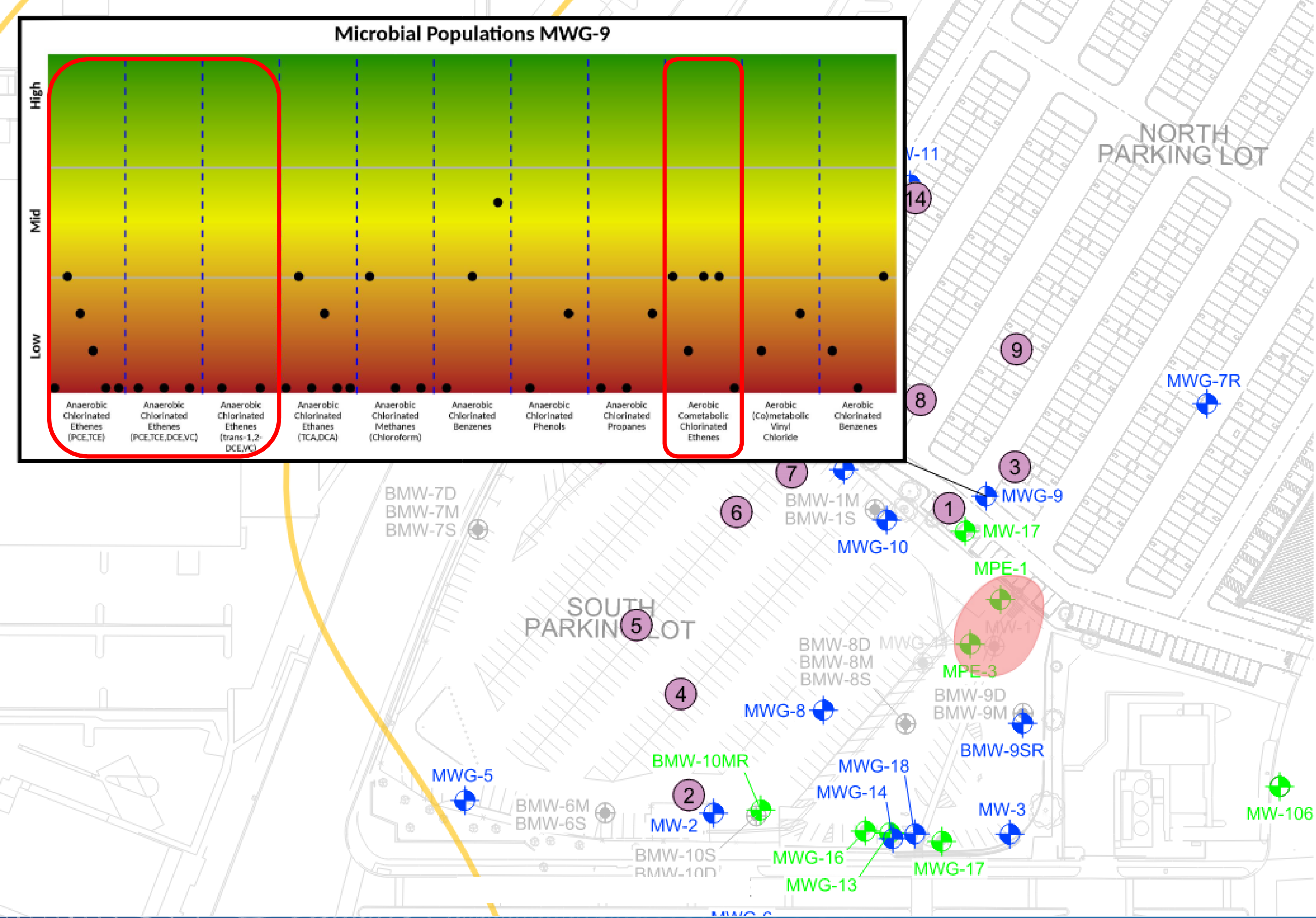


Overview

- Potential attenuation pathways:
  1. Reductive dechlorination (**RDC**) via hydrogenolysis
     - Historic data not supportive
     - *cis*-1,2-DCE detections at some wells
  2. Abiotic reductive dechlorination (**ARD**)
     - Historic data not supportive
  3. Aerobic cometabolic for TCE degradation (**ACD**)
     - Historic data somewhat supportive
     - 1,1-DCE detections may be indicative of ACD
     - Adequate DO concentrations



Source Area



Microbial Populations MWG-9
High
Mid
Low
Anaerobic Chlorinated Ethenes (PCE,TCE)
Anaerobic Chlorinated Ethenes (PCE,TCE,DCE,VC)
Anaerobic Chlorinated Ethenes (trans-1,2-DCE,VC)
Anaerobic Chlorinated Ethanes (TCA,DCA)
Anaerobic Chlorinated Methanes (Chloroform)
Anaerobic Chlorinated Benzenes
Anaerobic Chlorinated Phenols
Anaerobic Chlorinated Propanes
Aerobic Cometabolic Chlorinated Ethenes
Aerobic (Co)metabolic Vinyl Chloride
Aerobic Chlorinated Benzenes
NORTH PARKING LOT
SOUTH PARKING LOT
MWG-7R
MWG-9
MW-17
MWG-10
BMW-1M
BMW-1S
BMW-7D
BMW-7M
BMW-7S
MPE-1
MW-1
MPE-3
BMW-8D
BMW-8M
BMW-8S
BMW-9D
BMW-9M
BMW-9SR
MWG-8
BMW-10MR
MWG-5
BMW-6M
BMW-6S
MW-2
BMW-10S
MWG-18
MWG-14
MWG-16
MWG-13
MWG-17
MW-3
MW-106
1
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4
5
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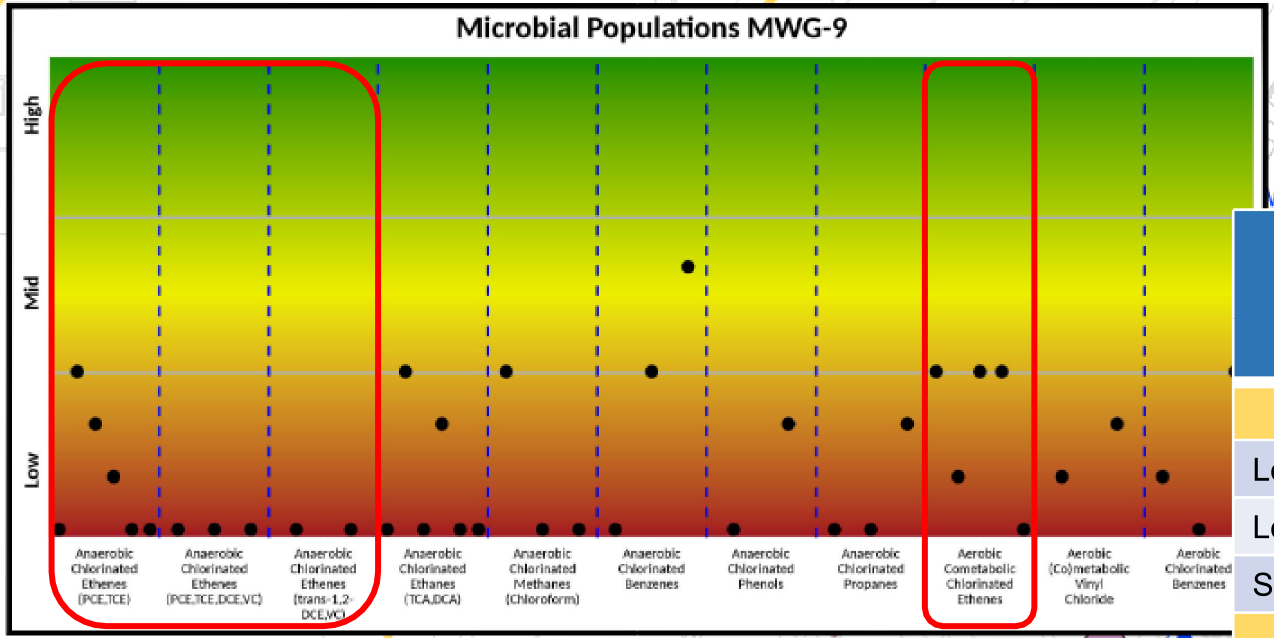
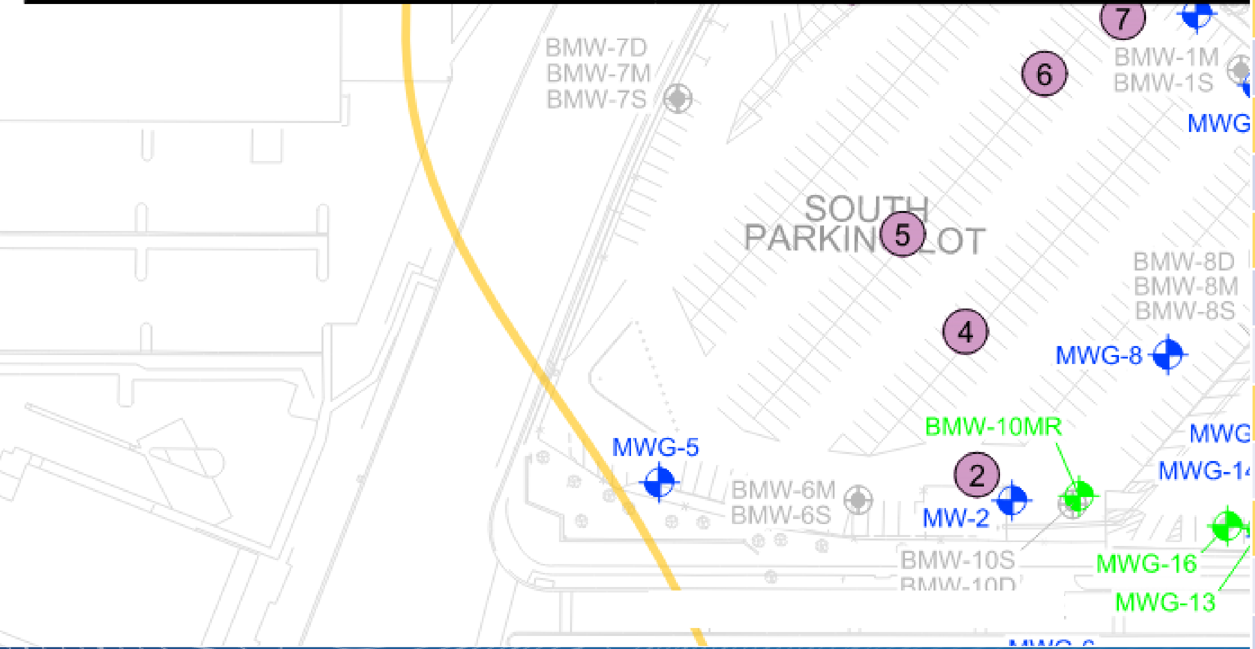
14

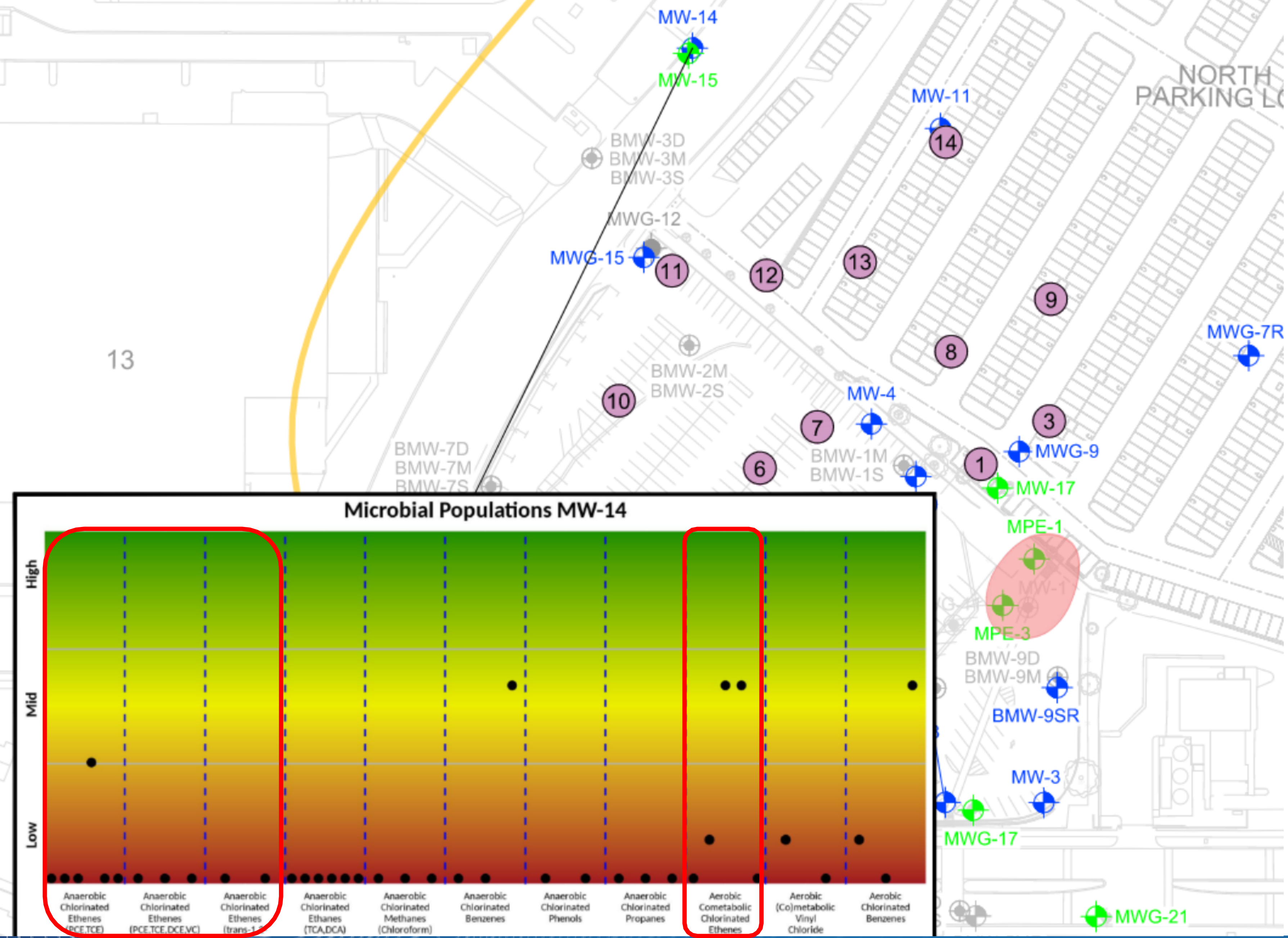
Source Area



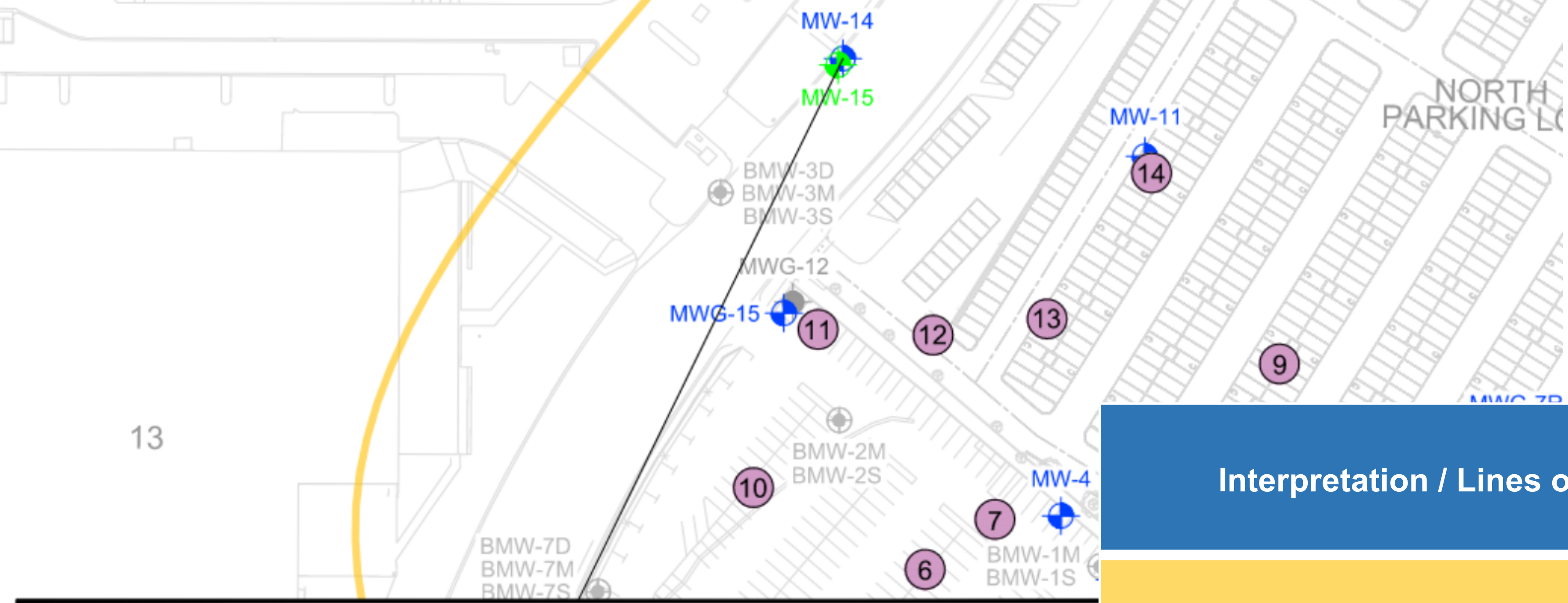


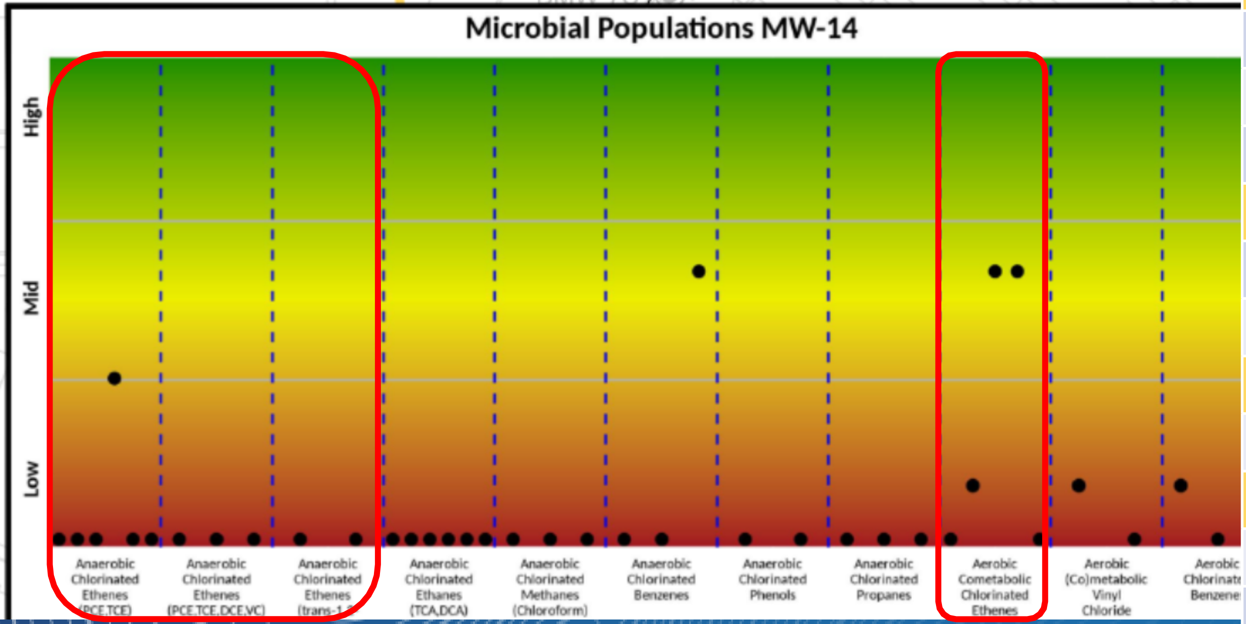
Interpretation / Lines of Evidence	Potentially Supportive of Pathway? RDC	ARD	ACD
MBT Results			
Low-Moderate populations of cometabolic degraders			✓
Low-Mod. populations of reductive PCE/TCE degraders	✓		
Some microbial diversity	✓	✓	✓
14C TCE Co-metabolism Results			
Negative			✗
cVOC Results (MWG-9)			
Low but increasing levels of cis-1,2-DCE	✓		
cVOC Results (HRSC-1)			
Low but detectable levels of cis-1,2-DCE	✓		
Low but detectable levels of 1,1-DCE			✓
Redox/Attenuation Parameter Results			
Mildly aerobic/oxic; more reducing than other wells	✓	✓	
Abiotic Degradation Indicator Results			
No acetylene detected		✗	
Moderate magnetic susceptibility results (HRSC-1)		✓	
Low sulfate levels		✗	
ND Fe(II) levels		✗	

Downgradient Plume



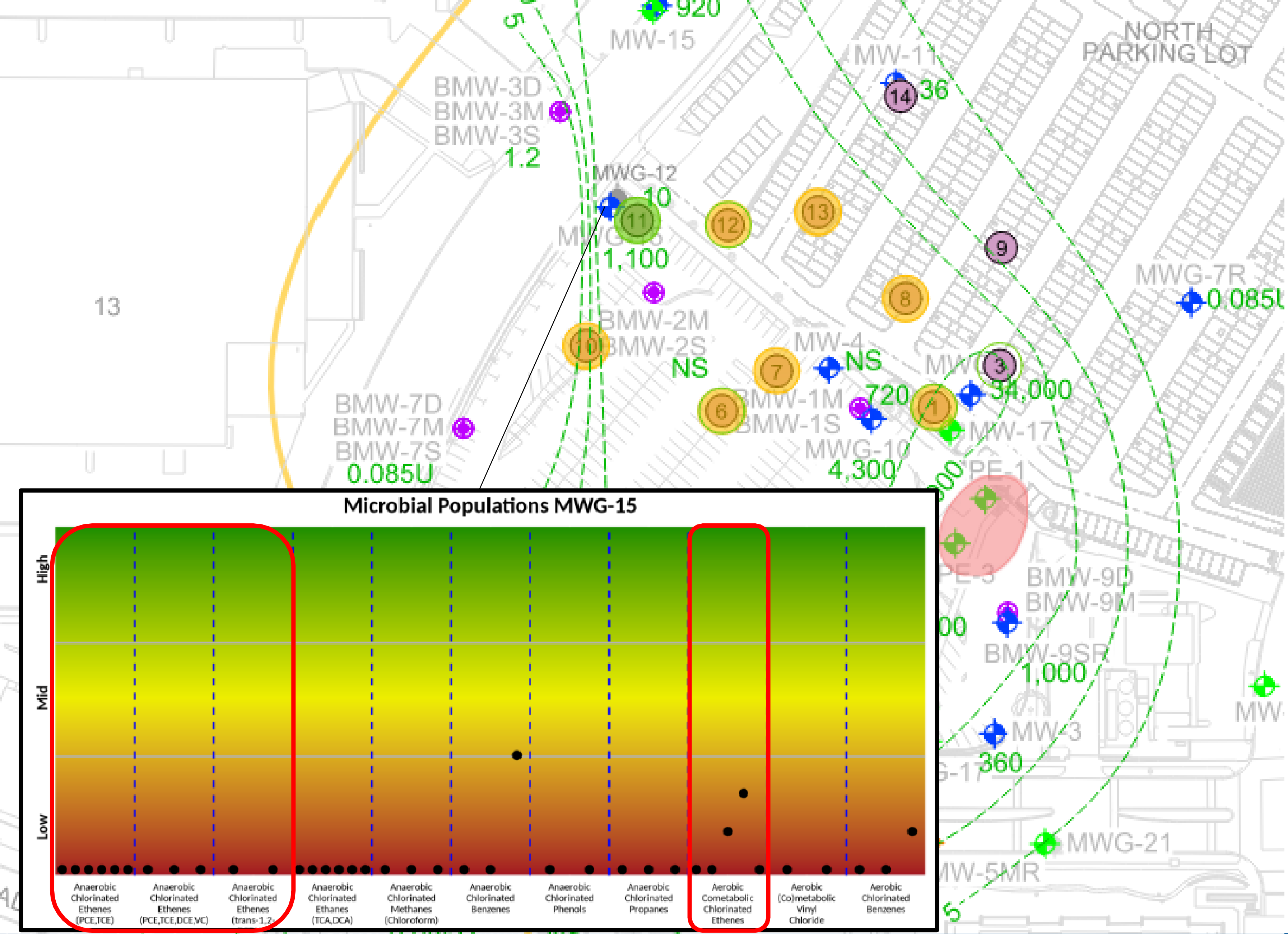
Downgradient Plume



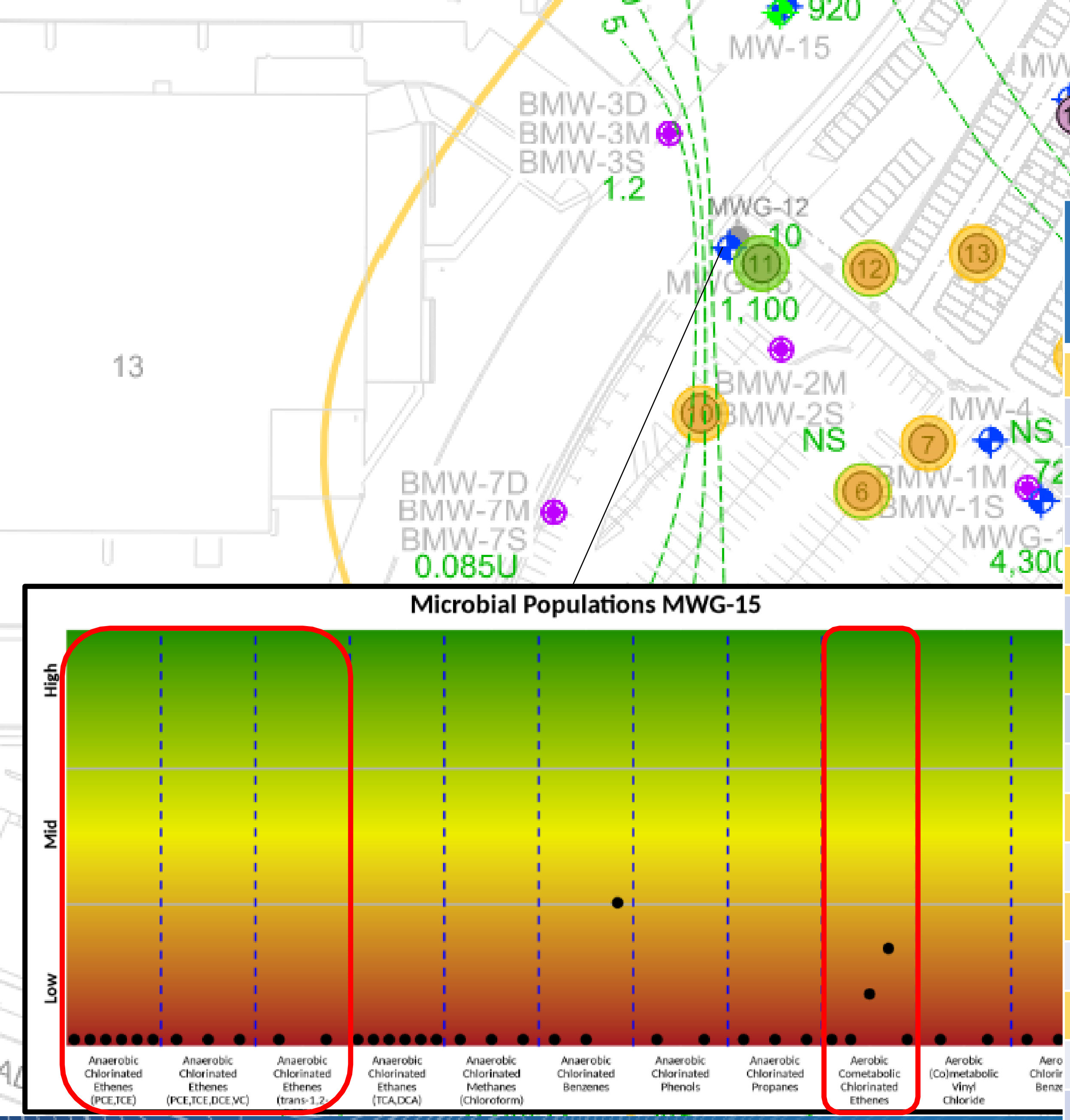


Interpretation / Lines of Evidence	Potentially Supportive of Pathway? RDC	ARD	ACD
MBT Results			
Moderate populations of cometabolic degraders			✓
Low-Mod. populations of reductive PCE/TCE degraders	✓		
Limited microbial diversity	✗	✗	✗
cVOC Results (MW-14)			
Low but detectable levels of cis-1,2-DCE	✓		
Low but detectable levels of 1,1-DCE			✓
Redox/Attenuation Parameter Results			
Aerobic/oxic conditions	✗	✗	✓
Abiotic Degradation Indicator Results			
No acetylene detected		✗	
Relatively high magnetic susceptibility results (HRSC-11)		✓	
Low to moderate sulfate levels		✗	
ND Fe(II) levels		✗	

Downgradient Plume



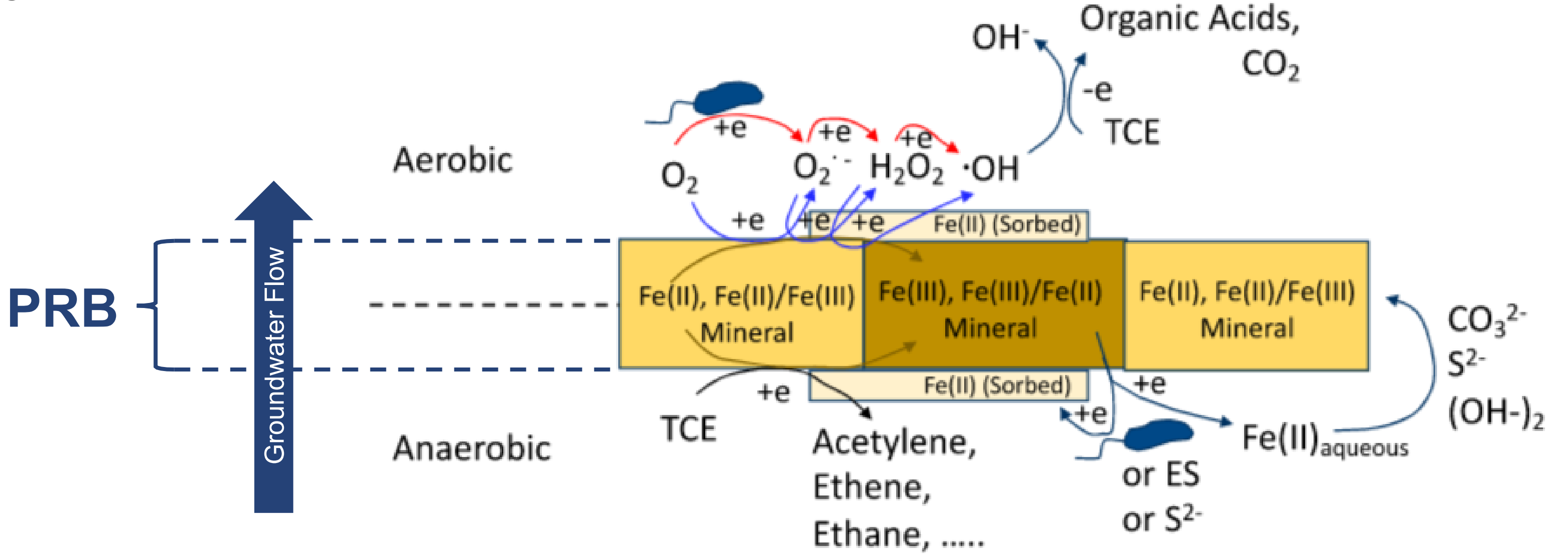
Downgradient Plume



Interpretation / Lines of Evidence	Potentially Supportive of Pathway?		
	RDC	ARD	ACD
MBT Results			
Low-Moderate populations of cometabolic degraders			✓
No populations of reductive PCE/TCE degraders	✗		
Limited microbial diversity	✗	✗	✗
14C TCE Co-metabolism Results			
Verified ACD at low degradation rate			✓
cVOC Results (MWG-15)			
Low but detectable levels of cis-1,2-DCE	✓		
Low but detectable levels of 1,1-DCE			✓
cVOC Results (HRSC-11)			
Low but detectable levels of 1,1-DCE			✓
Redox/Attenuation Parameter Results			
Aerobic/oxic conditions	✗	✗	✓
Abiotic Degradation Indicator Results			
No acetylene detected		✗	
Moderate magnetic susceptibility results (HRSC-1)		✓	
Low sulfate levels		✗	
Low to ND Fe(II) levels		✗	

Evaluation & Path Forward

- **Co-metabolism (ACD)** likely the predominant mechanism for TCE and daughter products, but **reductive dechlorination (RDC)** may contribute in discrete anaerobic zones
- Elevated temperatures may be promoting **RDC** near the former source area
- Minimal evidence of **abiotic degradation (ARD)**
- Proposed PRB approach
  - Promote biotic/abiotic reductive processes at PRB location
  - Stimulate aerobic biotic/abiotic process downgradient of PRB
  - Treatability testing (e-donor + iron)
  - Modeling



Conclusions / Lessons Learned

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Conclusions / Lessons Learned

- Historical data offer clues re: degradation pathways
- Tools needed to explain lack of VC at sites undergoing reductive dechlorination are now available
- Lack of VC presents potential opportunity to identify alternative pathways that can be leveraged for remediation (including MNA)
- CSM is critical to identifying mechanisms and selection data collection locations

Questions?