Bioremediation of Comingled 1,4-Dioxane and Chlorinated Solvent Plumes

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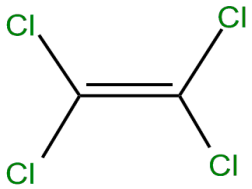
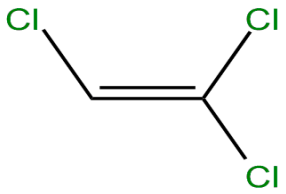
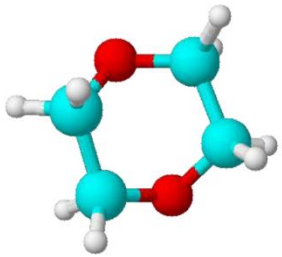
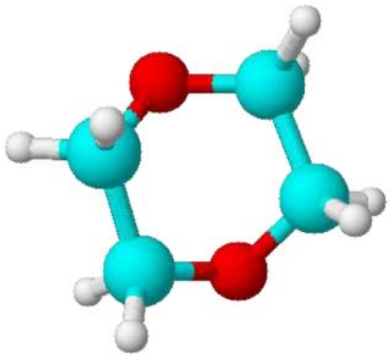






1,4-Dioxane (1,4-D)



- Cyclic ether; $C_4H_8O_2$
- Fully miscible in water
- Moderate vapor pressure
- Very low K_H
- Low Kow

- Does not readily sorb to soil or organic matter
- Highly mobile in groundwater
- Not amenable to air stripping

Property	1,4-D	MTBE	1,1,1-TCA
Formula	$C_4H_8O_2$	$C_5H_{12}O$	$C_2H_3Cl_3$
Aqueous Solubility (mg/L)	Infinite	50,000	950
Boiling Point (º C)	101	54	74
Vapor Pressure (mm Hg @ 20º C)	30	251	100
Henry's Law Const (K_H, atm-m^3/mol)	4.9×10^{-6}	1.5×10^{-3}	1.7×10^{-2}
Octanol-water partition coefficient (K_{OW})	0.5	16	309

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1,4-D Sources

Stabilizer in chlorinated solvents

- Primarily 1,1,1-TCA; 2-5% by vol
- May be present in TCE and other solvents

(Anderson et al. ,2012)

Trace amounts in personal care products, laundry detergents, shampoos, antifreeze, deicing fluids

Solvent/wetting Agent in textiles, paper manufacturing, specialty chemicals, pharmaceuticals

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Why care about 1,4-D

- Increased regulatory interest; no MCL established…yet
  - In EPA's Contaminant Candidate List 3
  - EPA Health Advisory Level = 0.35 ppb
  - EPA Region IX Tapwater Regional Screening Level (RSL) = 0.46 ppb
  - Risk-based guidelines vary from state to state

State	Action Level (ppb)	Guideline
North Carolina	**3**	**Groundwater quality standard**
California	1	Drinking water notification level
Colorado	0.35	Interim groundwater quality cleanup standard
Florida	3.2	Groundwater cleanup target level
Massachusetts	0.3	Drinking water guidance level
New Jersey	0.4	Interim ground water quality standard

Why care about 1,4-D

- Toxicology and human exposure
  - Class B2 Carcinogen (Probable Human Carcinogen) by all routes of exposure
  - Acute nervous system effects
  - Liver and kidney damage
- Environmental Detection
  - UCMR3 Occurrence Data– Results for 1,4-D (April ,2016)
    - 35,856 drinking water samples analyzed for 1,4-D
    - 4,145 (11.6%) had detectable levels of 1,4-Dioxane (≥ 0.07ppb)
    - 1,069 (3%) had 1,4-dioxane levels ≥ 0.35 ppb
  - Cary 2015 Annual Water Quality Report: 0.42 ppb
  - 1,4-D detection in Caper Fear Watershed
    (Dr. Detlef Knappe's Research Group, NCSU)

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1,4-D Remediation

- *Ex situ* Options (groundwater extraction + treatment)

Air stripping

Carbon adsorption

Advanced oxidation ($UV/H_2O_2/Fe$)

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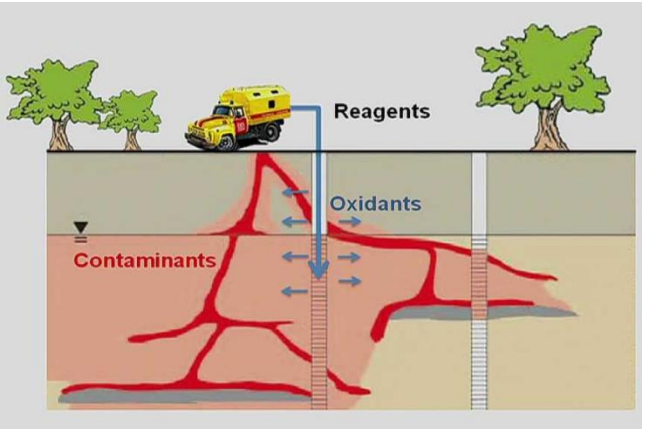
1,4-D Remediation

- *In situ* Options

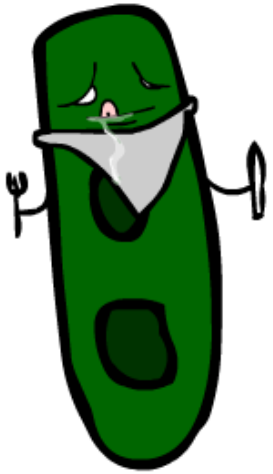
Air sparging /SVE



Chemical oxidation

Source

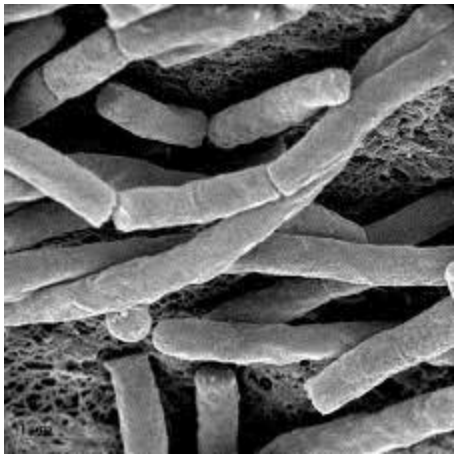
Plume



Bioremediation

1,4-D Biodegradation

- 1,4-D can be aerobically metabolized
- However….
  - Growth rates are very slow (*e.g.*, low cell yields; long doubling times)
  - Temperature sensitive (optimal growth at 30^{O}C)
  - Concentration sensitive; high half saturation constant



(**Pseudonocardia dioxanivorans CB1190**)

- Preliminary evidence of anaerobic 1,4-D degradation under iron-reducing conditions
  - Barajas et al. 2012, Battelle Monterey; Shen et al. 2008, Bioresource Technology

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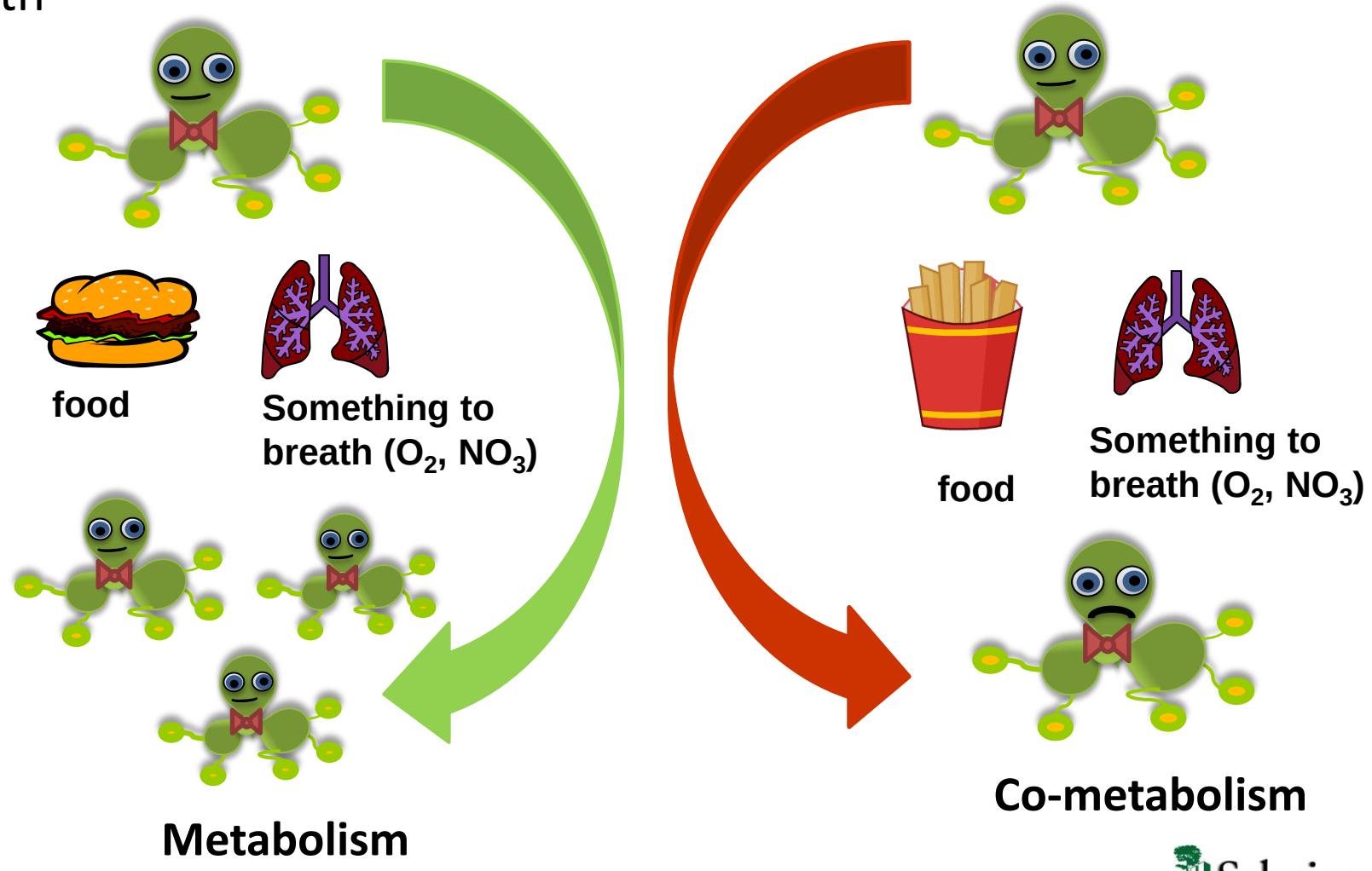
1,4-D Co-metabolism

Co-metabolism: Transformation of a compound that does not support growth



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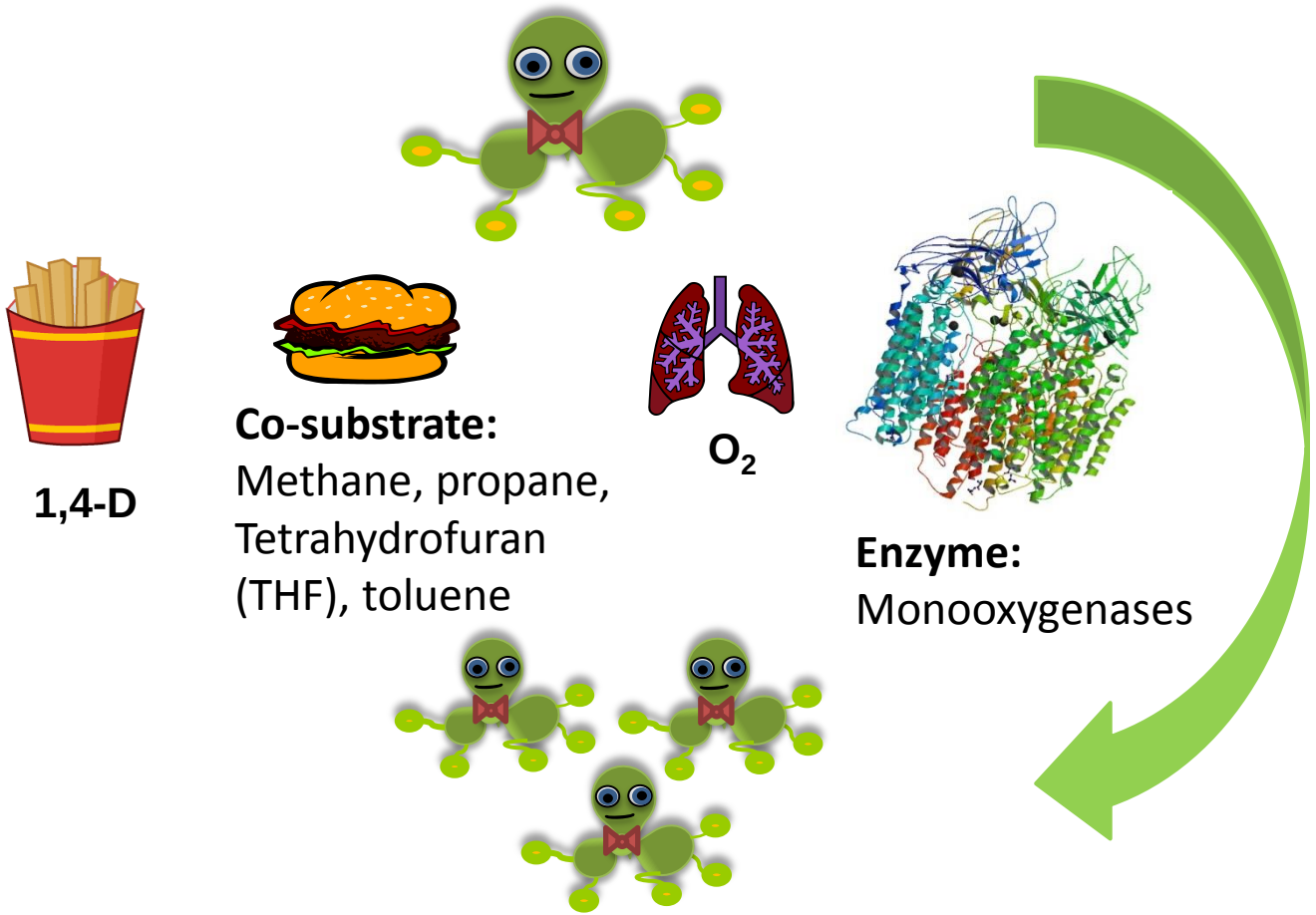
1,4-D Co-metabolism



- When using methane as a cosubstrate, 1,4-D was biodegraded at higher rates by the soluble methane monooxygenase (sMMO) than other oxygenases (Mahendra and Alvarez-Cohen, 2006, ES&T)

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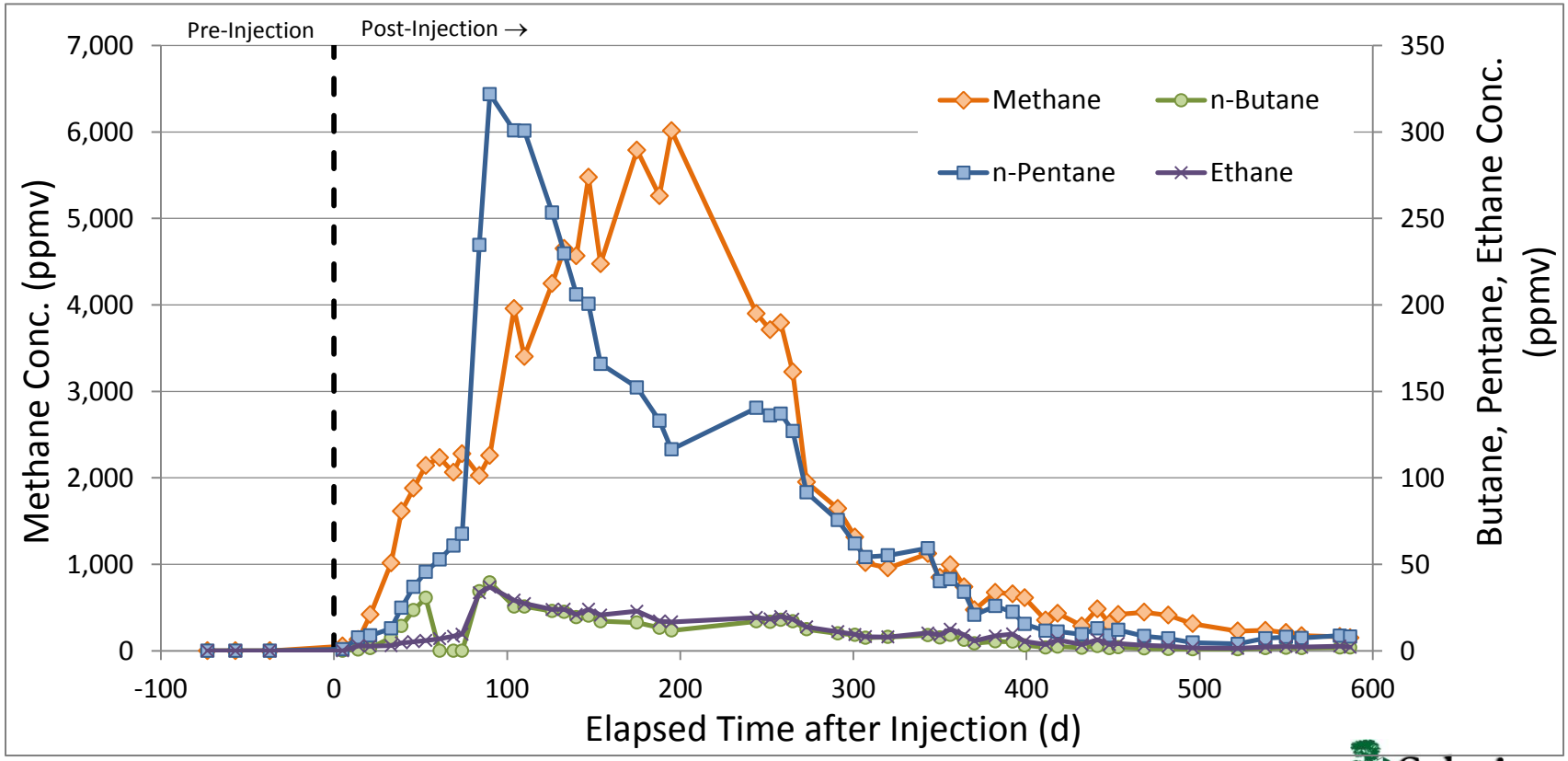
Methane Generation

- Significant amounts of methane from fermentation of organic substrates (e.g., lactates, molasses, vegetable oils) used for enhanced reductive dechlorination of CVOCs
- Methane production (vegetable oil injection)



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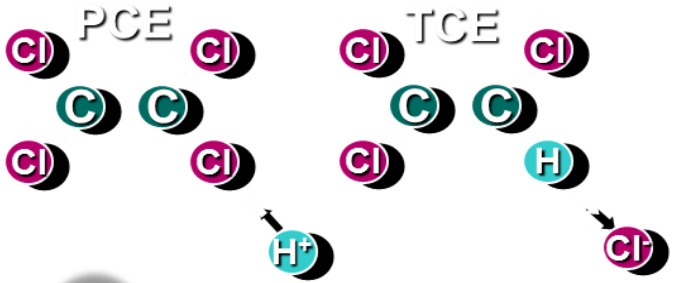
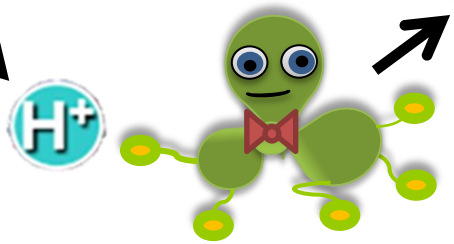
Enhanced Reductive Dechlorination

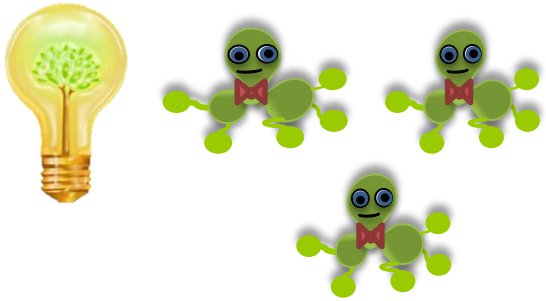
Electron Donor + **Electron Acceptor** =

Fermentation

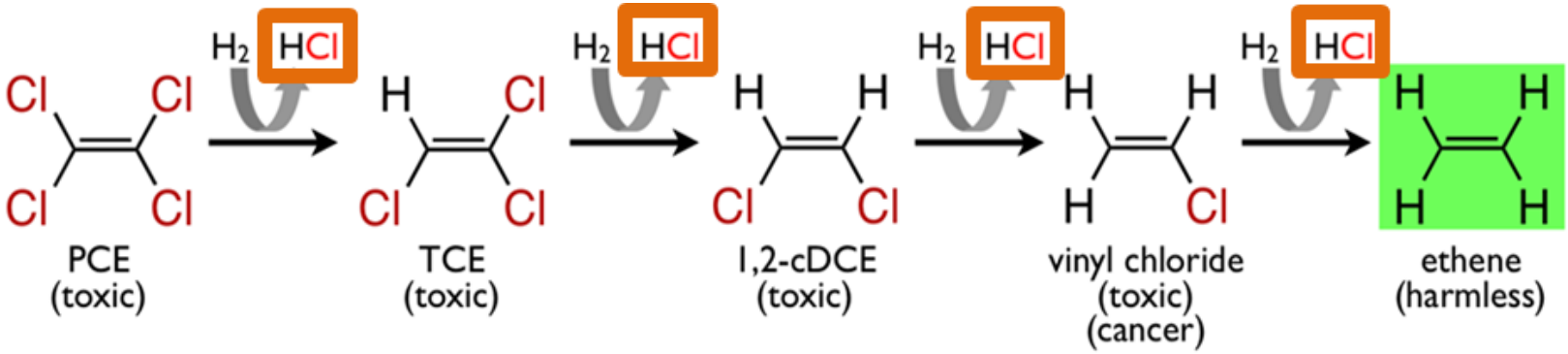
Respiration







Waste
CO_2, Water



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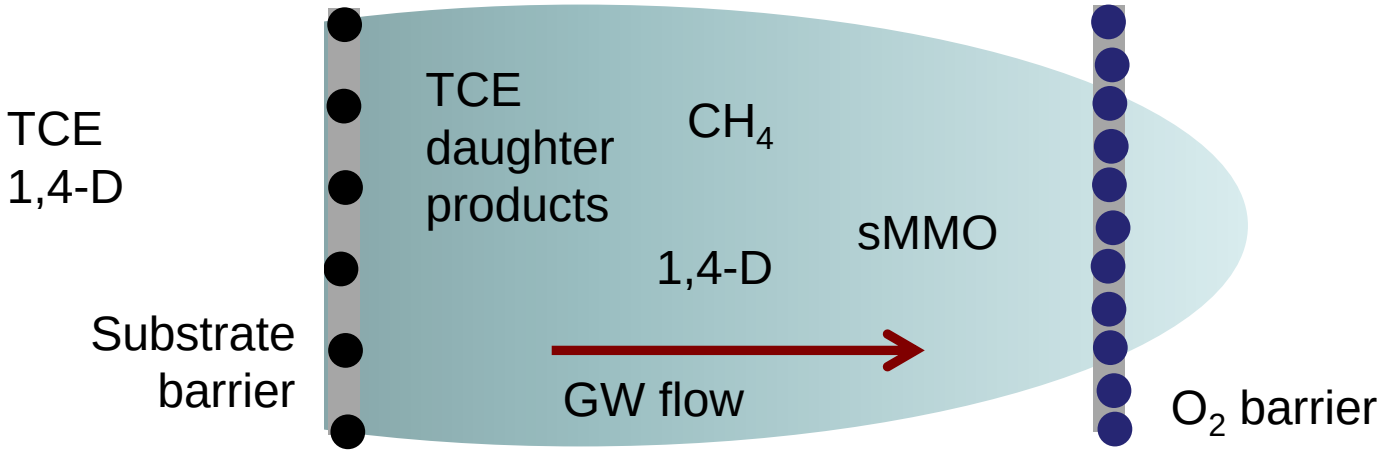
Proposed Strategy

- Problem: Cosubstrates and oxygen are rarely at the same location
- Solution: Engineered contact using a two-barrier system
- Objective: To demonstrate a simple, low-cost approach for enhancing *in situ* cometabolic biodegradation of 1,4-D and TCE using a two-barrier system



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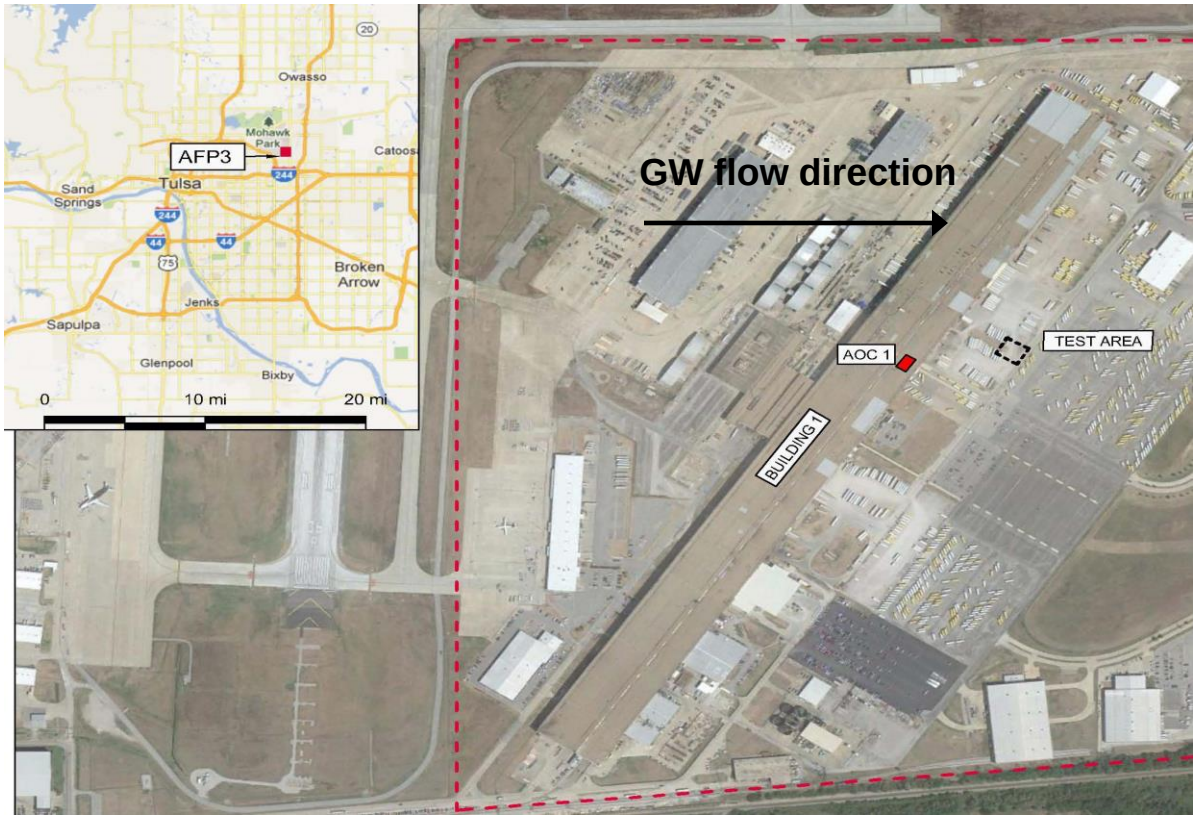
Site Background

Former Air Force Plant 3 (AFP 3), Tulsa, Oklahoma

- AOC-1, eastern side of Building 1
- Historically, two vapor degreasers housed within (or near) Building 1 for solvent reuse
- Former TCE degreaser was located sub-grade within a sump
- Former TCA degreaser was above grade
- Identified CVOCs and 1,4D plumes migrating towards Mingo Creek



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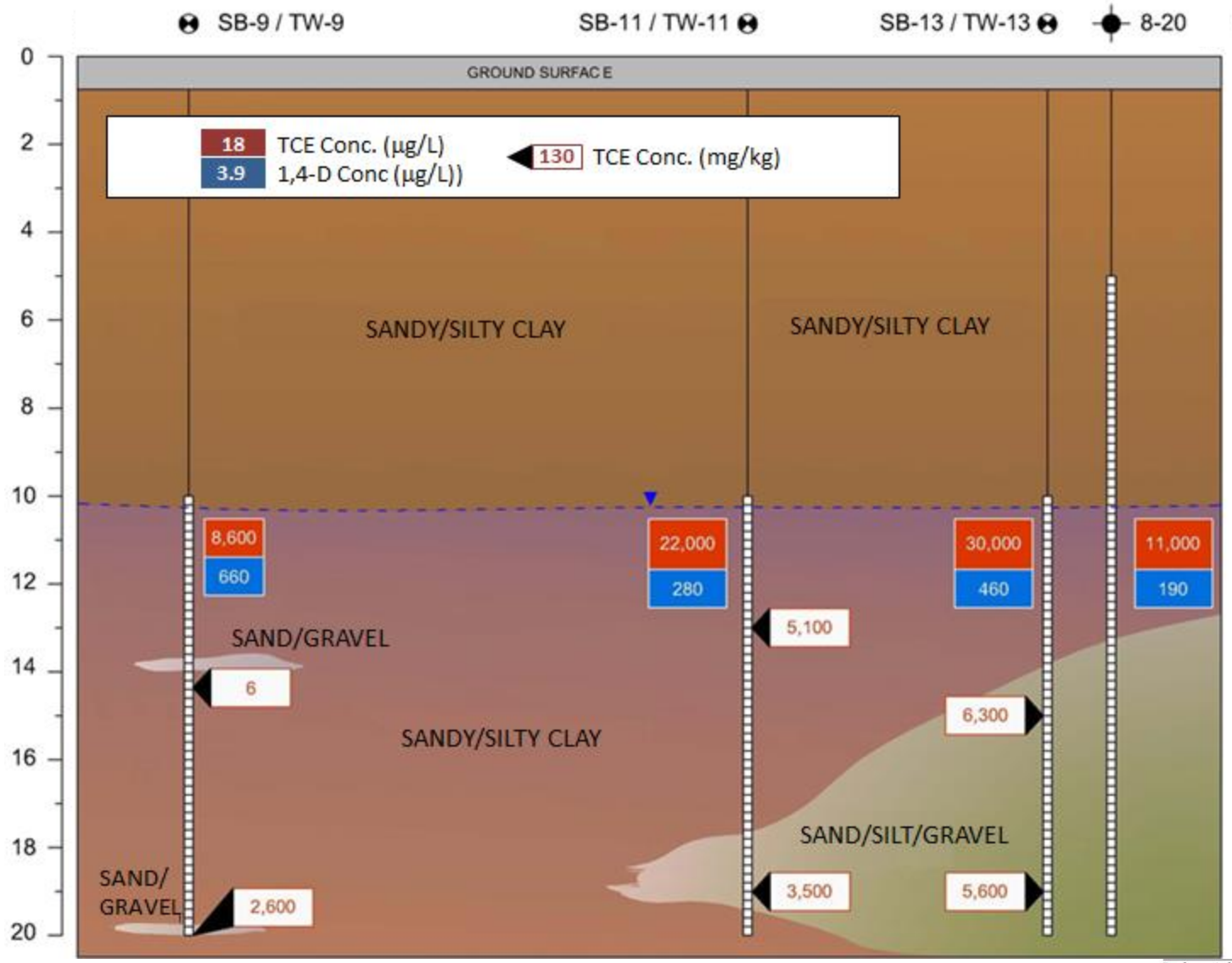
Site Background



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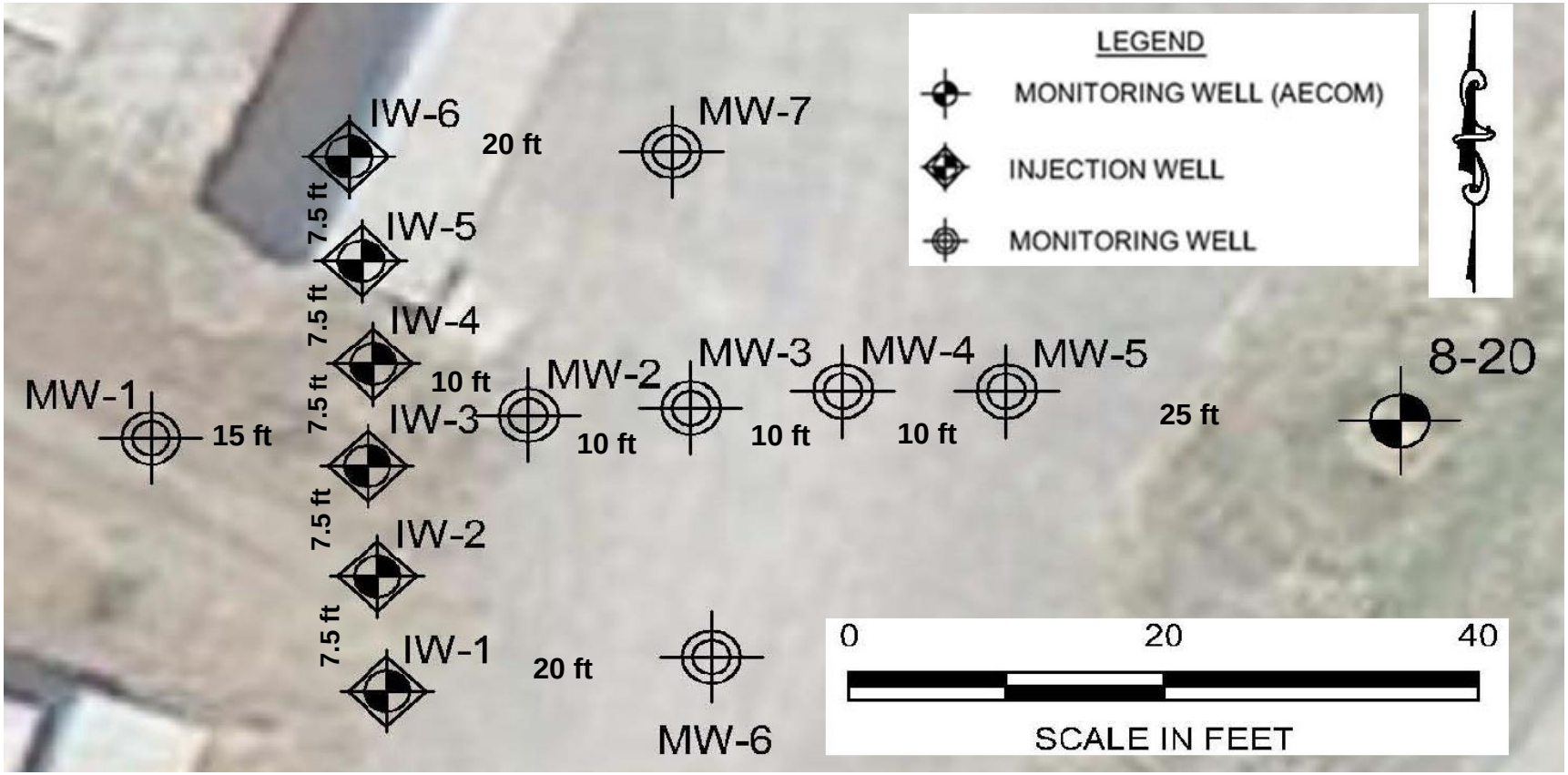
Injection

- 6 injection (PRB) and 7 monitoring wells; screened from 10 to 20 ft bgs
- August 2013, Injected ~ 300 gal of diluted EVO + chase water



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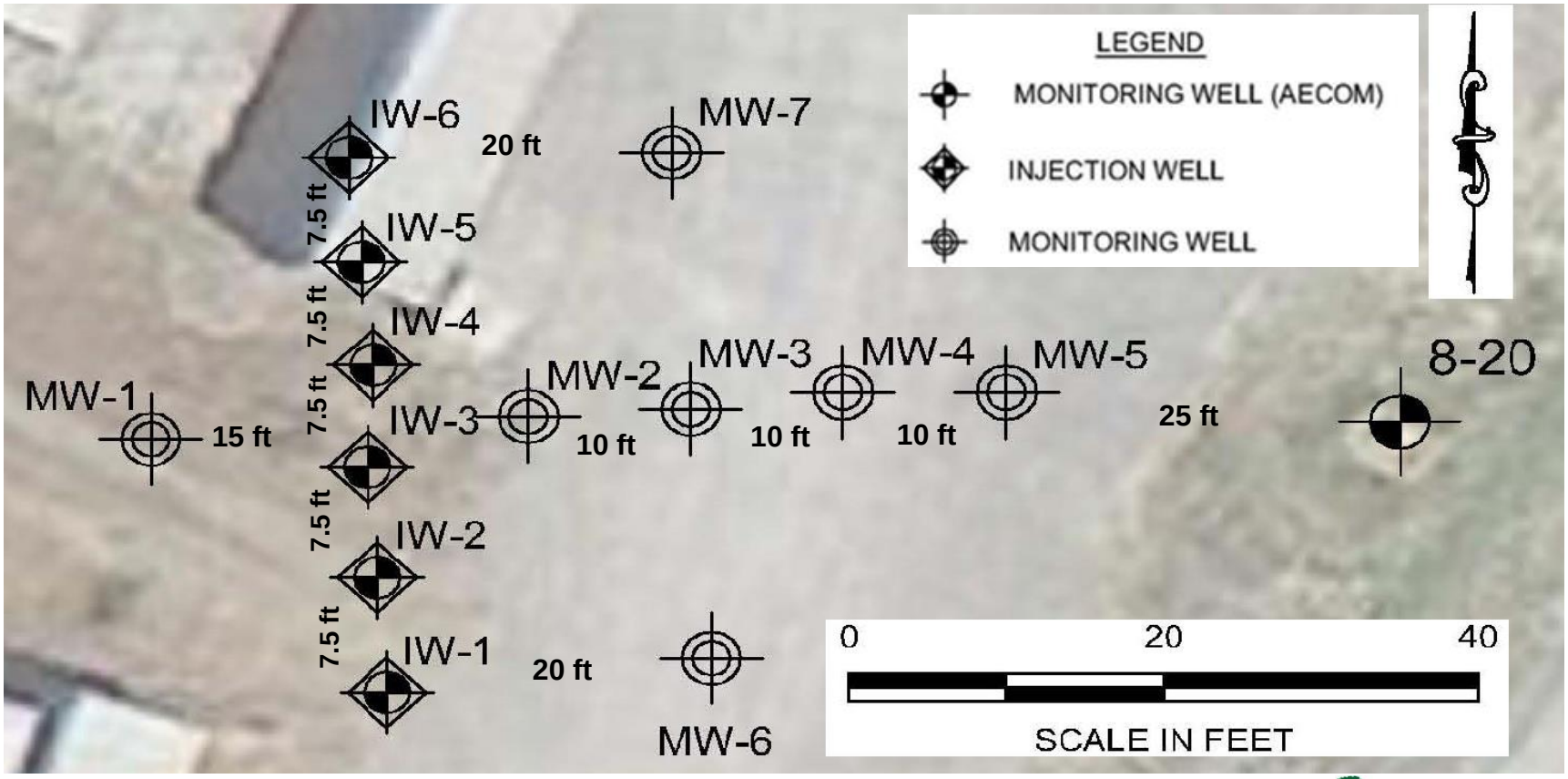
Injection Design

- Bioaugmentation to increase the abundance of DHCs
- Groundwater monitoring: 2, 4, 6, 8, 16, 22 and 28 months after injection



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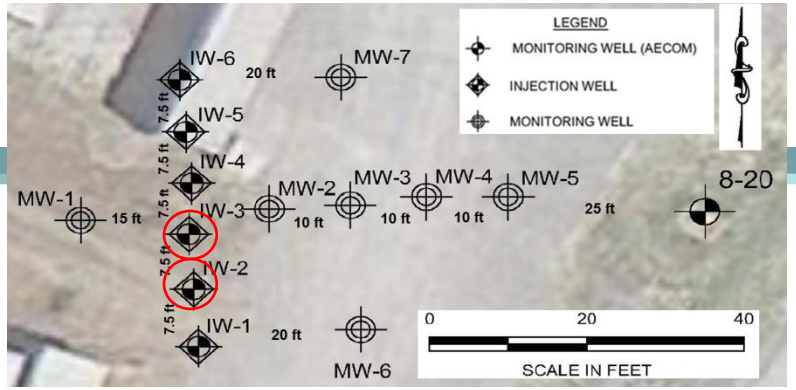
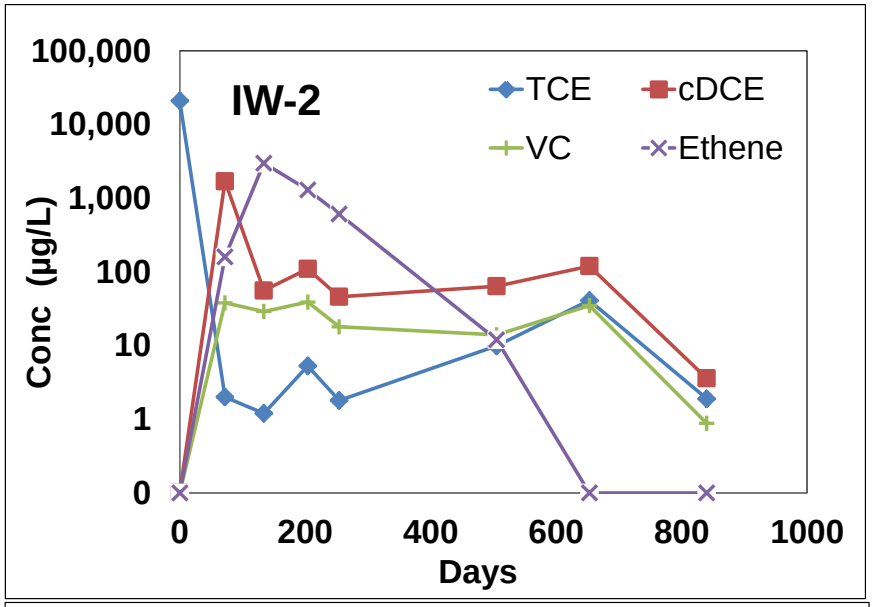
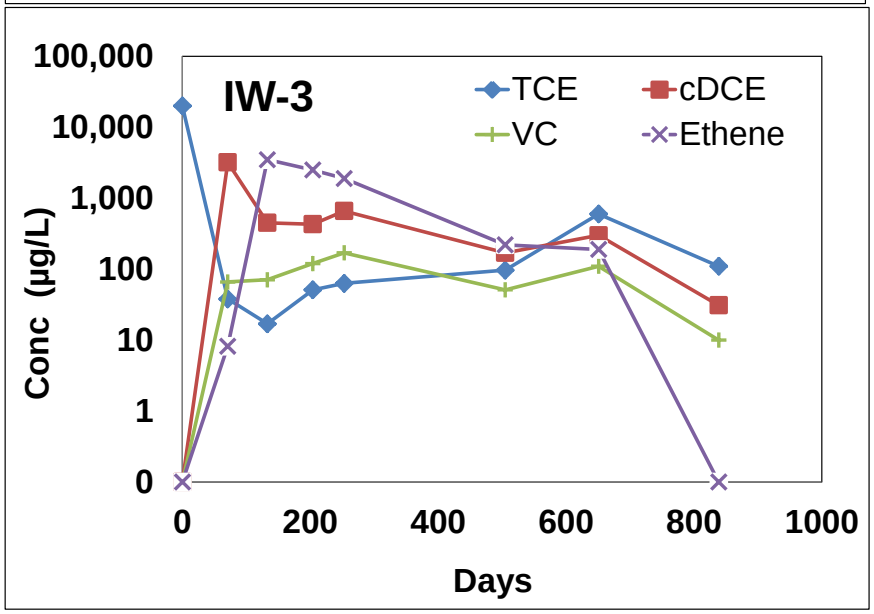
Results to Date







- >99% decrease in TCE concentrations
- cDCE and VC increase
- Significant ethene formation

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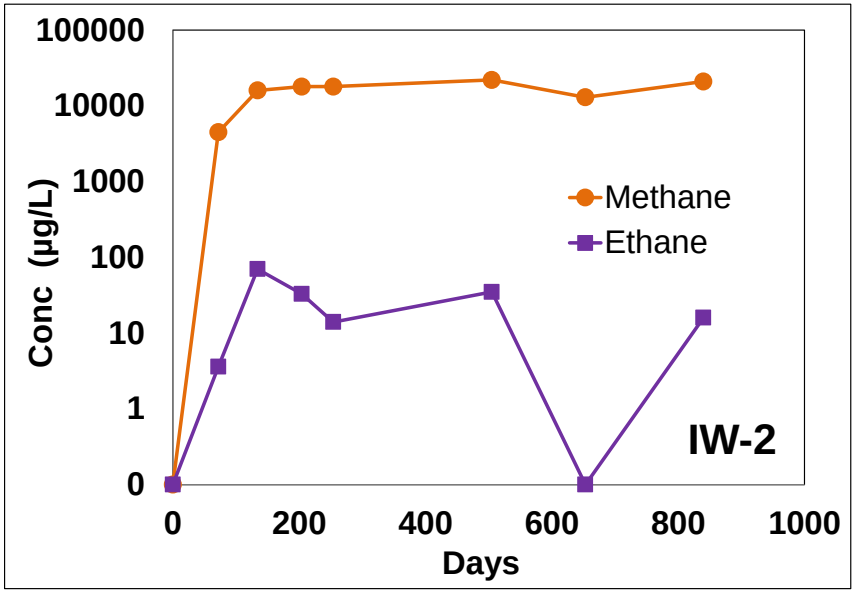
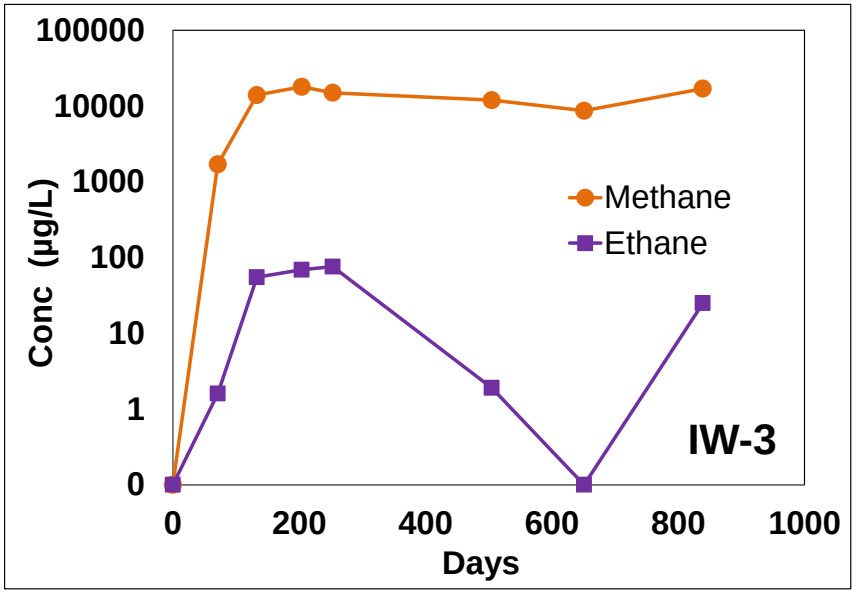
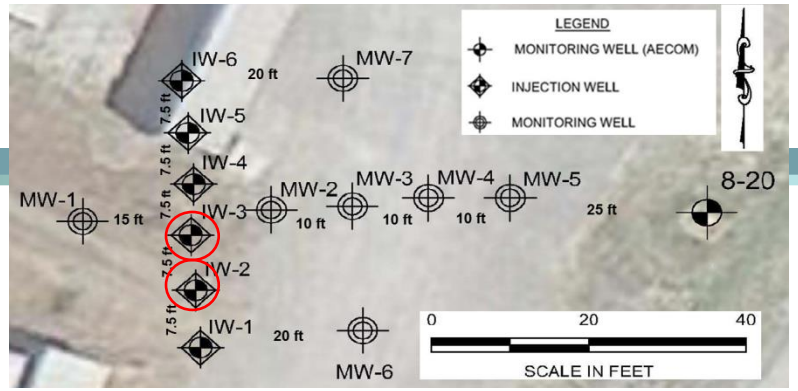
Results to Date







- >99% decrease in TCE concentrations
- cDCE and VC increase
- Significant ethene formation
- Significant methane formation
- Some ethane formation

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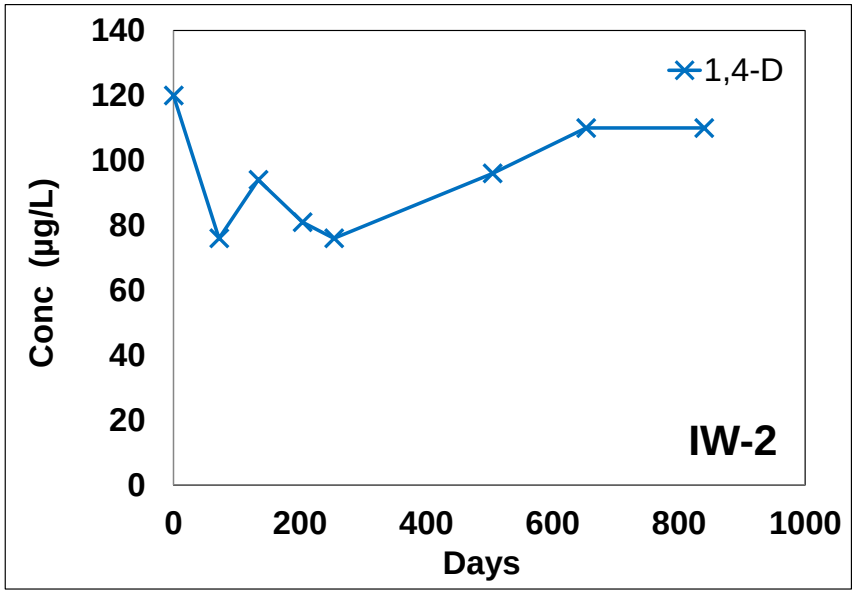
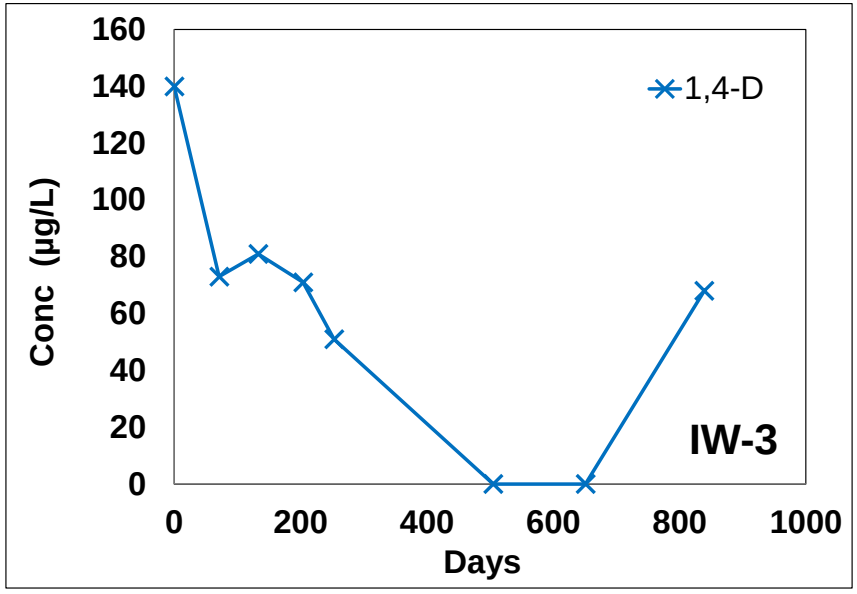
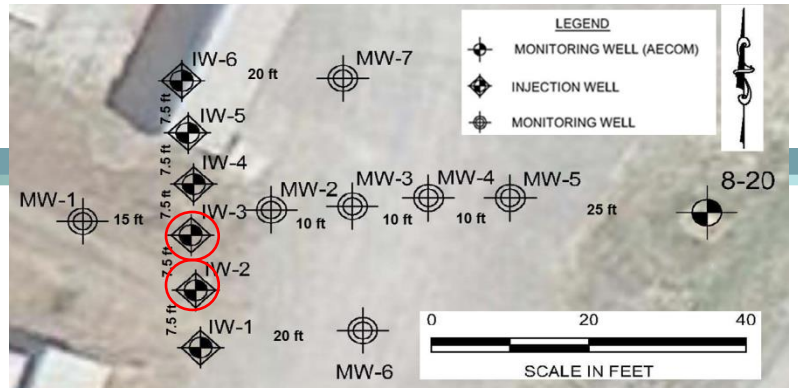
Results to Date







- >99% decrease in TCE concentrations
- cDCE and VC increase
- Significant ethene formation
- Significant methane formation
- Some ethane formation
- 1,4-D decline – ND in some injection wells

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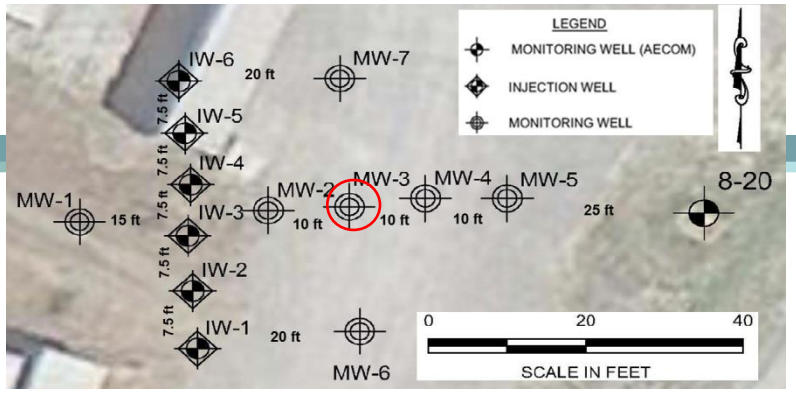
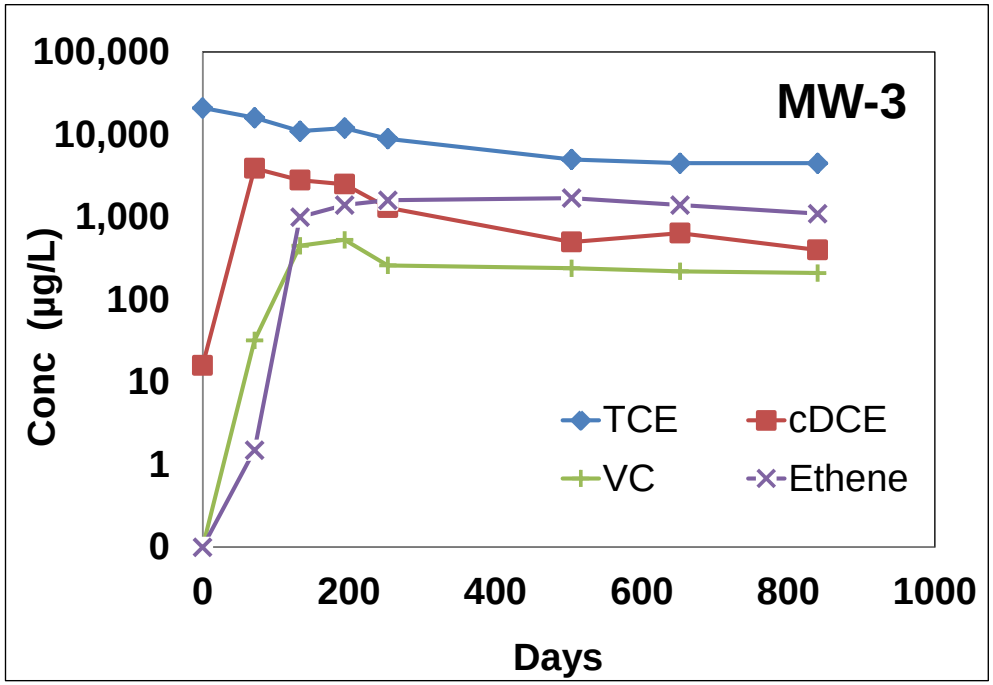
Results to Date





- ~85% TCE decrease in MW-3
- Evidence of reductive dechlorination

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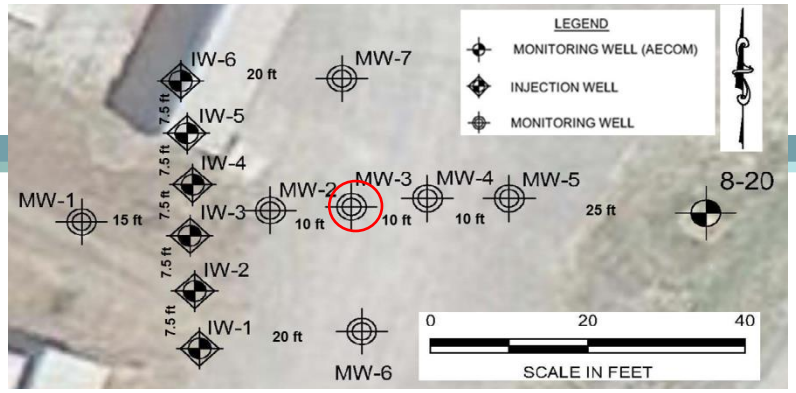

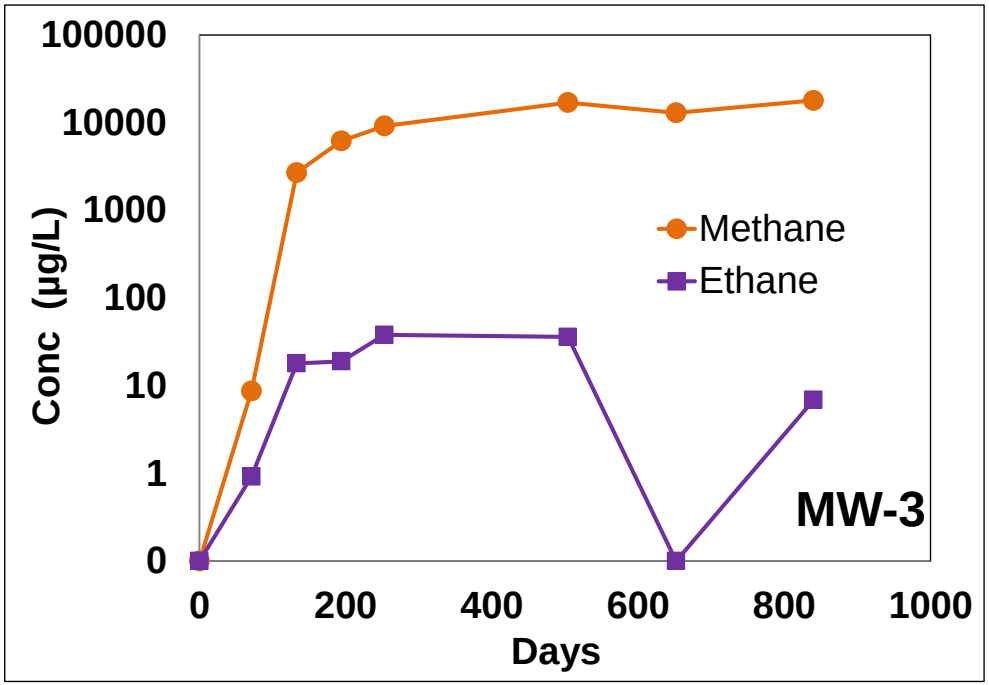

- ~85% TCE decrease in MW-3
- Evidence of reductive dechlorination
- Significant methane
- Some ethane formation

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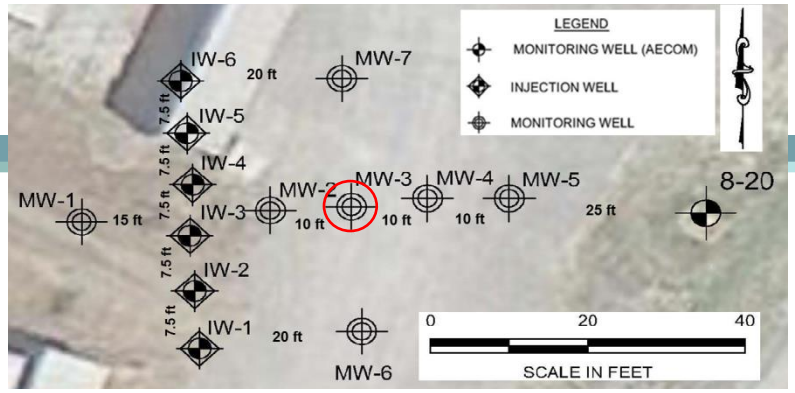
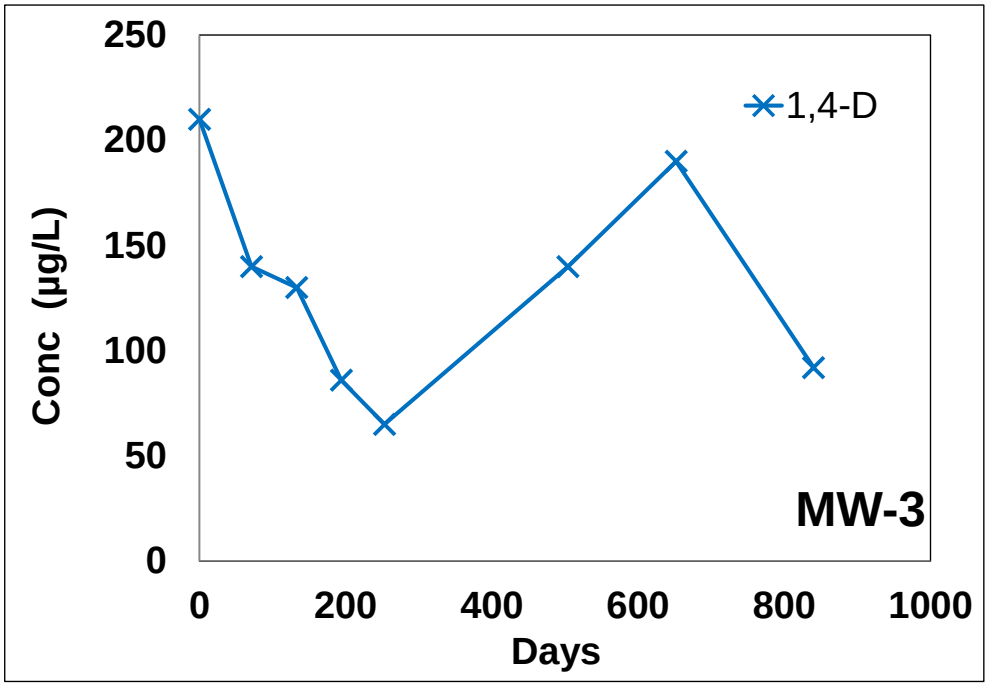
Results to Date





- ~85% TCE decrease in MW-3
- Evidence of reductive dechlorination
- Significant methane
- Some ethane formation
- An initial decrease in 1,4-D concentration then increase

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Column Study

Dr. Paul Hatzinger, CB&I:

- Packed with 500 gr of site sediment mixed with sand
- Artifical GW simulating site background GW
- Flowrate = 4 ml/min
- T = 230C
- Columns were treated with different co-substrates: methane, ethane, ethane, propane

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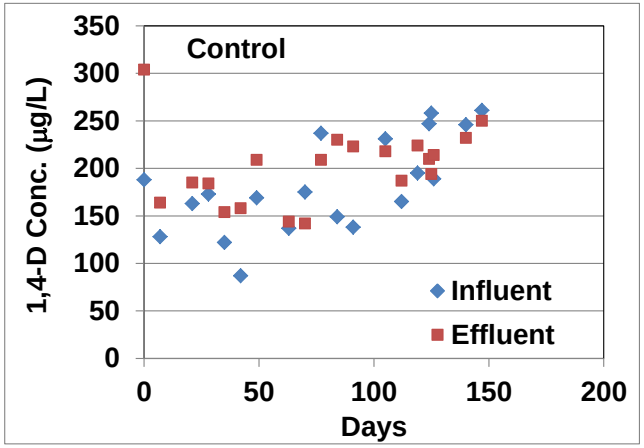
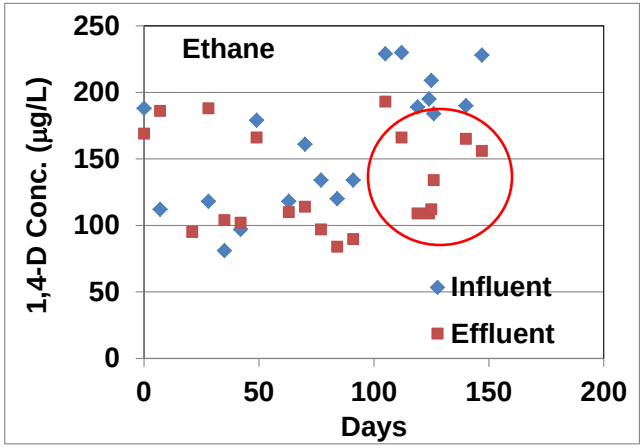
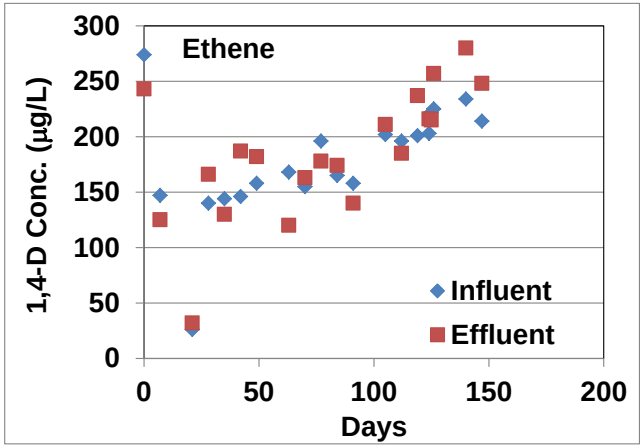
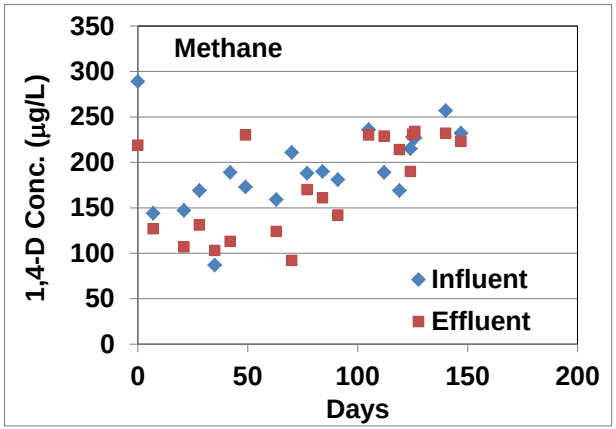
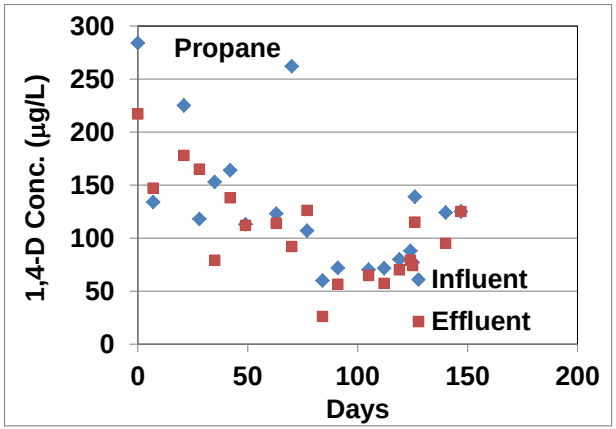
Column Study











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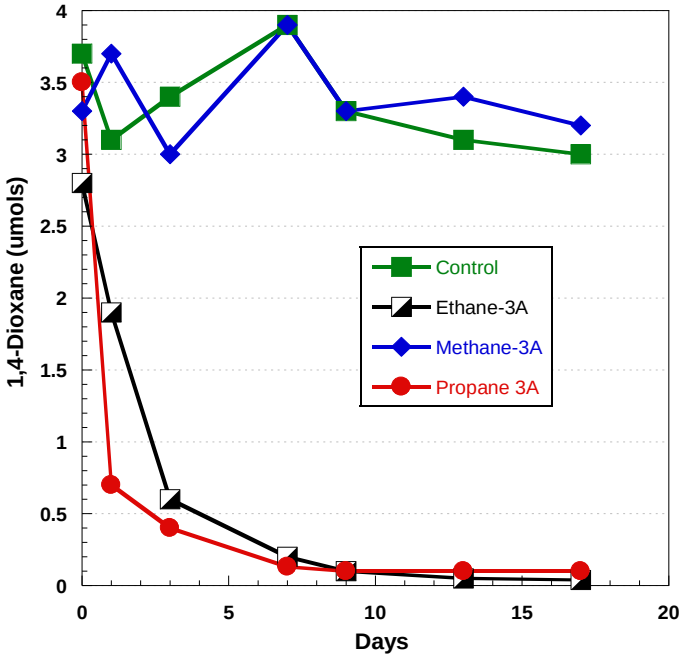
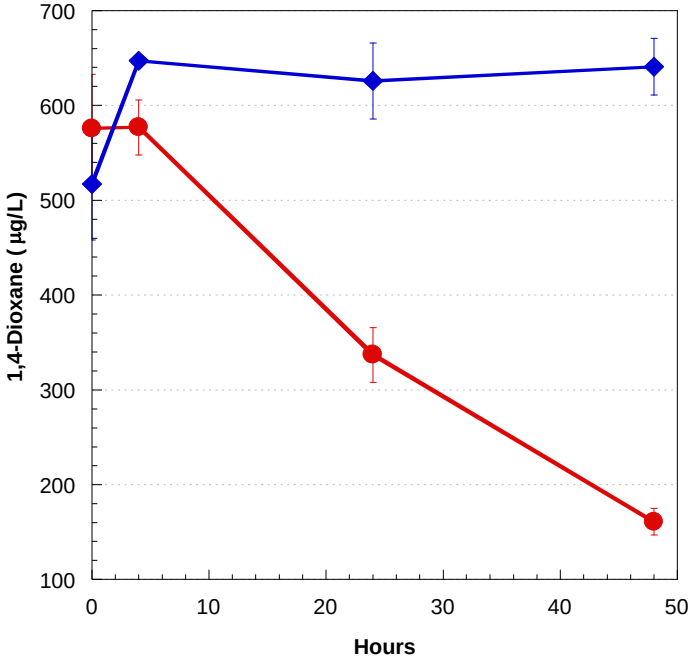
Ethane co-metabolism



Mixed enrichment culture (Myrtle Beach AFB)



Ethanotroph *Mycobacterium sphagni* ENV482 (Cape Cod)

Courtesy of Dr. Paul Hatzinger, 2015

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Issues

- TCE rapidly declined in injection wells but is still high in downgradient wells
- High concentrations of TCE may inhibit cometabolic degradation

  ⟶ not feasible to inject oxygen and stimulate 1,4-D degradation
- Ethene production is usually limited until TCE completely degraded

  ⟶ high ethene concentrations downgradient
- High TCE and ethene concentrations in downgradient wells
  - two distinct zones with high transmissivity at downgradient?
  - due to mixing of treated and untreated water? (10 ft screen)

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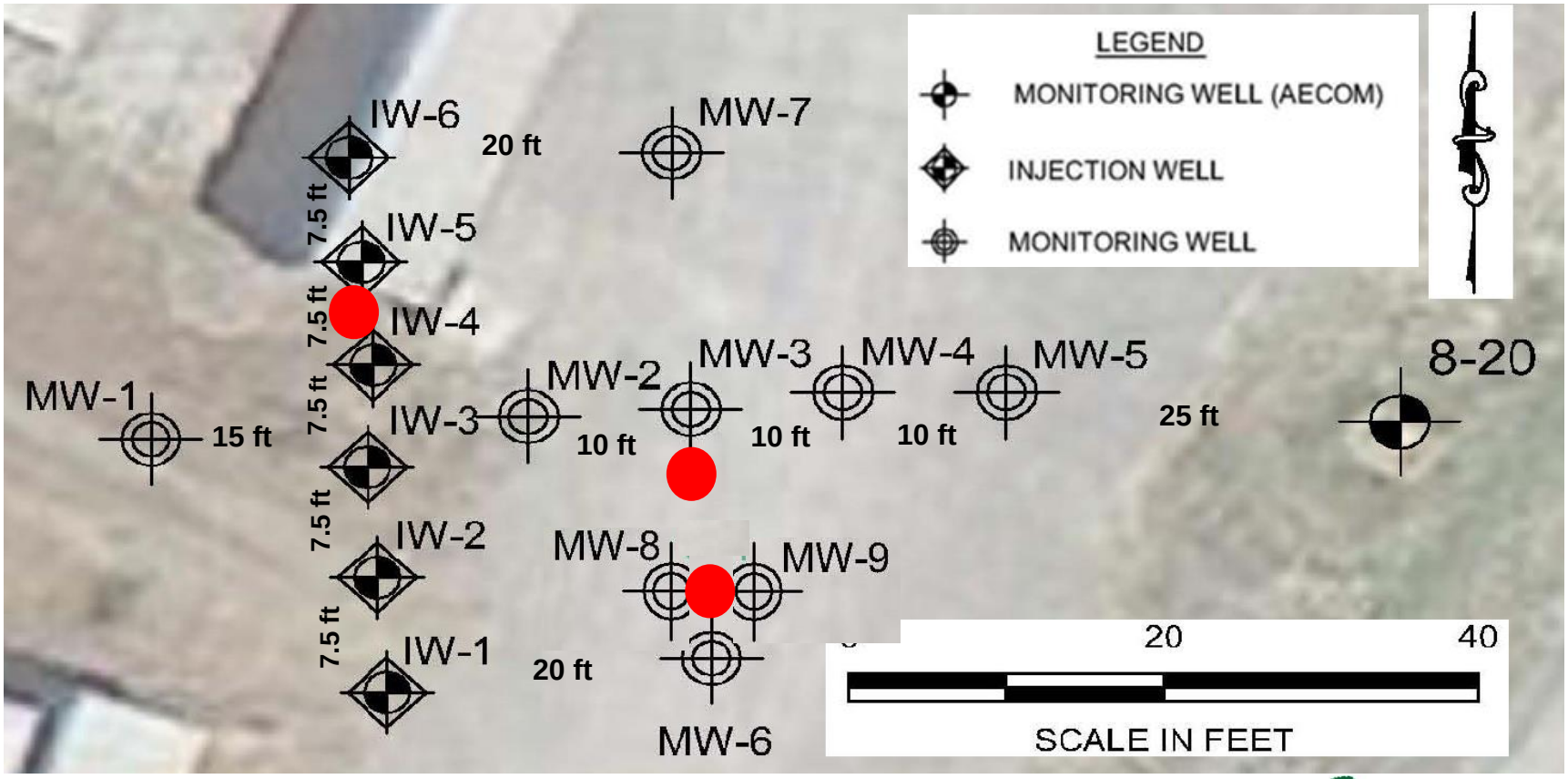
Supplemental Characterization

- 3 continuous macrocores
- 2 new monitoring wells with shorter screens at different depths



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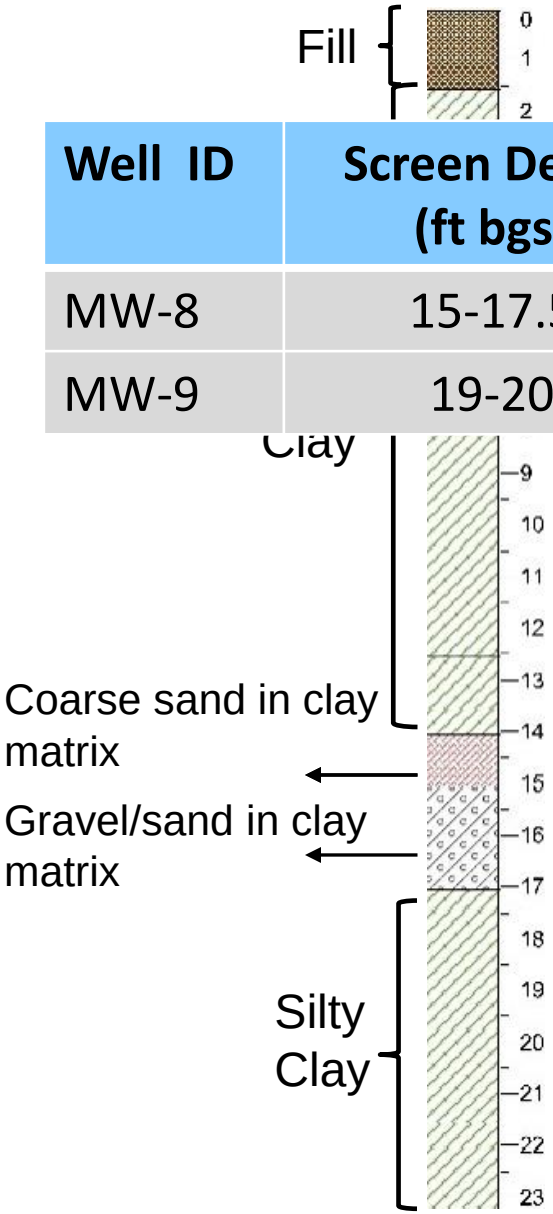
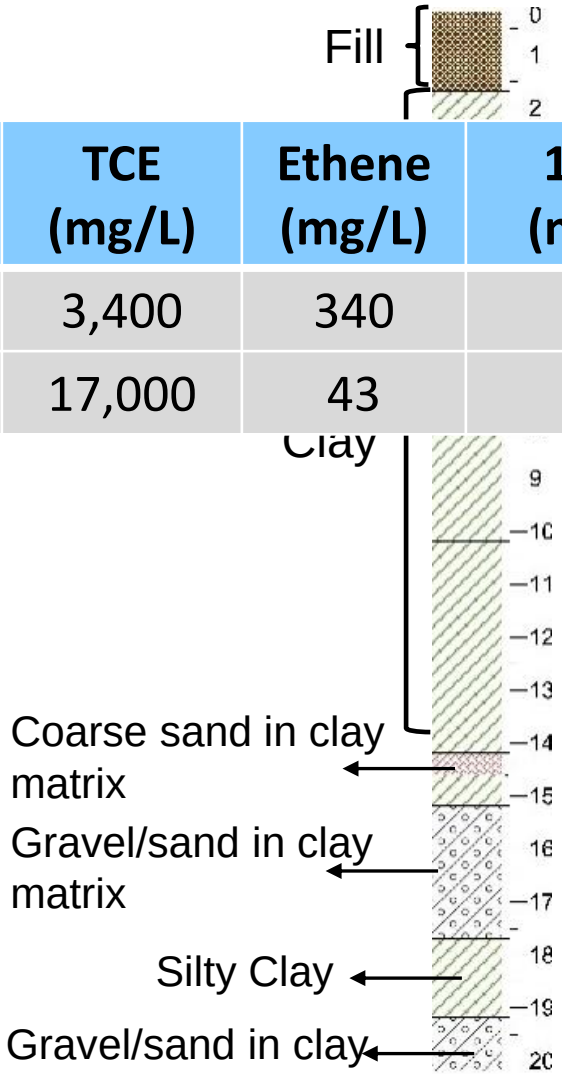
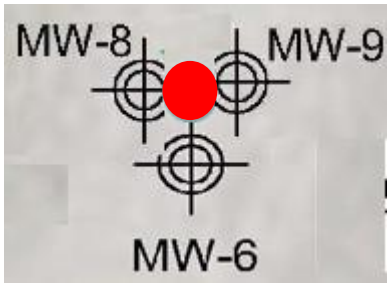
Supplemental Characterization

Well ID	Screen Depth (ft bgs)	TCE (mg/L)	Ethene (mg/L)	1,4-D (mg/L)
MW-8	15-17.5	3,400	340	79
MW-9	19-20	17,000	43	79







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Summary

- 1,4-D concentrations appear to decline in both injection and monitoring wells
  - Anaerobic?
  - Co-metabolic? Ethane?
  - Additional Microbial Analysis → Genomic Analysis
    - determine which biodegradative pathways are actively expressed
    - highlight which nutrients and conditions are important for degradation metabolism
  - Activity based protein profiling (ABPP)- Dr. Michael Hyman, NCSU
    - enables the detection, identification and quantification of specific enzymes in complex mixtures
    - targets bacterial monooxygenases
  - Oxygen injection?
- Complex subsurface geology
  - Very thin discontinuous bodies of sand and gravel are preferential conduits for substrate
  - More detailed site characterization

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