Microbial chain elongation: A more efficient process for promoting and sustaining in situ bioremediation of chlorinated solvents

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Site history

- Superfund Site, chlorinated volatile organic compounds (CVOCs) released from leak in below grade wastewater treatment system in 1970’s
  - Trichloroethene (TCE), and its breakdown products (*cis*-1,2-dichloroethane (*cis*-DCE) and vinyl chloride) are the primary CVOCs detected

- Groundwater extraction (GWE) was the remedy selected in the Record of Decision (ROD)
- In situ bioremediation (ISB) implemented to expedite groundwater treatment
- A pilot test is being implemented to support amending the ROD to replace GWE with ISB

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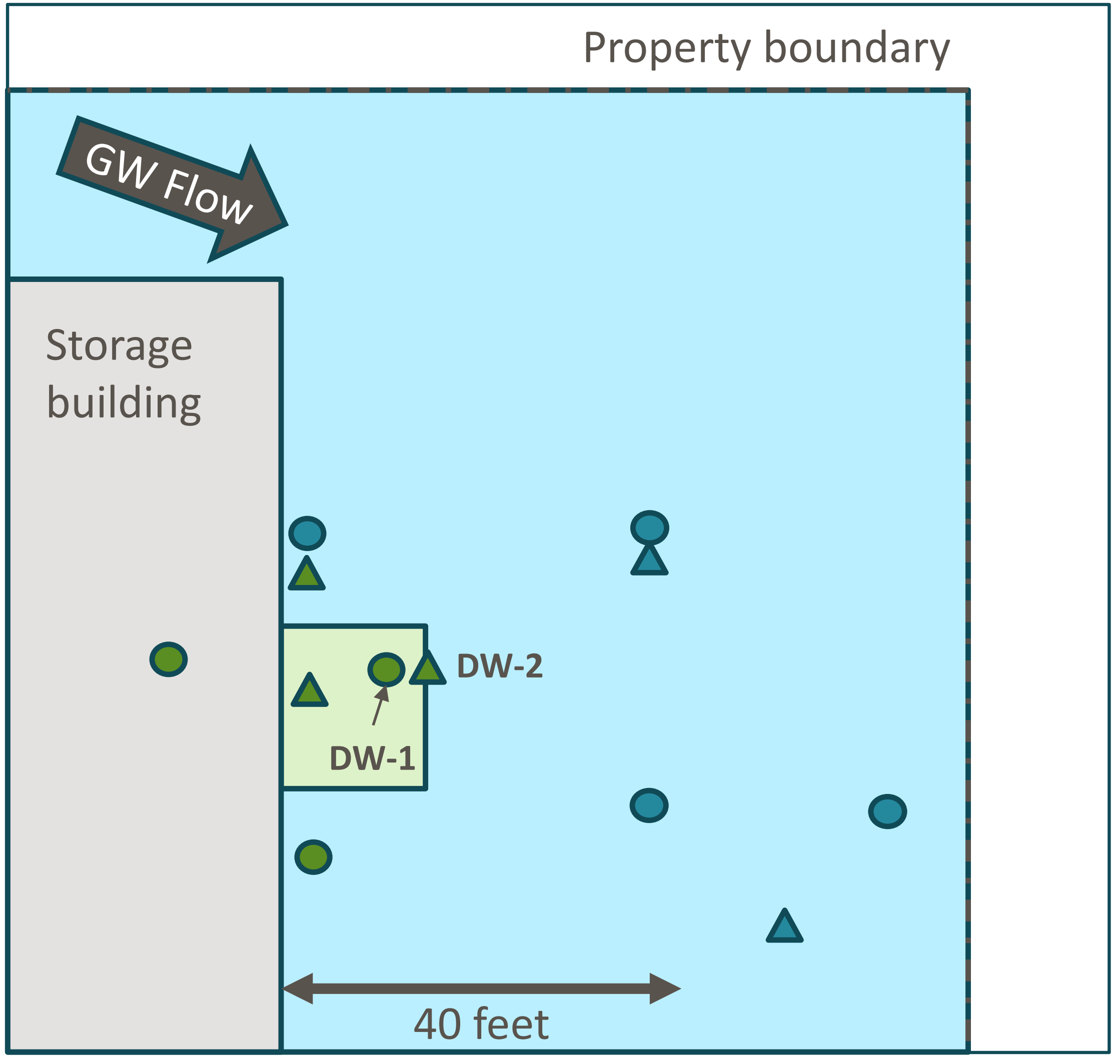
ISB overview



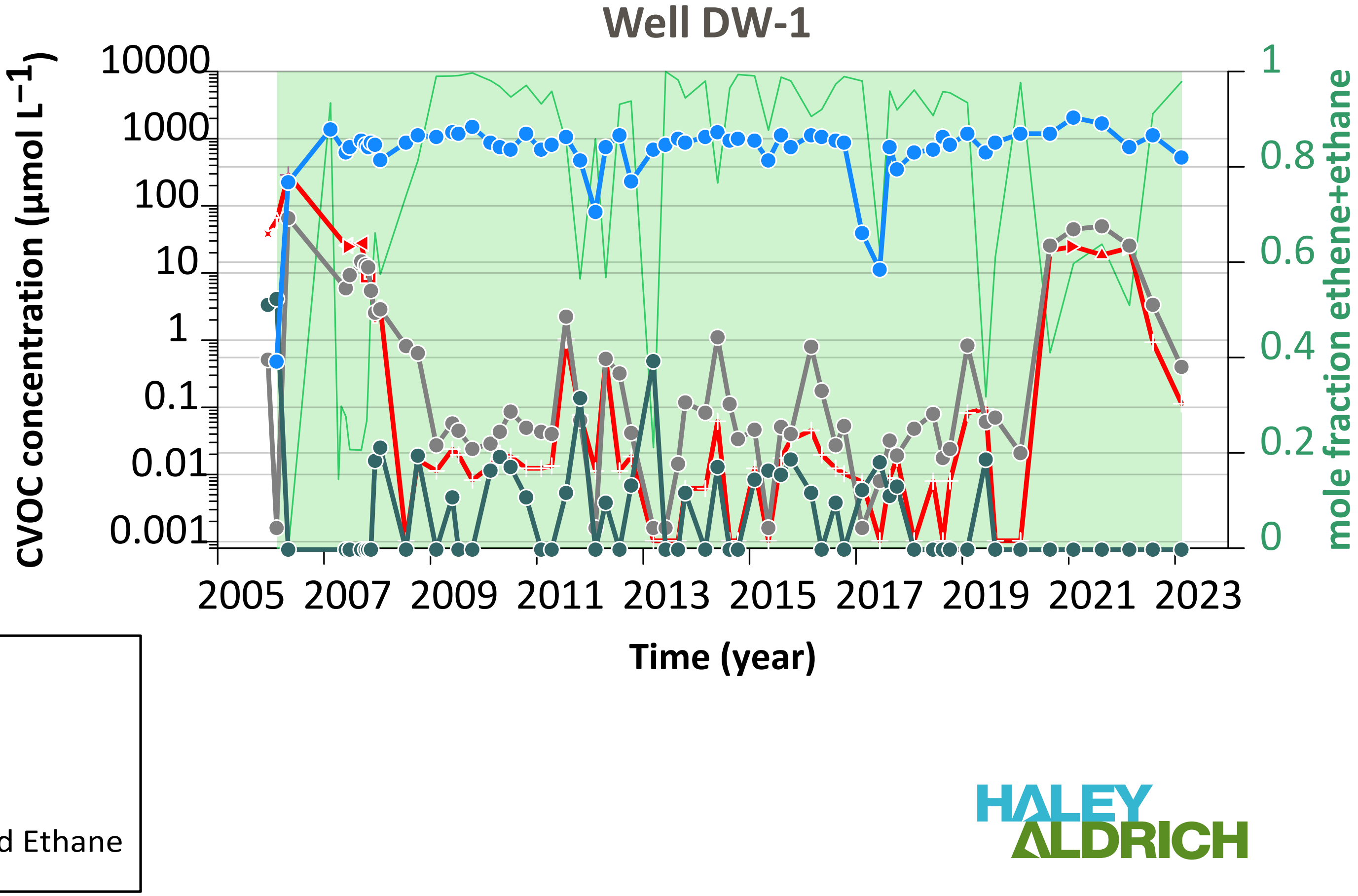
- A network of groundwater injection and extraction wells for delivering electron donor substrates via groundwater circulation
- Three stratigraphic intervals targeted between 10 and 50 feet below grade
- Rapid initial treatment with full scale operation (2006 to 2008) and greater than 10 pore volume (PV) exchanges
- Residual CVOCs treated with a 10-day circulation event targeting one PV circulation volume every 1 – 2 years

Former source excavation
A-zone extraction
A-zone injection
B-zone extraction
B-zone injection

Challenges at the in situ bioremediation system

Complete conversion of TCE to ethene, but a degree of rebound occurred between applications, prompting a search for longer lasting substrates…

- Longer-lasting substrates (emulsified oils/lecithin) resulted in:
  - Clogged injection wells
  - Biogenic toluene production
  - High methane concentrations



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Evolving the state of in situ bioremediation with academic collaborations

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Microbial Chain Elongation and Subsequent Fermentation of Elongated Carboxylates as H_2-Producing Processes for Sustained Reductive Dechlorination of Chlorinated Ethenes

Aide Robles, Theodora L. Yellowman, Sayalee Joshi, Srivatsan Mohana Rangan, and Anca G. Delgado*

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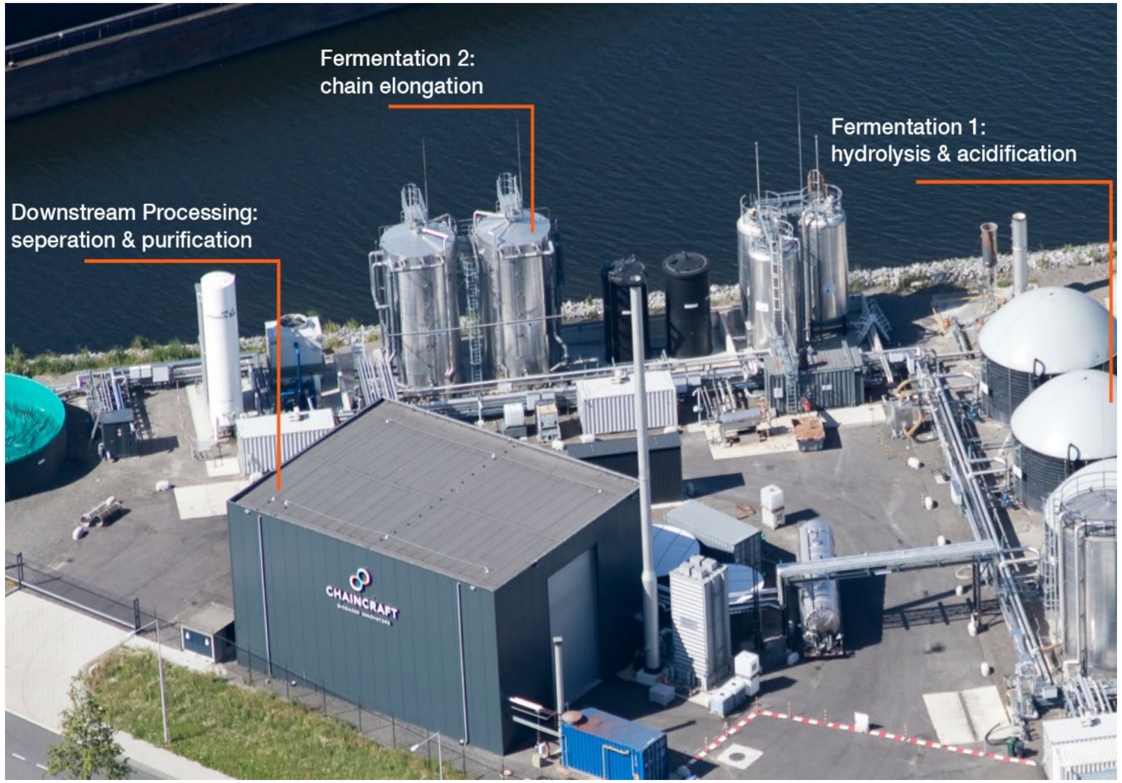
Microbial chain elongation for resource recovery



All images from: https://www.chaincraft.nl/

organic streams (agriculture waste, food waste, etc.)

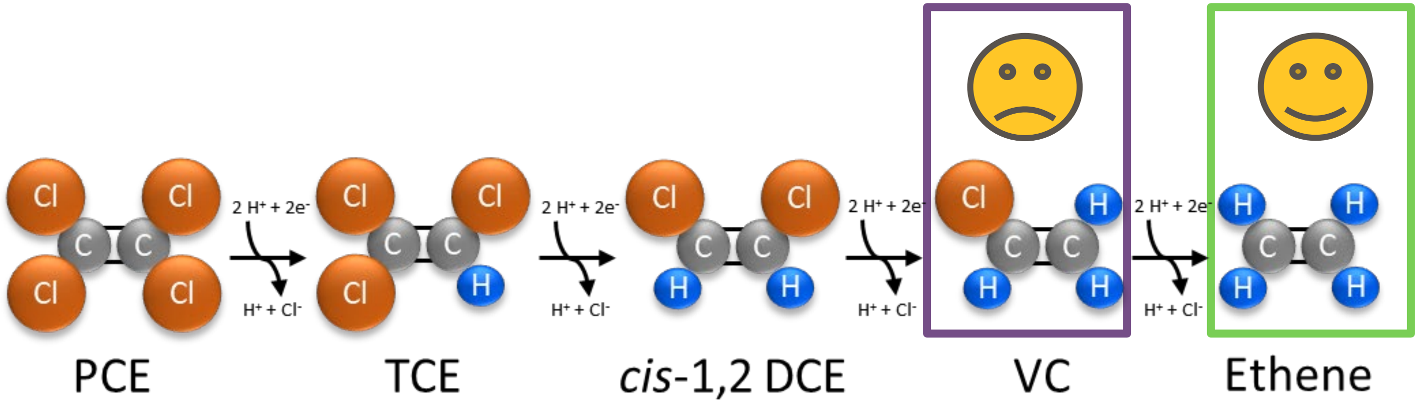
butyrate (C4), caproate (C6), butanol, etc. & **H_2**

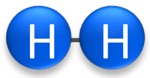
   

5 Ethanol + 3 Acetate$^-$ → 4 *n*-Butyrate$^-$ + H^+ + 4 H_2O + 2 H_2

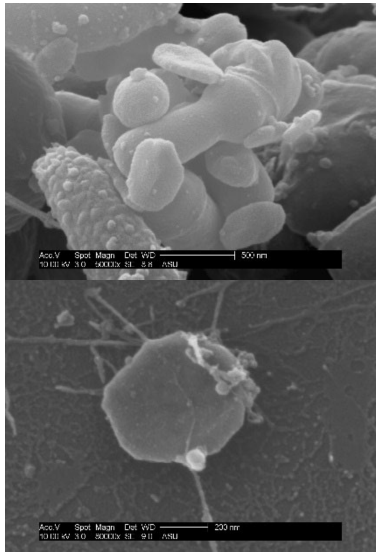
5 Ethanol: (2 Carbon) electron donor
3 Acetate: (2 Carbon)
4 *n*-Butyrate: (4 Carbon)

Reductive dechlorination





electron donor: hydrogen (H_2)



Dehalococcoides mccartyi

Delgado et al *Environ. Sci. Technol.* **2017**, 51, 11297-11307.

Why source H_2 from MCE?

- Reliably produces H_2 without producing CO_2 for methanogenesis
- MCE products (butyrate, butanol, etc.) are fermented for more H_2
- Naturally occurring microbes are commonly found in soil matrices
- Acetate and ethanol are low-cost substrates that are also easy to handle

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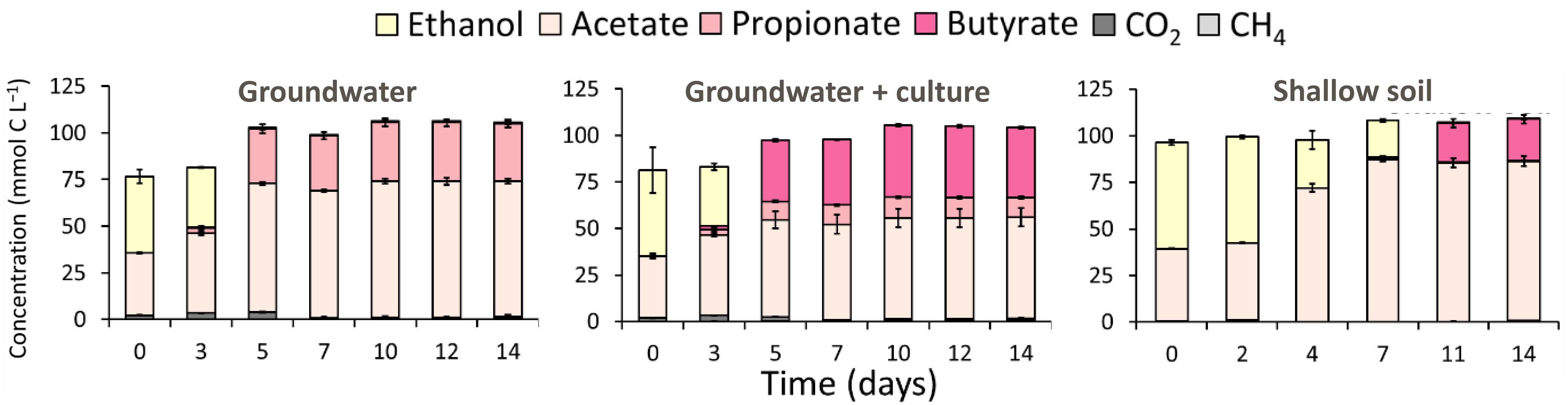
Initial material screening



- Bioremediation relevant MCE (27 mM ethanol & 16.2 mM acetate) substrate concentrations can suppress methanogenesis
- Site groundwater receptive to bioaugmentation
- Shallow site soil contains chain elongating microorganisms not found in treatment zone groundwater

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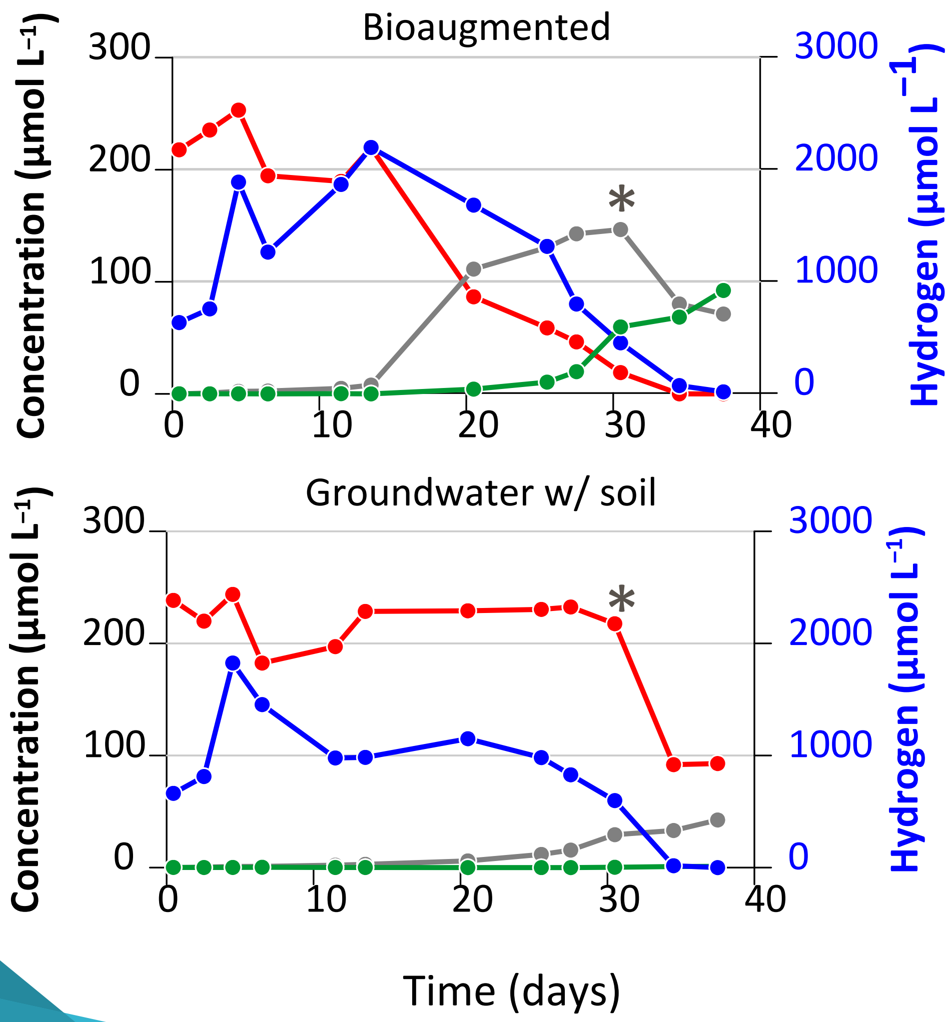
Reductive dechlorination in groundwater



- Microcosms amended with 3.6 mM acetate, 32.4 mM ethanol, and culture demonstrated conversion of *cis*-DCE to ethene
- Adding shallow site soil instead of culture resulted in lower conversion to ethene
- No CO_2 production observed

*Day 31 added groundwater

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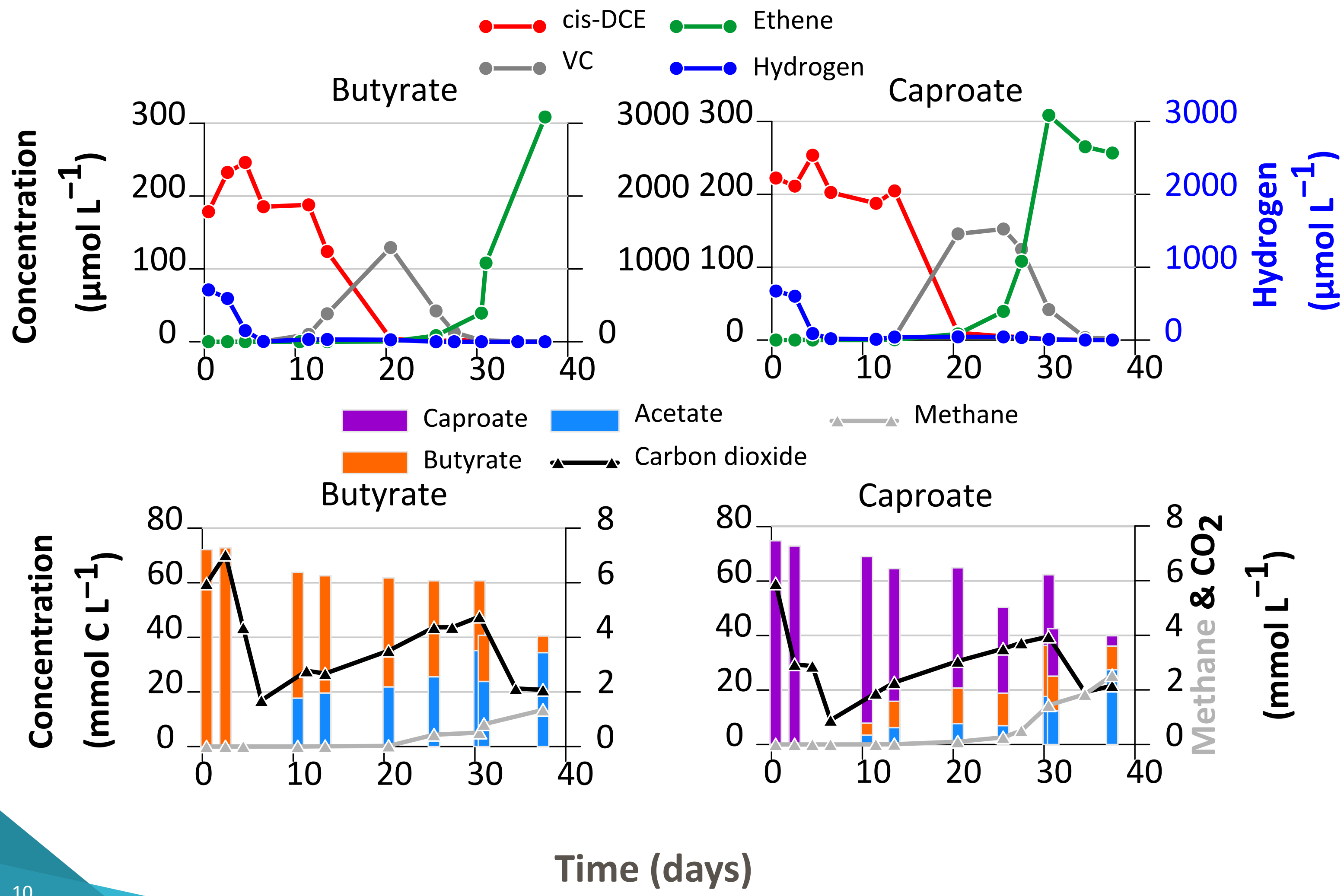
Direct use of MCE products



- Complete conversion of *cis*-DCE to ethene
- Sequential fermentation of caproate and butyrate to acetate and H_2
- Minimal CO_2 and CH_4 production

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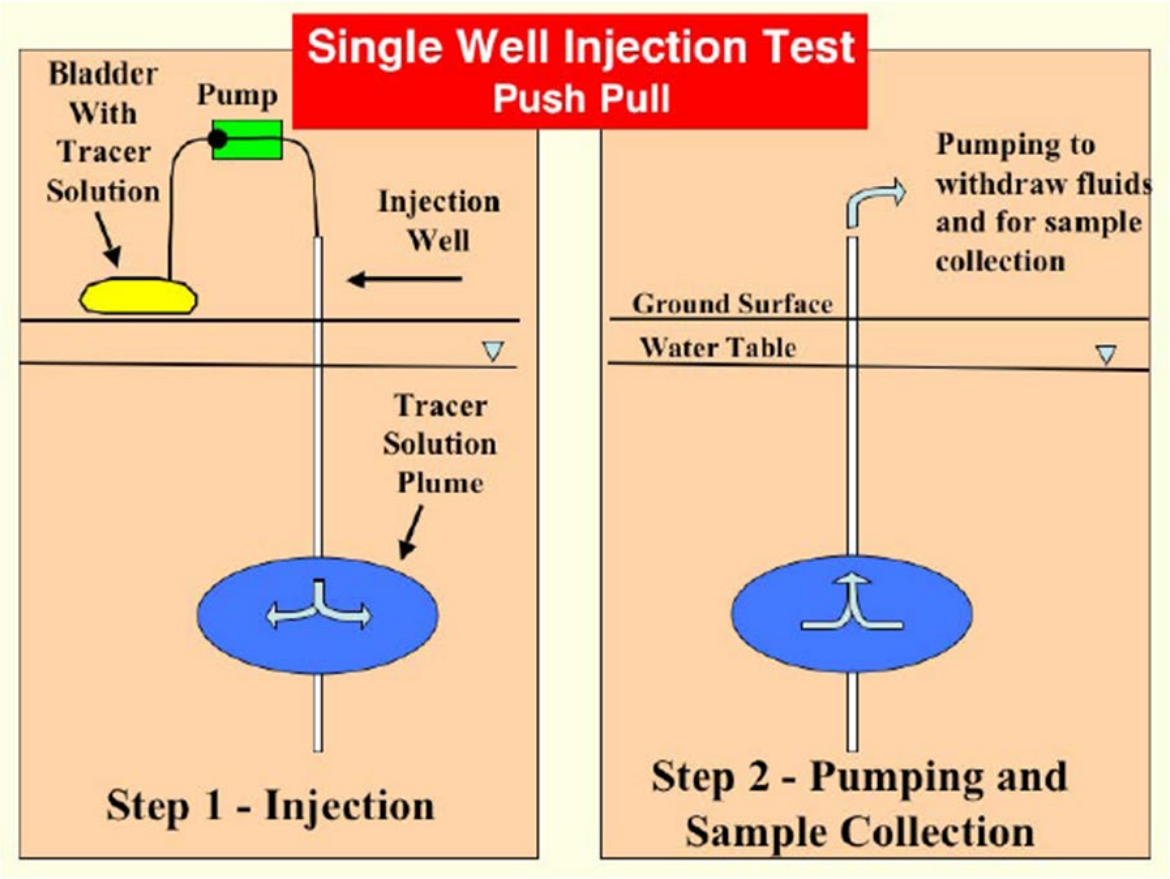
Two-stage push-pull pilot test



Stage 1: DW-2 Groundwater

3.9 mM acetate, 35 mM ethanol, **without** bioaugmentation and **no VOCs**. Test period 3 weeks.

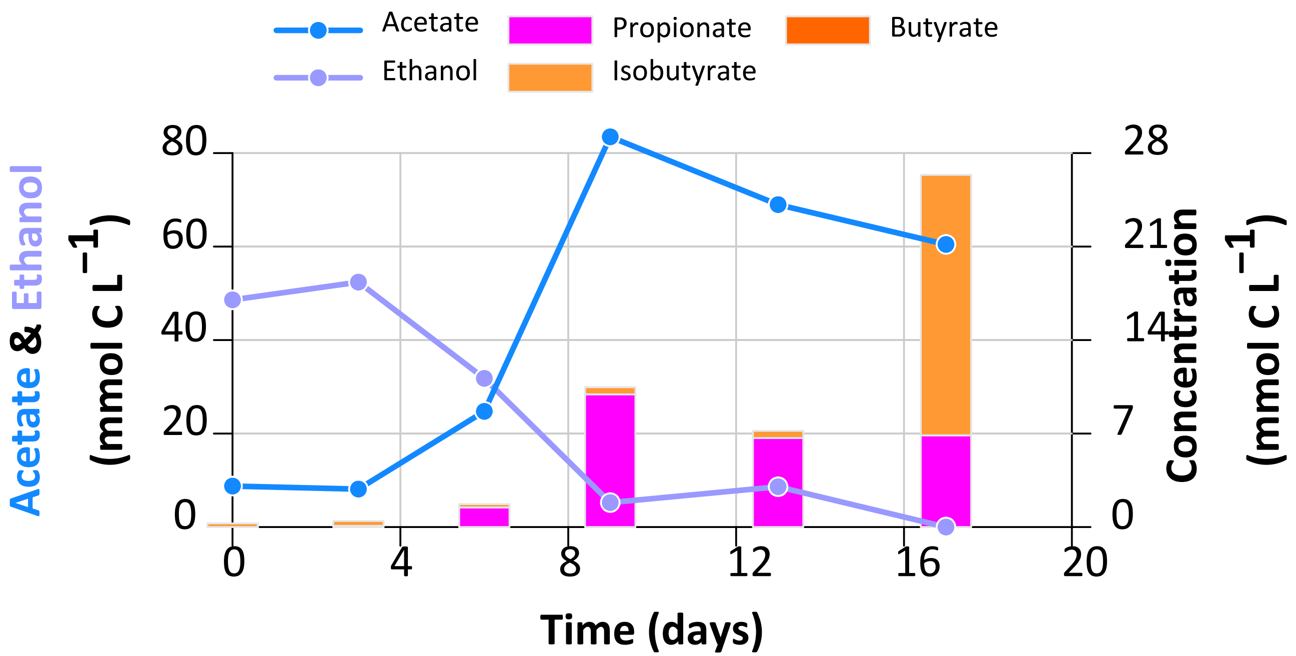
Stage 2: DW-1 Groundwater

Same as above but **with VOCs*** and **bioaugmentation with culture MAT-1**. Test period is 5 weeks.

*contains: *cis*-DCE, VC, ethene, and ethane

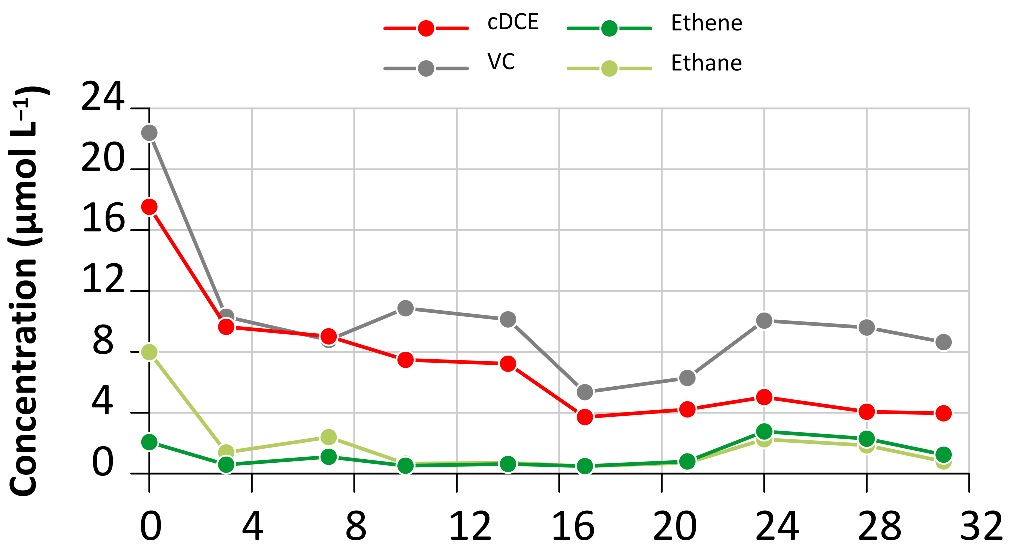
Push-pull test: Stage 1 w/out bioaugmentation

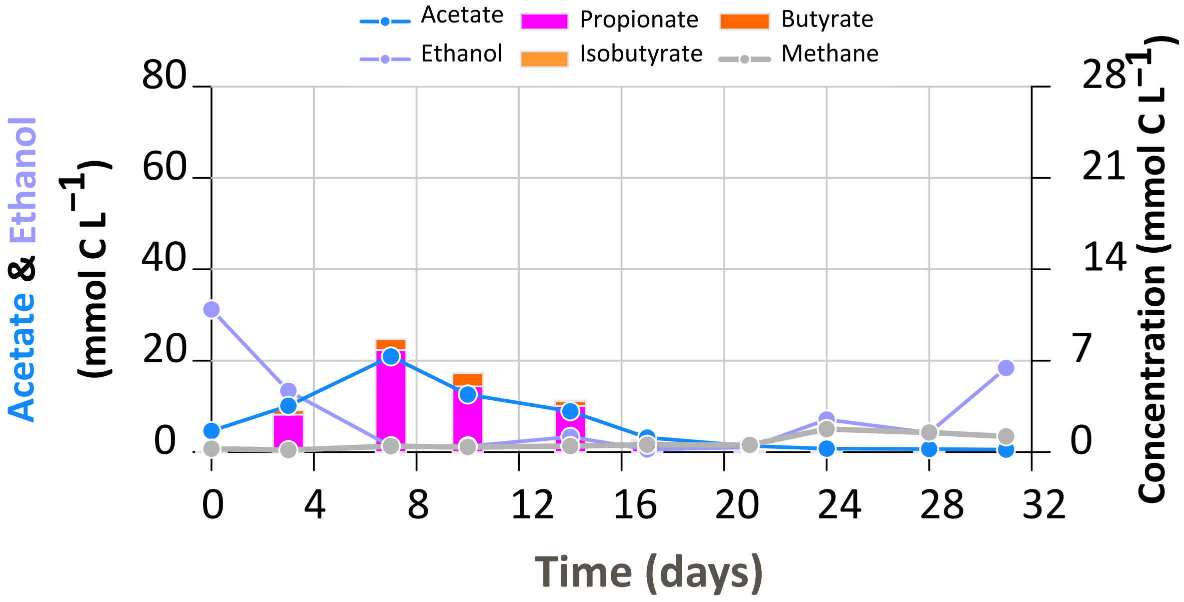
- Confirmed bench-scale study findings
- Propionate & isobutyrate generated instead of butyrate or caproate (MCE products of ethanol & acetate)
- Acetate generated partly by ethanol oxidation
- Bioaugmentation will be required to drive MCE processes

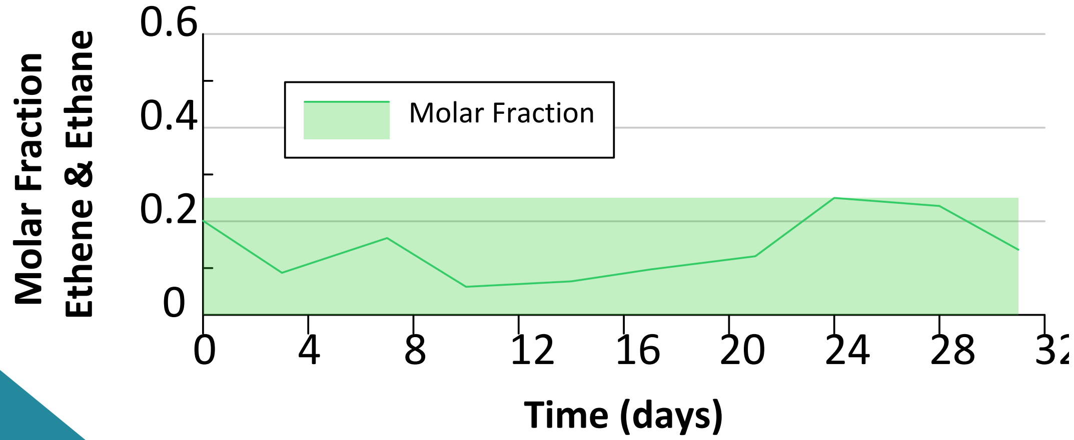


Push-pull test: Stage 2

- Production of butyrate and trace amounts of isobutyrate, valerate, and isovalerate!
- Less methane generation than with previous amendments
- VOC concentrations lower than expected yet conversion to ethene was achieved







Practical considerations for full field application at this site

- Bioaugmentation with MAT-1 will promote MCE processes
- MCE substrates provide greater and faster H_2 release than conventional substrates
- Expecting ~50% reduction in methane generation
- MCE substrates and products are soluble and do not cause clogging

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Thank you for listening! Questions?

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Background

Activated carbon-based PRBs:

- Intercept groundwater plumes
- Retard downgradient contaminant migration

R&D efforts produced:

- Plant-based, sub-micron, fermentable bioremediation amendment
- Sustains in-situ bioremediation within a PRB
- Co-injectable with activated carbon at low pressures

Discussed in the Poster

- ***AquiFix***
- ***Treatability Study and Results***
- ***Longevity Experiment***
- ***Field-Scale Case Study and Results***

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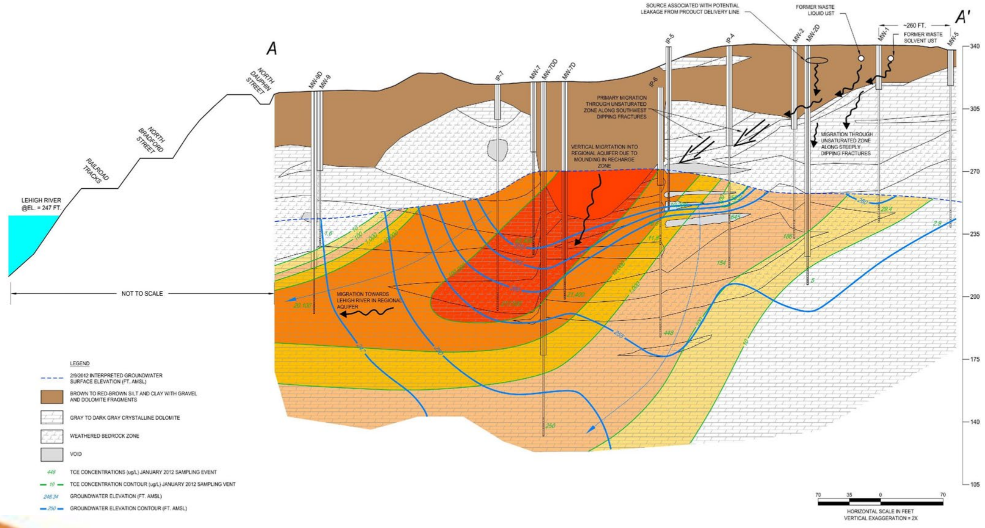
Source Area BioRemediation in Fractured Bedrock with Karst Features Revisited as Sustainable and Resilient Remediation

ERM

- A manufacturing facility operating in central Pennsylvania experienced releases of tetra and trichloroethene through leaking underground waste storage tanks (UST) that were installed on top of fractured bedrock.
- Initial investigation identified shallow saprolite soil impact and GW impact to depths of ~250' bgs
- HRSC including sorbers identified elevated concentrations of TCE and degradation products ir the bedrock aquifer at depths of ninety-five to almost two-hundred feet below ground surface (bgs) at concentrations exceeding 300,000 µg/L.
- Semi-quantitative sustainability assessment was conducted comparing pump and treat, thermal, in situ chemical oxidation and in situ bioremediation



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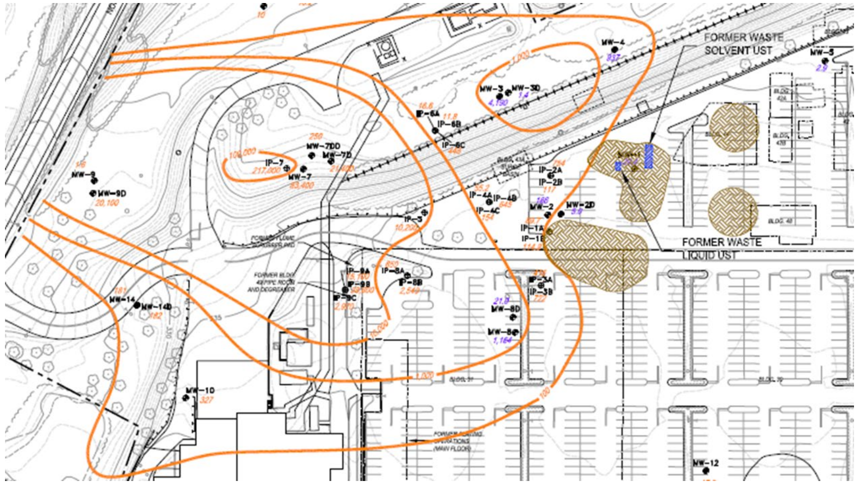
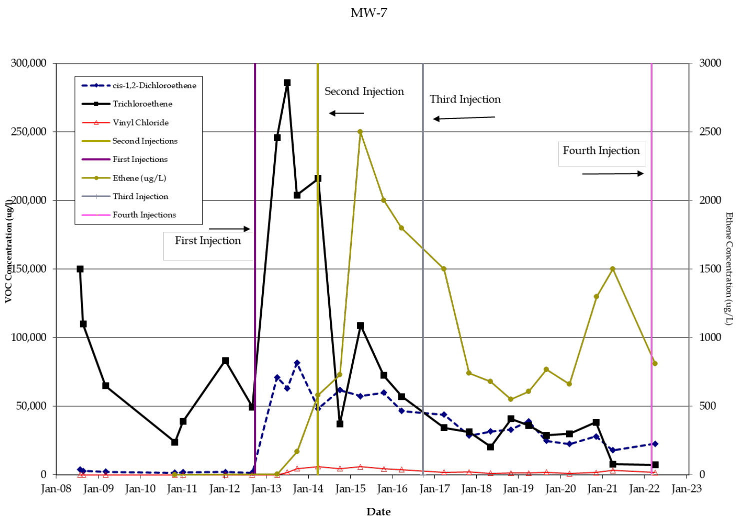
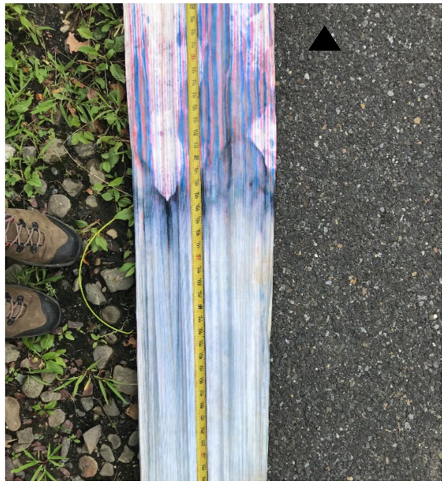
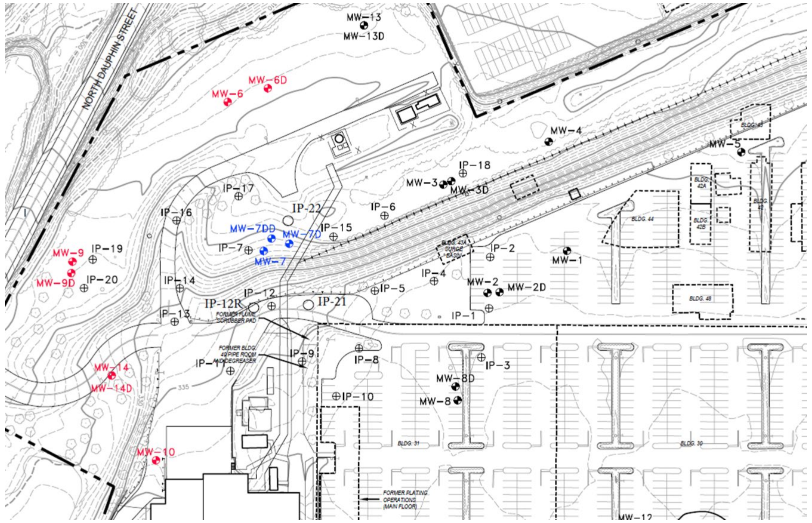
Source Area Bioremediation in Fractured Bedrock with Karst Features Revisited as Sustainable and Resilient Remediation

- Remedy included installation of 18 injection well clusters focused in the source area and downgradient as a biobarrier
- Injection well clusters installed from 95 to 170’ bgs starting in 2014 with injections every 3 years
- Injected an 8% emulsified vegetable oil solution using groundwater from well development
- Also bioaugmented with DHC consortium after reducing conditions were established
- 12 bioborings installed in DNAPL source area and immediately downgradient in 2021
- Bioborings installed from 100’ to a depth of 120’ bgs









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