DCE 'Stall' – Causes and Cures

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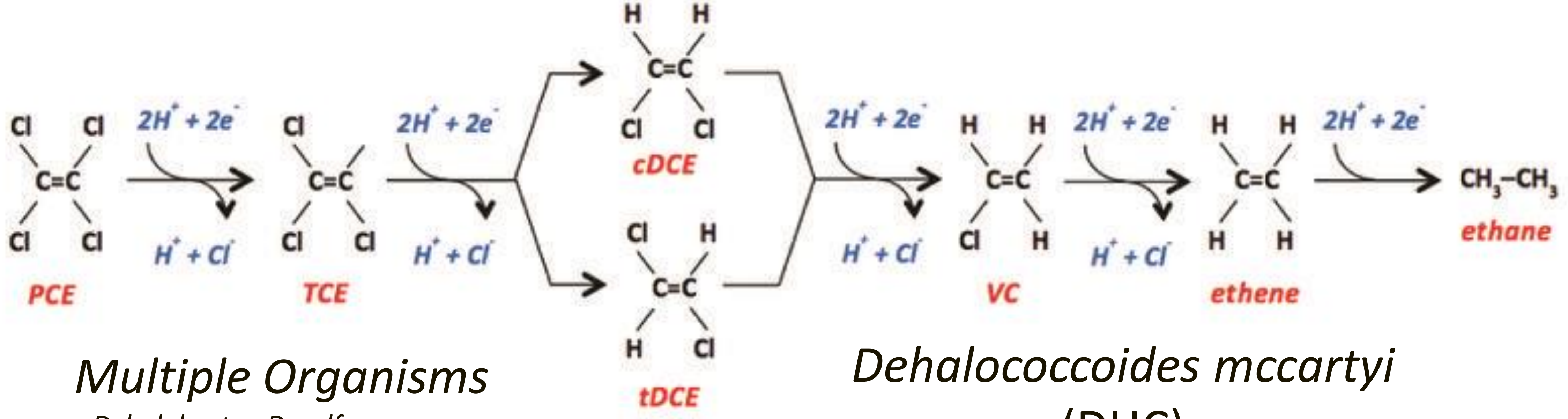
Anaerobic Bioremediation with Emulsified Vegetable Oil (EVO)

- Experience
  - >20 years experience with this process
  - 1000’s of sites worldwide, tens of millions Kg
- Process
  - Dilute EOS Pro 1:4 and inject
  - Inject additional chase water
    - distribute emulsion throughout treatment zone
    - Flush oil out of injection well
  - Oil droplets eventually stick to sediment surfaces
  - Oil slowly ferments to H_2 and acetate
  - H_2 and acetate drive anaerobic biodegradation
  - Bioaugment if needed
  - Reinject after 3 – 5 years

Chloroethene Respiration



Multiple Organisms

Dehalobacter, Desulfuromonas, Sulfurospirillum, Geobacter, Desulfitobacterium

Grow rapidly

Use H_2 or Acetate

Can fix N (produce NH_4)

Can produce B_{12}

pH > 5.5

Dehalococcoides mccartyi

(DHC)

Grows slowly

Requires H_2

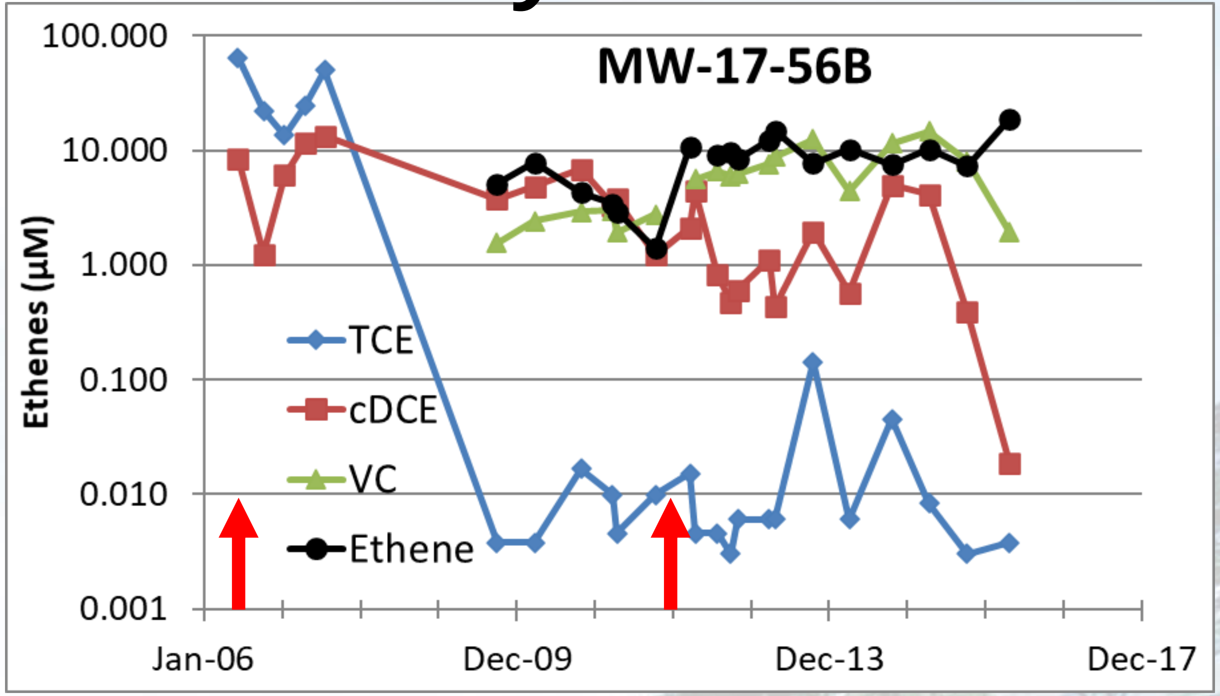
Requires NH_4

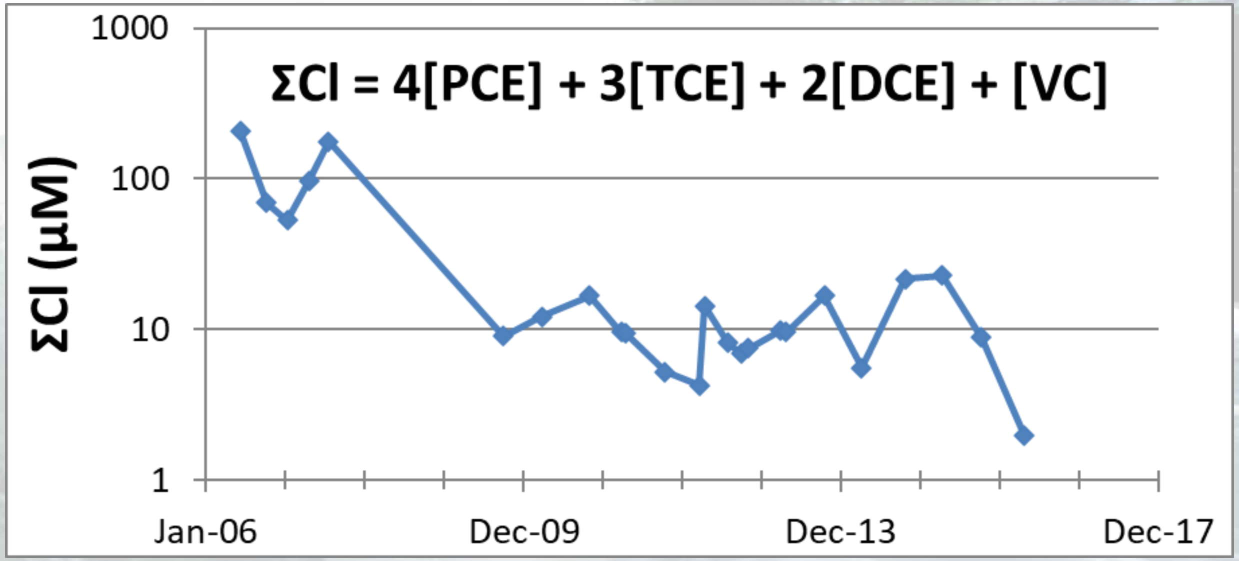
Requires B_{12}

pH > 6.3

MW-17-56B Data Analysis

- EOS Pro in 2006 and 2012
- 2006 to 2009
  - **99.99%** TCE removal
  - High cDCE and VC conc.
  - Lots of ethene (> 100 µg/L)
  - Is ERD Working?
- 2009 to 2014
  - ΣCl ~ constant
- Interpretation → Not a 'DCE Stall'
  - Continuing upgradient source
  - TCE decay rate > cDCE decay rate
- Recommendations
  - Locate upgradient source and treat
  - Increase cDCE & VC decay rate to reduce cleanup time / save money





Post-Remediation Evaluation of EVO Treatment: How Can We Improve Performance?

- Lessons Learned
  - PCE & TCE → cDCE FAST
  - cDCE → VC → Ethene SLOWER

ESTCP

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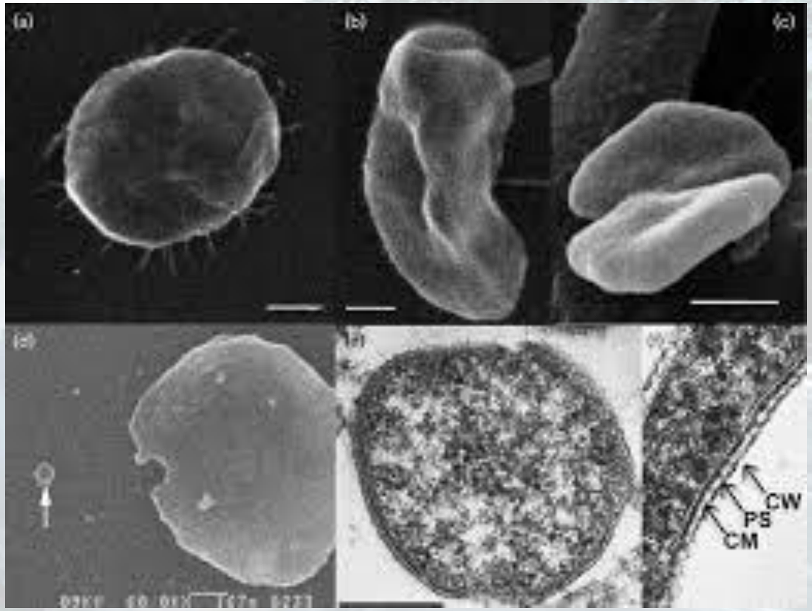
- Note – this is **NOT** a ‘DCE stall’
  - Ethene is being produced
  - TCE degradation rate > DCE degradation rate
  - Increasing DCE degradation rate → shorter cleanup time → save money
- Causes of **Slow** cDCE → Ethene
  - Significant PCE / TCE still present → bugs prefer TCE to DCE/VC
  - Low DHC numbers → bioaugment
  - B_{12} or nutrient limitation → add nutrients + B_{12}
  - cDCE and VC not in direct contact with H_2 → improve oil distribution
  - Low pH inhibition → add buffer to raise pH

Bioaugmentation

- Addition of specialized bacterial cultures to enhance contaminant biodegradation
  - Indigenous bacteria cannot degrade target pollutants
  - Reduce lag time
- Example
  - Bacteria that convert TCE → cis-DCE (very common, grow rapidly)
  - Bacteria that convert cis-DCE → VC → ethene (not always present, grow slowly)
- Should you bioaugment?
  - Cons: Bugs and injection labor are significant
  - Pros: Will save time, even if not ‘required’
- Conclusion
  - Waiting is expensive (monitoring, mobilization)
  - We recommend bioaugmentation whenever qPCR counts are low

Dehalococcoides mccartyi



Vegetable Oil Fermentation

- Natural fats → Triglycerides
  - glycerol
  - three long chain fatty acids (LCFA)
  - Anaerobes cannot degrade LCFA when attached to glycerol
  - Bacteria hydrolyze ester linkages releasing glycerol and LCFA
- Glycerol (Very soluble, Easily biodegraded)
- Beta Oxidation of LCFA (e.g. linoleic acid or $C_{18}H_{32}O_2$)

$C_{18}H_{32}O_2 + 2H_2O \rightarrow C_{16}H_{30}O_2 + C_2H_4O_2 + H_2$

$C_{16}H_{30}O_2 + 2H_2O \rightarrow C_{14}H_{28}O_2 + C_2H_4O_2 + H_2$

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$C_{18}H_{32}O_2 + 16H_2O \rightarrow 9C_2H_4O_2 + 14H_2$

Acetic Acid

Hydrogen (H_2) vs Acetate

- LCFA (linoleic acid + NaOH = Soap)
  - Precipitates with Ca^{+2}, Mg^{+2}, Fe^{+2}, Mn^{+2} (soap scum)
  - Essentially immobile → low bioavailability
  - Slowly ferments releasing both **acetate** and $\mathbf{H_2}$

- Acetate (stimulates PCE → TCE → cDCE)
  - Low energy yield → Slow consumption
  - Will migrate some distance downgradient

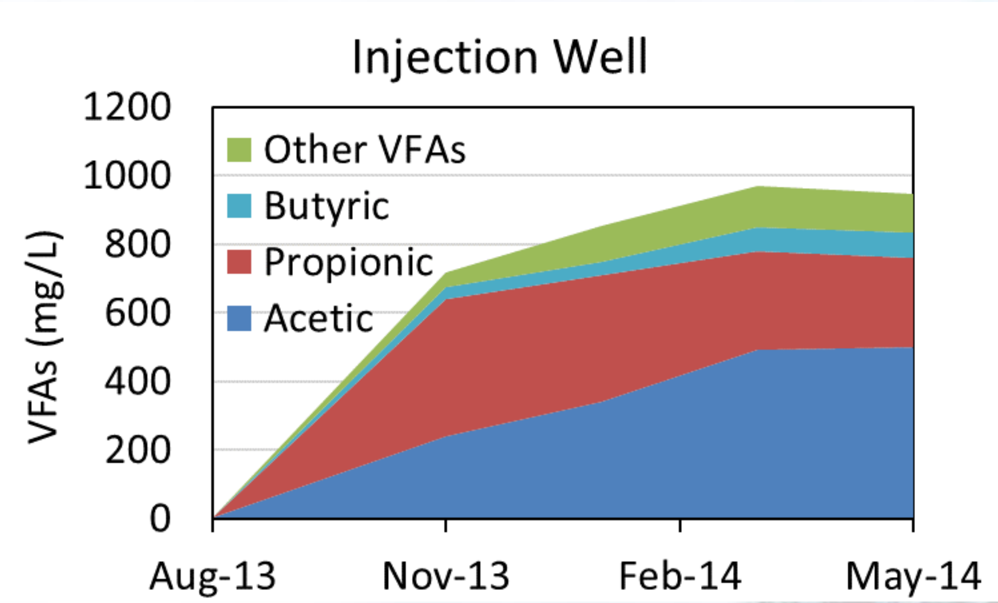
- H_2 (required for cDCE → VC → ethene)
  - High energy yield → Rapid consumption
  - Excellent electron acceptor for CVOCs **AND** Fe(III), SO_4, and CO_2
  - H_2 does not migrate any significant distance
  - H_2 **is** produced from LCFA, proprionate, butyrate, valerate, , ,

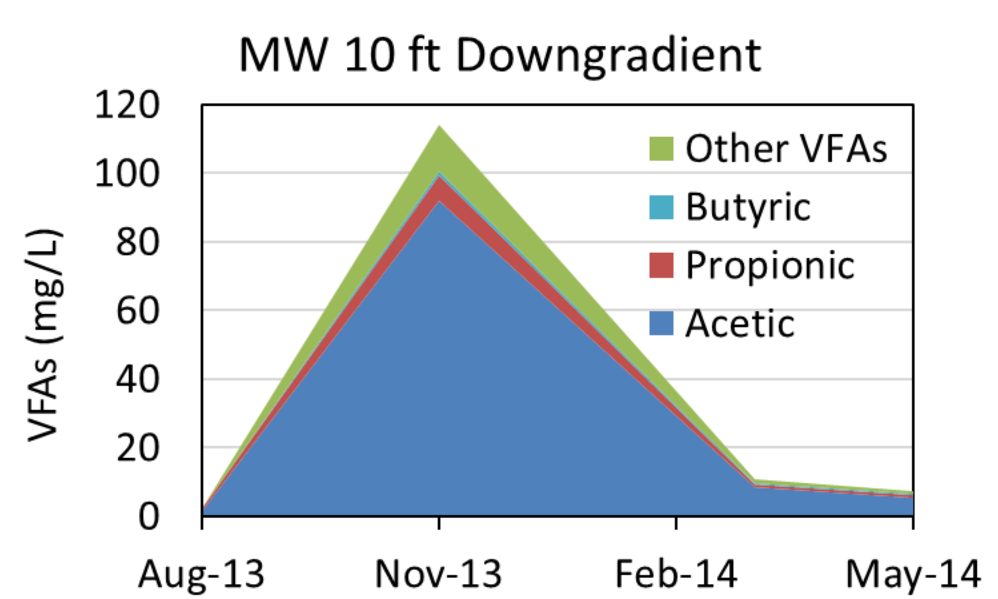
Need direct contact between cDCE/VC and oil, proprionate, butyrate, etc

Acetate will not stimulate cDCE→VC→ ethene

Fermentable Carbon

- EOS Pro Injection Wells
  - Direct contact with oil
  - Good fermentable carbon
  - Complete dechlorination of TCE → ethene
- 10 Ft Downgradient
  - Some soluble TOC
  - Primarily acetate
  - ‘No’ fermentable carbon
  - Good TCE → DCE
  - Poor DCE → ethene



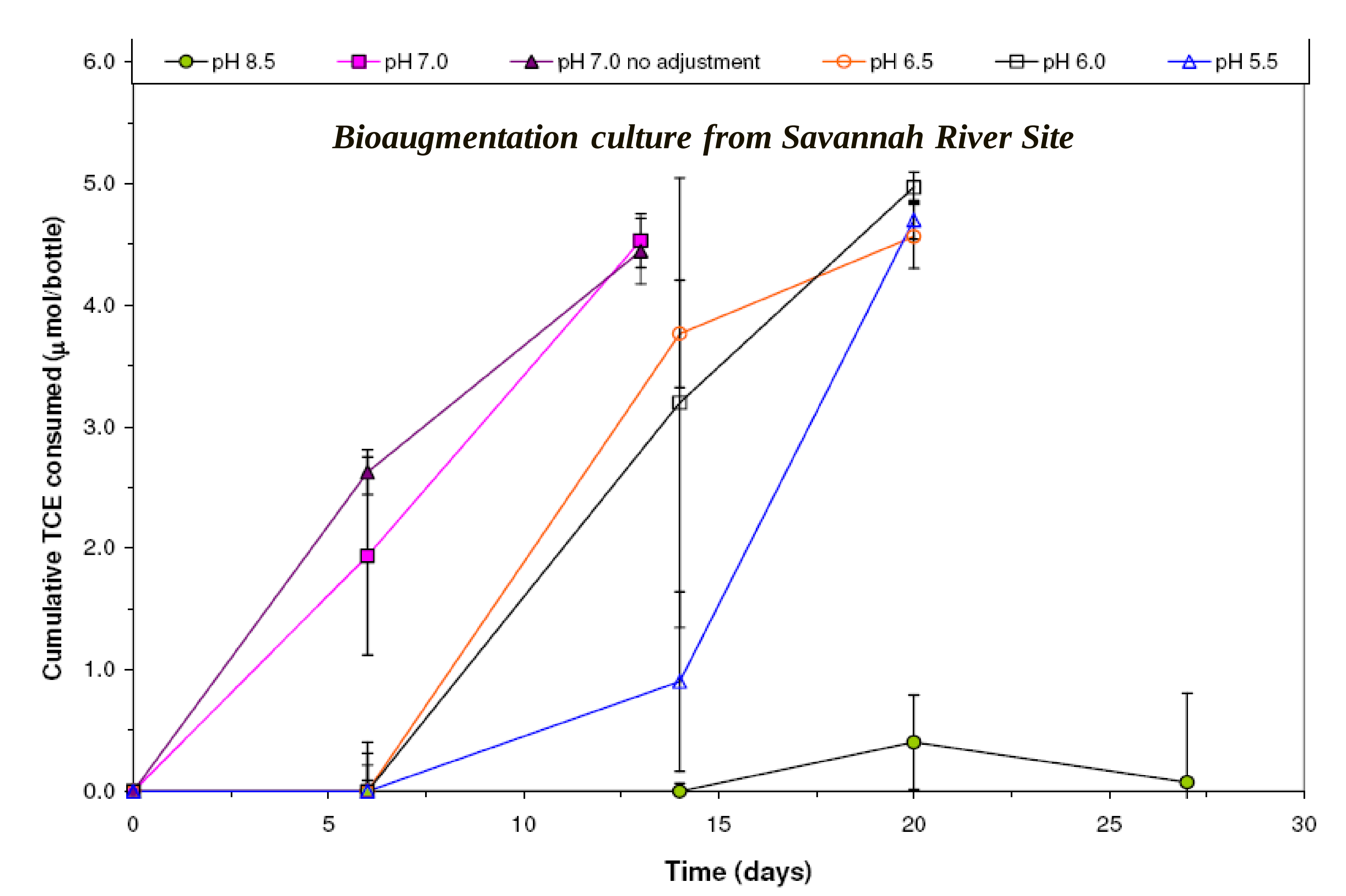


Bring oil into direct contact with contaminant

Effect of pH on TCE Dehalogenation

TCE → DCE

- pH= 7
  - Optimum
- pH= 6.5 – 5.5
  - Inhibition, followed by complete degradation

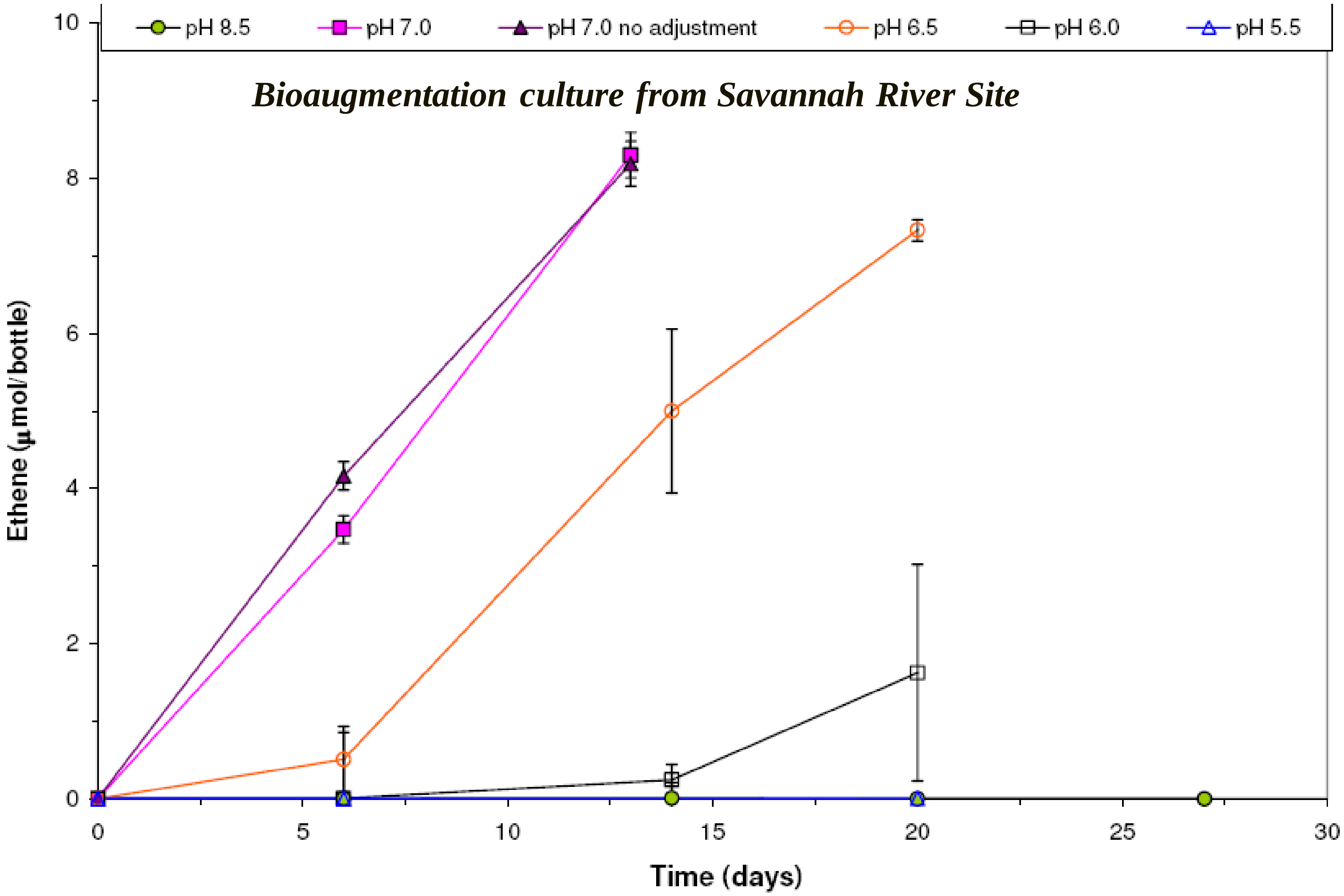


Ashley Eaddy, 2008. Scale-Up and Characterization of an Enrichment Culture for Bioaugmentation of the P-Area Chlorinated Ethene Plume at the Savannah River Site. M.S. Thesis, Clemson University, under the direction of David Freedman.

Effect of pH on VC Dehalogenation

VC → ethene

- pH= 8.5
  - Complete inhibition
- pH= 7
  - Optimum
- pH= 6.5
  - Some inhibition
- pH= 6.0
  - Strong inhibition
- pH= 5.5
  - Complete inhibition



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Lessons Learned

- ERD is a robust and effective treatment technology
- Required for efficient cDCE→VC→ethene
  - Low TCE levels
  - Good bug counts
  - Adequate nutrients (N, P, B_{12})
  - Neutral pH
  - Direct contact between bugs, H_2, and cDCE/VC
- Solutions
  - Bioaugment and provide nutrients
  - Bring oil into direct contact with cDCE & VC (Friday short course)
  - Provide sufficient buffer to maintain pH > 6.3 (Friday short course)

Questions?

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