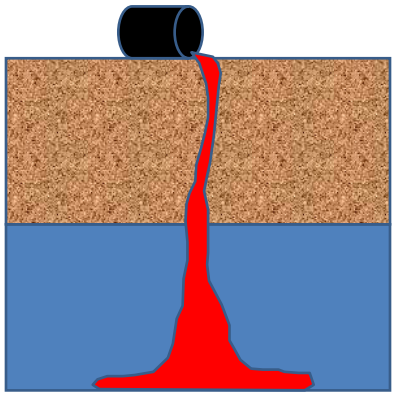
Enhanced Remediation of Chlorinated Solvents from Contaminated Groundwater using a Bioreactor System

Charles Walker and Michelle Lorah

Chlorinated Organic Solvents

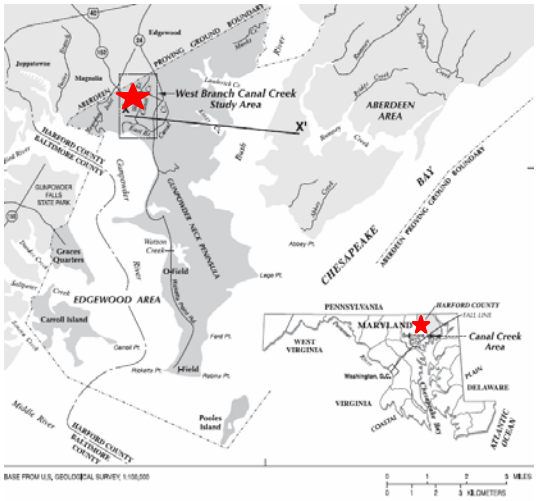
- Useful for degreasing oils, fats and resins
- Generally are harmful to human and environmental health
- Suspected carcinogens
- Many different phases in environment
  - Non Aqueous Phase Liquid (NAPL)
  - Dissolved
  - Vapor
- Most are heavier than water
  - Dense NAPL
- Volatile Organic Compound (VOC)

DNAPL



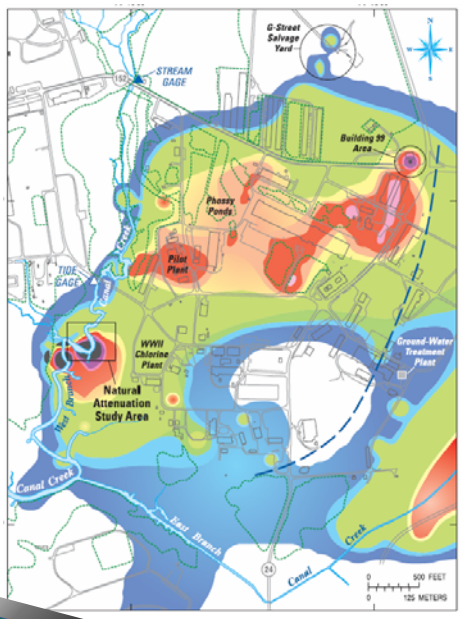
Aberdeen Proving Grounds

- Chlorinated solvents were used as decontaminating agents and degreasers
- Wastes were discharged directly into the creek, or through overland runoff
- Led to the contamination of the Canal Creek Aquifer
- 1990, APG was placed on National Priorities List, established under CERCLA (Superfund)



Phelan and others 2002

Site Contamination



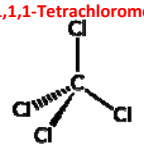
TOTAL VOLATILE ORGANIC COMPOUND (VOC) CONCENTRATIONS, in micrograms per liter

- Greater than 10,000
- 5,000-9,999
- 1,000-4,999
- 500-999
- 100-499
- 50-99
- 10-49
- Less than 10

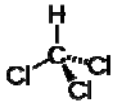
Majcher and others, 2007; Weston Solutions, 2005

Common Chlorinated Solvents Found at APG

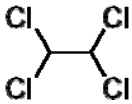
1,1,1,1-Tetrachloromethane



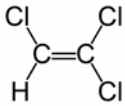
Trichloromethane



1,1,2,2-Tetrachloroethane



Trichloroethene



Name	Abbreviation	Use
1,1,1,1-Tetrachloromethane (carbon tetrachloride)	CT	Agent manufacturing, fire extinguishers, refrigerant
Trichloromethane (chloroform)	CF	Agent manufacturing, solvent
Trichloroethene	TCE	Anaesthetic
1,1,2,2-Tetrachloroethane	1,1,2,2-PCA TeCA	Solvent, decontaminating agent

Current Groundwater Treatment

- Pump and Treat System
- Extracts groundwater from eight groundwater recovery wells
- 200 gallons per hour
- Removes chlorinated solvents using specialty resin
  - Short lifespan
- Fouls easily with metals
  - Metals removal
- 100 ug/L total VOC effluent limit
- TeCA is the main contaminant
- Expensive to run

Material Safety Data Sheet
1,1,2,2-Tetrachloroethane MSDS

Section 1: Chemical Product and Company Identification

Product Name: 1,1,2,2-Tetrachloroethane
Catalog Codes: SLT1927
CAS#: 79-34-5
RTECS: KI8575000
TSCA: TSCA 8(b) inventory: 1,1,2,2-Tetrachloroethane
CIM: Not available.
Synonym:
Chemical Name: Not available.
Chemical Formula: C2H2Cl4

Contact Information:
Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396
US Sales: 1-800-901-7247
International Sales: 1-281-441-4400
Order Online: ScienceLab.com
CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300
International CHEMTREC, call: 1-703-527-3887
For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
(1,1,2,2-)Tetrachloroethane	79-34-5	100

Toxicological Data on Ingredients: 1,1,2,2-Tetrachloroethane: ORAL (LD50): Acute: 350 mg/kg [Rat]. DERMAL (LD50): Acute: 6400 mg/kg [Rabbit]. VAPOR (LC50): Acute: 2250 ppm 4 hour(s) [Mouse].

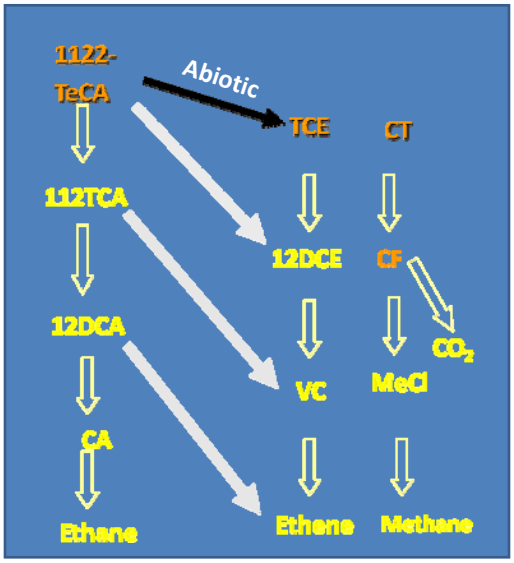
Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (irritant, permeator). Inflammation of the eye is characterized by redness, watering, and itching.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Classified + (PROVEN) by OSHA. Classified 2 (Reasonably anticipated.) by NTP.
MUTAGENIC EFFECTS: Not available.
TERATOGENIC EFFECTS: Not available.
DEVELOPMENTAL TOXICITY: Not available.
The substance is toxic to blood, kidneys, the nervous system, liver.
Repeated or prolonged exposure to the substance can produce target organs damage.

Natural Degradation Pathways

- The majority of degradation is biologically mediated
- Replace chlorine atoms with hydrogen atoms
- Anaerobic conditions
- Requires electron donors
  - Carbon substrate
  - Hydrogen gas

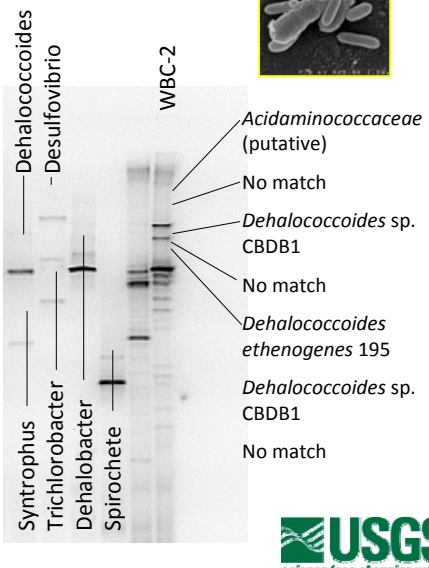


Time for some 'Culture'

- Characterization studies in the wetland area around West Branch Canal Creek found natural degradation occurring.
- Sediments from this area were collected
- Culture was enriched
- Complete degradation
- Sediment free media

WBC-2 Microbial Composition

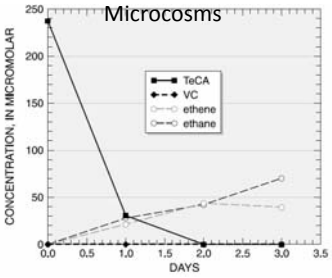
- "West Branch Consortia"
- Contains at least 17 and 21 distinct *Bacteria* phylotypes based on DGGE and clone library analysis, respectively
- *Acetobacterium* (40%), *Dehalobacter* (19%), and Acidaminococcacea (9%) most prominent; *Dehalococcodies* 5%



WBC-2 Culture in Action

- Only known culture capable of degrading such a broad mixture of chlorinated alkanes, alkenes, and methanes
- The culture was successfully used to bioaugment a reactive mat at APG
- Can we create a pump and treat system with WBC-2?

WBC-2 Culture + TeCA Microcosms



Reactive Mat

Project Goals and Objectives

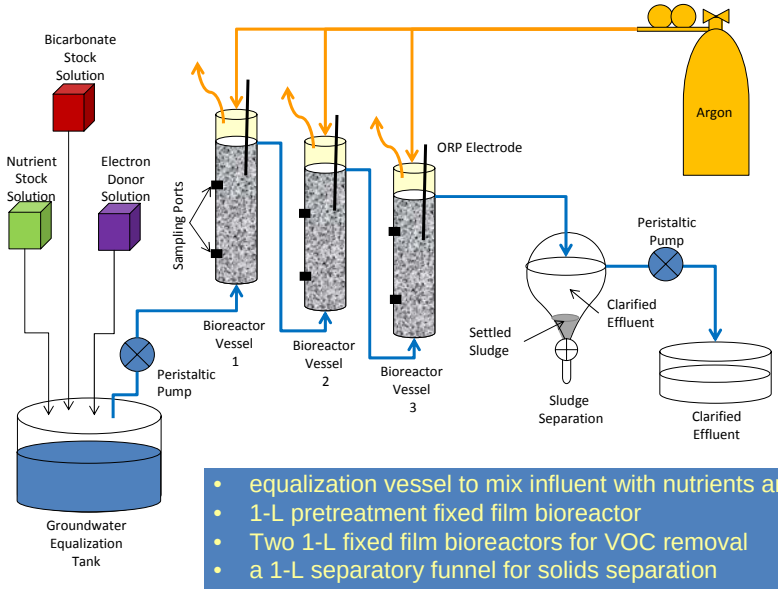
Goal:

Conduct pre-design testing necessary to evaluate the effectiveness of WBC-2 for treating chlorinated VOCs in a bioreactor application.

Objectives:

- Determine if a flow-through bioreactor system can support the WBC-2 Culture and remove VOCs below the discharge limit.
- Determine operational parameters, such as pH, ORP, Temp, and HRT to aid in the design for a larger scale system.
- Determine the optimum electron donor.

Bench Scale Bioreactor Design



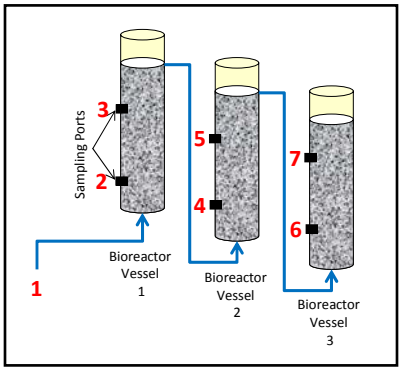
- equalization vessel to mix influent with nutrients and donor
- 1-L pretreatment fixed film bioreactor
- Two 1-L fixed film bioreactors for VOC removal
- a 1-L separatory funnel for solids separation

Operations

- Two bioreactor systems, D (Design) and (E)
- Reactors contained a polyurethane foam and polypropylene support matrix, which was seeded with WBC-2.
- Nutrients, electron donor, and TeCA were added to the treatment plant influent in equalization tank
- Pumped to first vessel and then gravity fed
- Monitored for chlorinated solvents, pH, nutrients, oxidation reduction potential and flow rates.

Monitoring

- Samples removed from sampling ports
  - Analyzed for VOCs
    - Immediately with GC-MS
  - ORP, pH, N, P, COD
- Continuous Monitoring
  - ORP, pH, flow, temperature



Results

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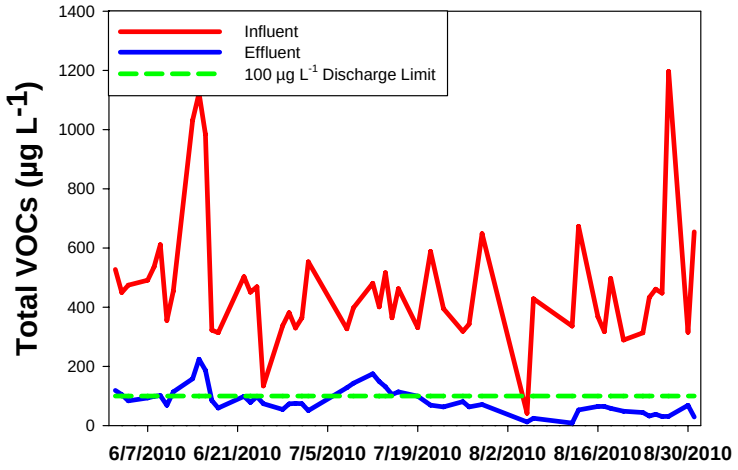
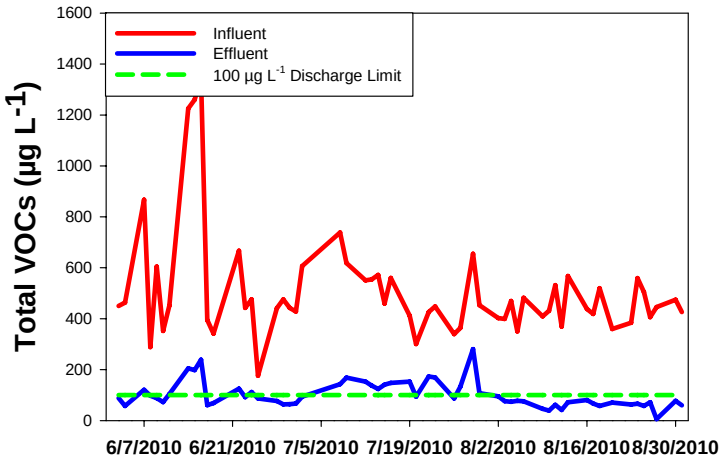
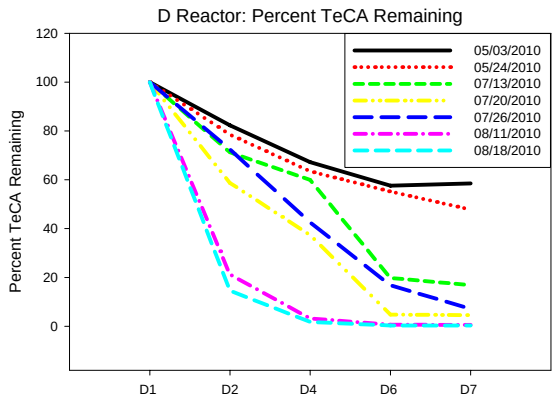
Total VOCs in D Reactor

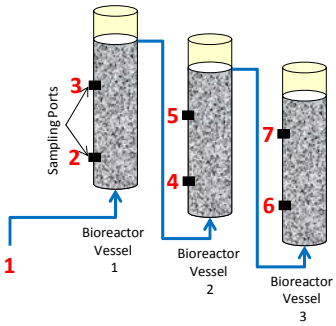


Total VOCs in E Reactor

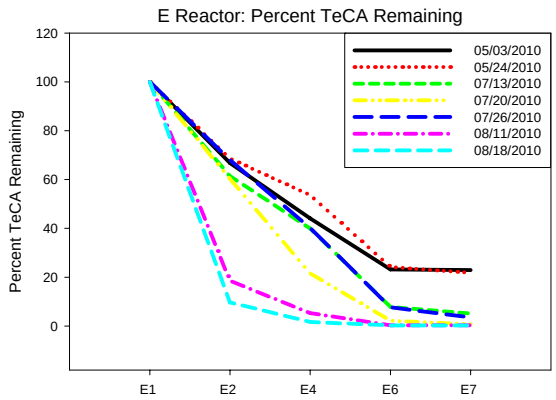


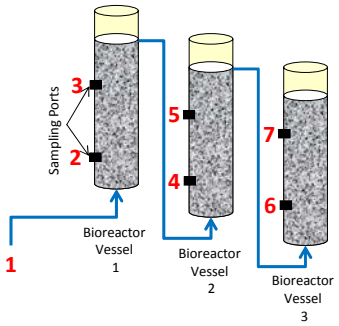
TeCA Removal in D Reactor



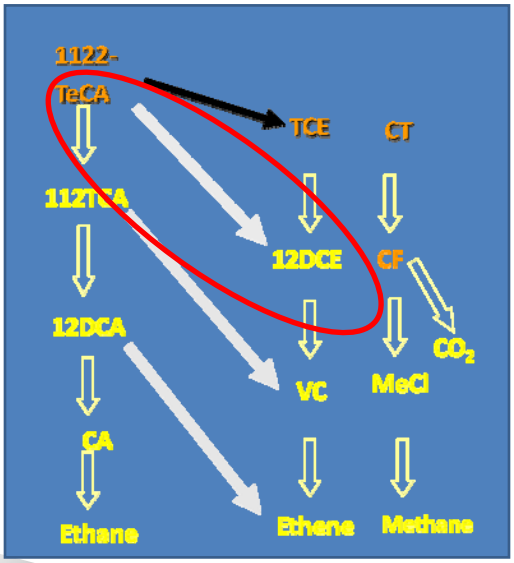


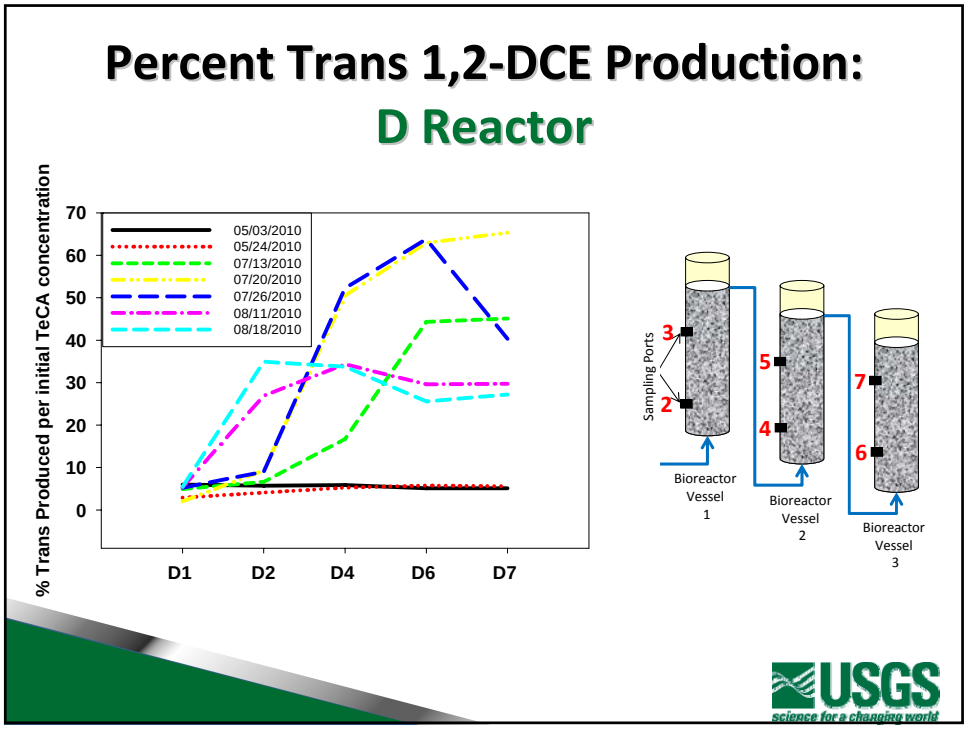
TeCA Removal in E Reactor

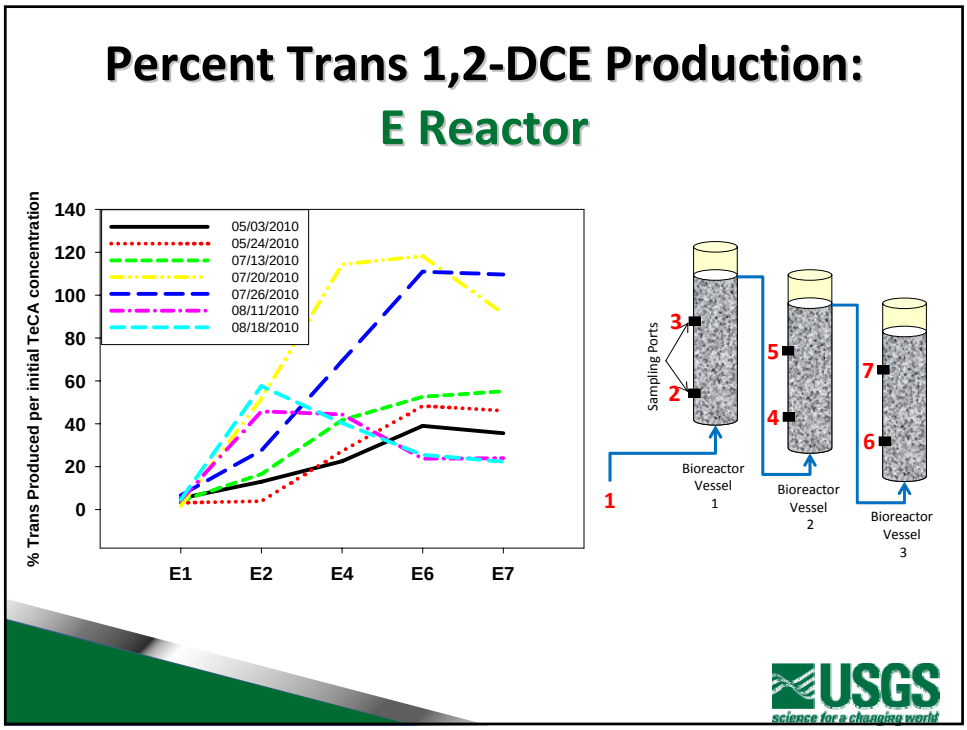




Formation of Daughter Products




Percent Trans 1,2-DCE Production:
D Reactor
% Trans Produced per initial TeCA concentration
70
60
50
40
30
20
10
0
05/03/2010
05/24/2010
07/13/2010
07/20/2010
07/26/2010
08/11/2010
08/18/2010
D1
D2
D4
D6
D7
Sampling Ports
3
2
5
4
7
6
Bioreactor Vessel 1
Bioreactor Vessel 2
Bioreactor Vessel 3
USGS
science for a changing world


Percent Trans 1,2-DCE Production:
E Reactor
% Trans Produced per initial TeCA concentration
140
120
100
80
60
40
20
0
05/03/2010
05/24/2010
07/13/2010
07/20/2010
07/26/2010
08/11/2010
08/18/2010
E1
E2
E4
E6
E7
Sampling Ports
3
2
5
4
7
6
1
Bioreactor Vessel 1
Bioreactor Vessel 2
Bioreactor Vessel 3
USGS
science for a changing world

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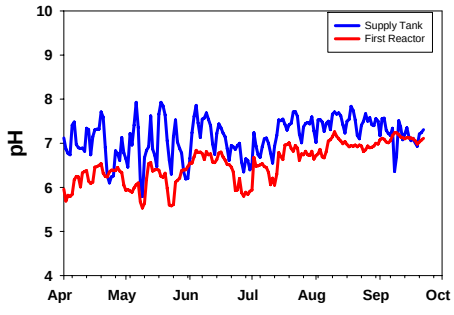
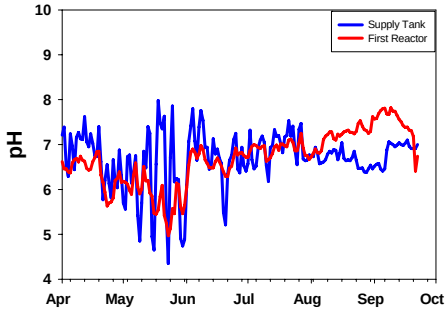
Operational Parameters: pH

D Reactor pH

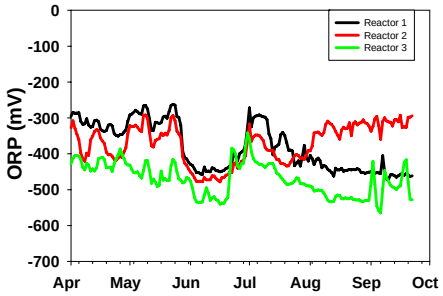


E Reactor pH

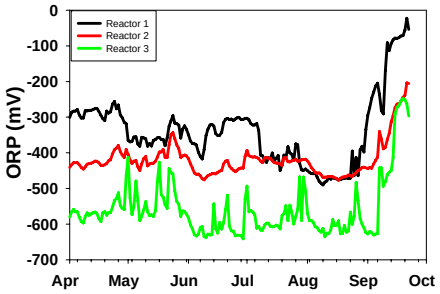


Operational Parameters: ORP

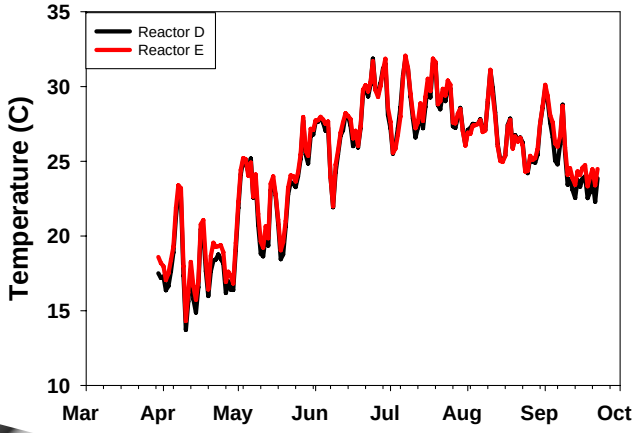
D Reactor ORP



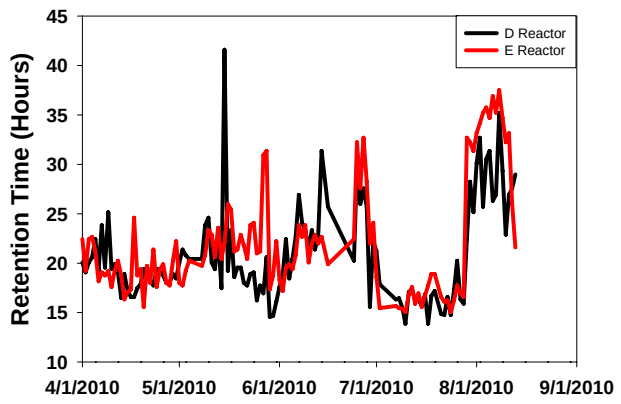
E Reactor ORP



Operational Parameters: Temperature



Operational Parameters: HRT



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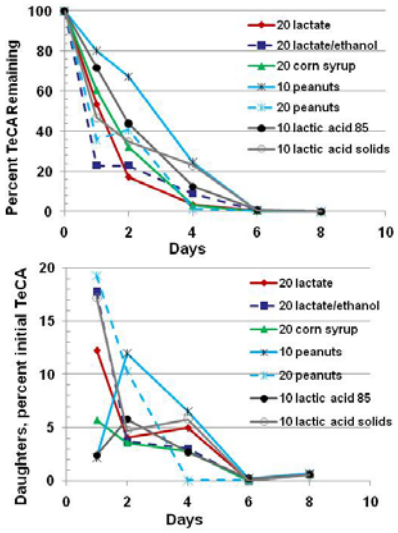
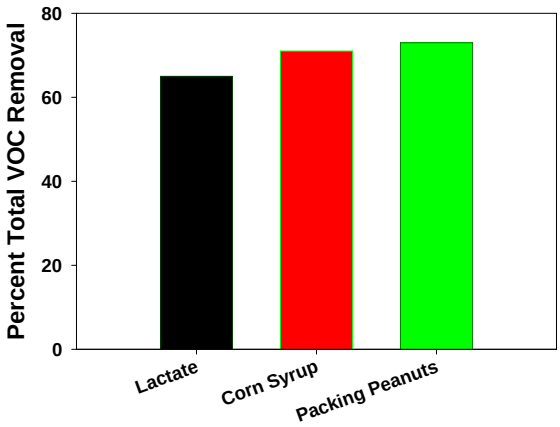
- **Determine the optimum electron donor.**

Donor Microcosms

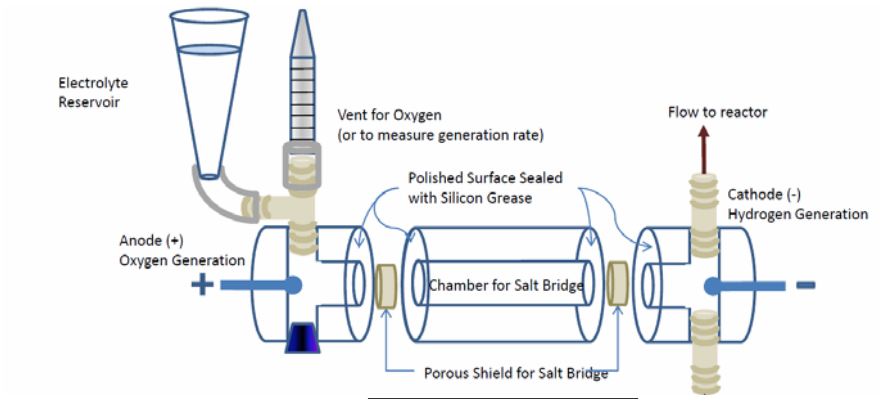
- Tested different donors in microcosms first
  - Lactate
  - Lactate/ethanol
  - Corn Syrup
  - Corn Starch Packing Peanuts
  - Lactic Acid
  - Lactic Acid Solids



Donors in Bioreactor

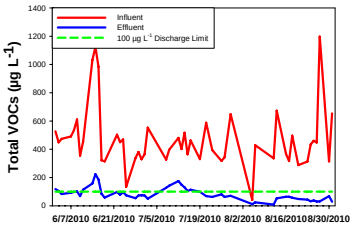


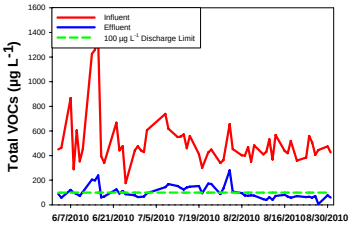
Next Donor: Hydrogen Generator



Conclusions

- WBC-2 culture was successfully established in a bioreactor system
- Effluent discharge limits are being met
- Despite varying operational parameters, effluent discharge concentrations were relatively stable



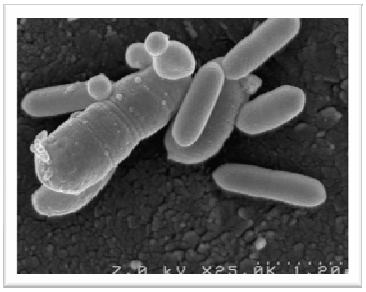


Conclusions

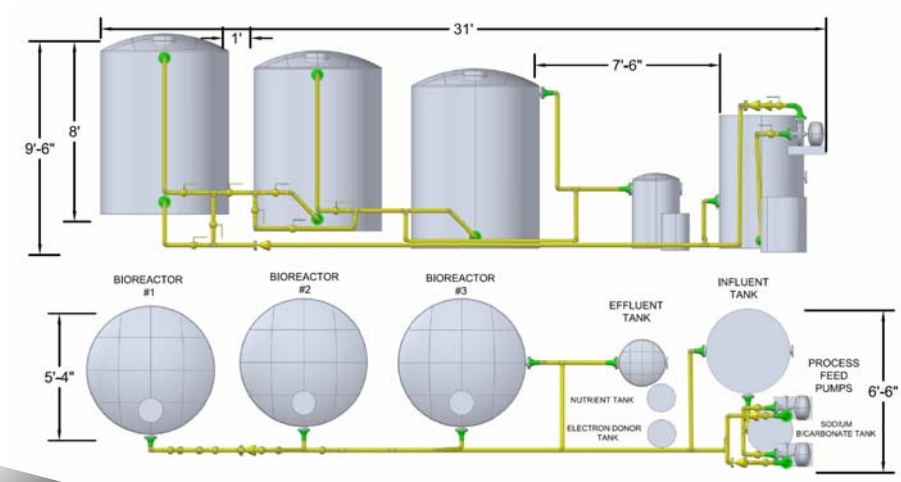
- The bioreactors operated efficiently with a 15-20 hour retention time
- pH was best controlled with Sodium Bicarbonate
- Corn syrup appears to be a good choice for donors
- Hydrogen generators may also be potential donors

Conclusions

- The WBC-2 culture can adapt to different environments and degrade many different types of chlorinated organic compounds



Future Work: Pilot Plant



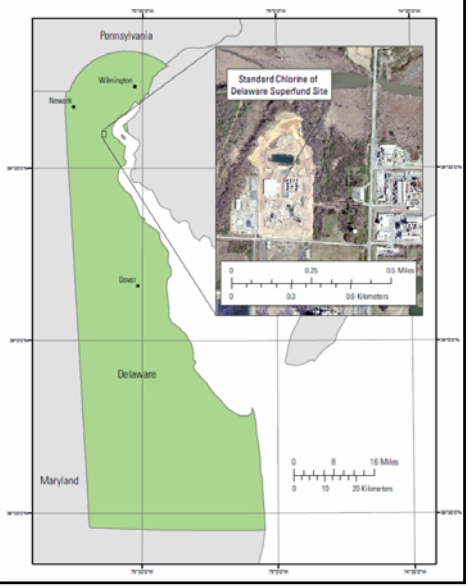
Future Work: Pilot Plant

3 mL/min to 3 gal/min

1 bottle per 3 months to 5 gal/1.5 weeks

Future Work: Standard Chlorine of Delaware

- Superfund Site
- Starting wetlands work
- WBC-2 and Chlorobenzenes



Acknowledgments

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- General Physics
  - Dennis Donovan
- ARMY
  - John Wrobel
  - Jeff Aichroth

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