Coupled Technologies and Bioenhanced Dissolution for Improved DNAPL Source Zone Bioremediation

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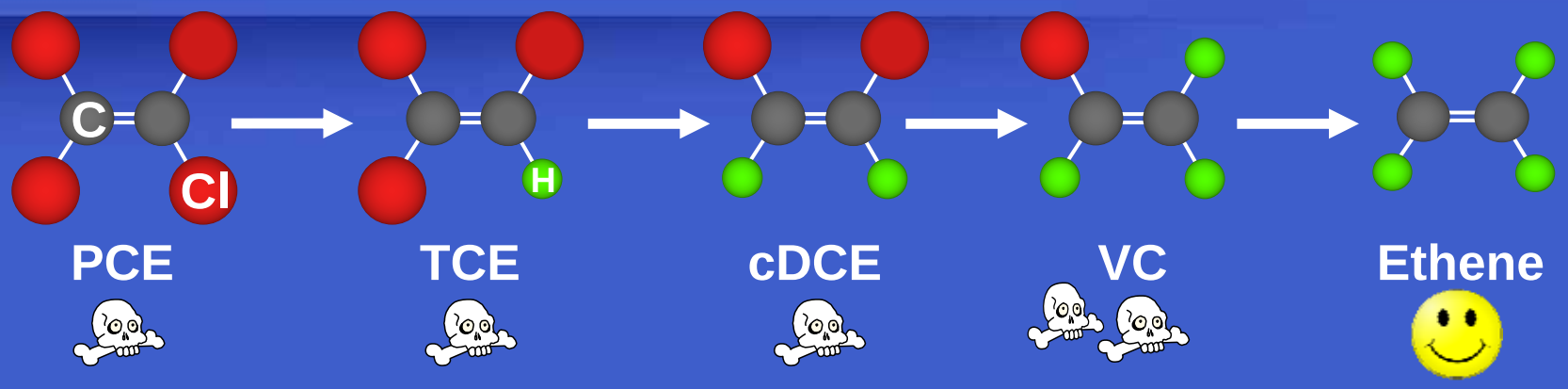
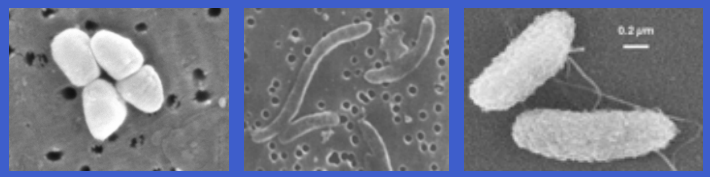
Microbial Reductive Dechlorination



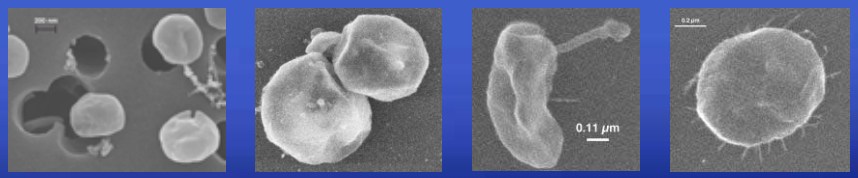
Incomplete Dechlorination

***Sulfurospirillum, Geobacter, Dehalobacter, Desulfuromonas, Desulfitobacterium*, etc.**



Conversion to Ethene

***Dehalococcoides* spp.**



He et al., 2003. Nature. 424:62-65
Sung et al., 2006. AEM. 72:1980-1987

Bioremediation: Plume Containment

- Currently a plume containment technology
- Successfully implemented in the field
- Gaining acceptance in the remediation community
- Commercially marketed

Biostimulation

REGENESIS

HRC® HYDROGEN RELEASE COMPOUND

Bioaugmentation

Shaw SDC-9™

Bio-Dechlor INOCULUM™ (Dechlorinating Microbes)

KB-1™ DECHLORINATOR

GeoSyntec Consultants

Assessment

Gene Trac Dehalococcoides Testing

SiREM Site Recovery & Management

mi microbialinsights

Bio-Dechlor CENSUS

Bioremediation: Source Zones

Conventional Wisdom

- **DNAPL and high PCE concentrations are toxic to microbes**
- **Complete dechlorination to ethene does not occur**
- **Dechlorination rates are insufficient to be relevant**

Recent Advances

- **Dechlorinating cultures reported to dechlorinate at saturated PCE concentrations**
  - Contradictory reports regarding inhibitory concentrations
- **Bioenhanced DNAPL dissolution has been experimentally observed**
  - 1.3-14 times enhancement over abiotic dissolution alone
  - Potential to reduce cleanup times and costs

Technical Motivation

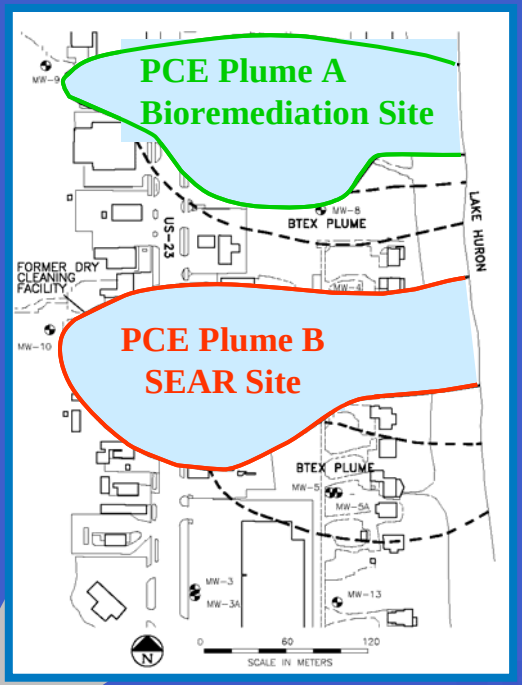
- Despite documented successes of source zone mass reduction, none of the currently employed stand-alone technologies are expected to remove all DNAPL contamination

- Residual contamination may lead to continued and persistent contaminant elution that poses risks to human health and the environment

- Synergistic effects of coupling physical-chemical remedies with biological activity are insufficiently understood

Coupled Technologies

- Field evidence suggests enhanced effectiveness of coupled technologies
- Potential to overcome challenges associated with each technology when used in isolation



Bachman Road Site

- PCE-DNAPL
- Surfactant Enhanced Aquifer Remediation (SEAR)
- Fortuitous stimulation of reductive dechlorination in the presence of Tween 80
- Surfactant degradation promoted anaerobiosis and supplied electron donors (cis-DCE formation)

(Abriola et al. 2005; Ramsburg et al. 2005 in ES&T)

Bio-Box Set-up

Fully screen end chambers and inlet injection well

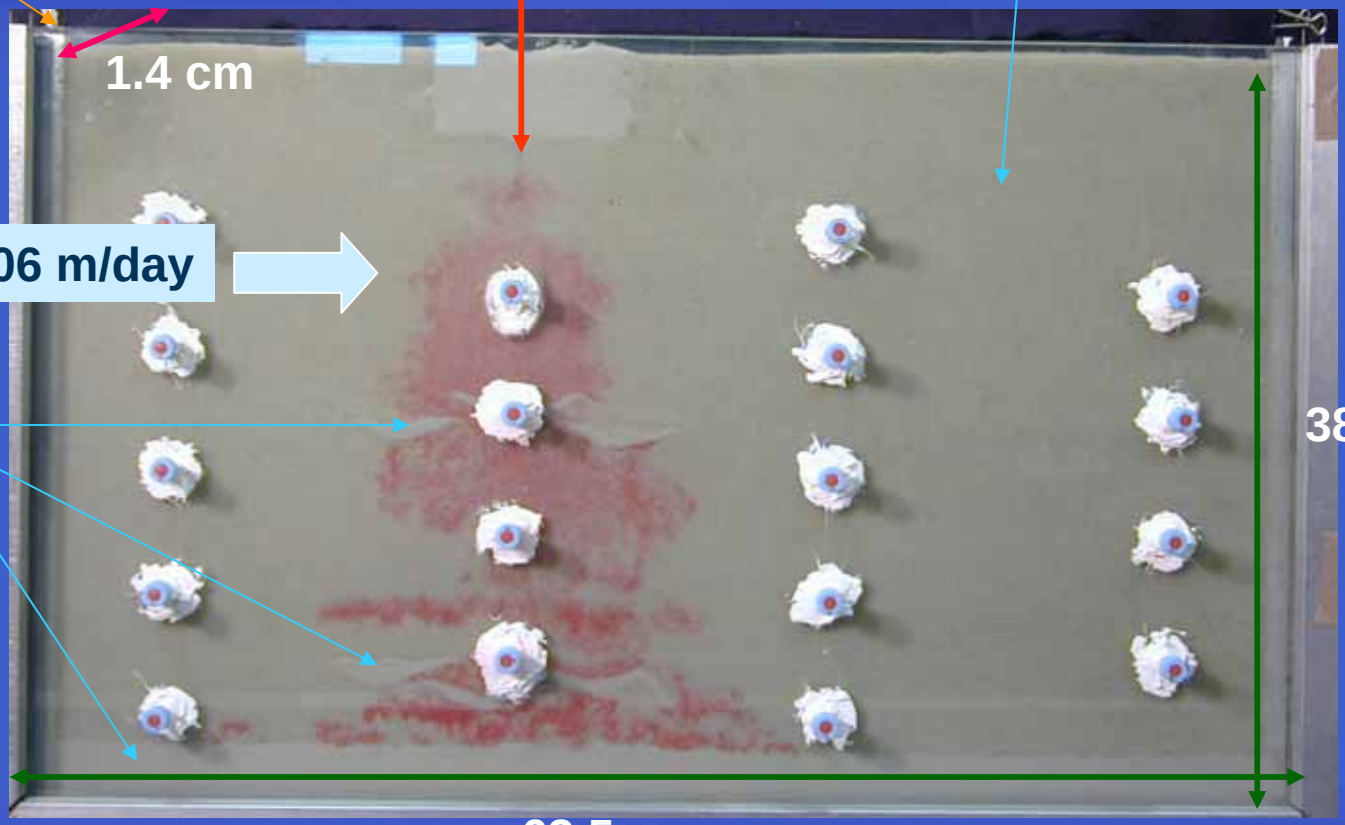
Source Addition

Accusand: 50% 40/50 and 50% 20/30

1.4 cm

Flow = 0.06 m/day

F70 Ottawa sand lens



38 cm

63.5 cm

Source Zone: 40 mL of anoxic PCE dyed with Oil-Red-O added at 0.5 mL/min, and allowed to redistribute for 24 hr.

Surfactant Floods

- A total of 2.3 pore volume (1 PV= 1450 mL) of surfactant (4% by weight Tween 80 dyed with Ergioglaucine A) solution injected at 4 mL/min (v= 2.4 m/day)
- Followed by degassed water injected at 1.5 mL/min (v=0.9 m/day)
- Pictures taken every 30 minutes over 14 hours

Surfactant Flood & Light Transmission Summary

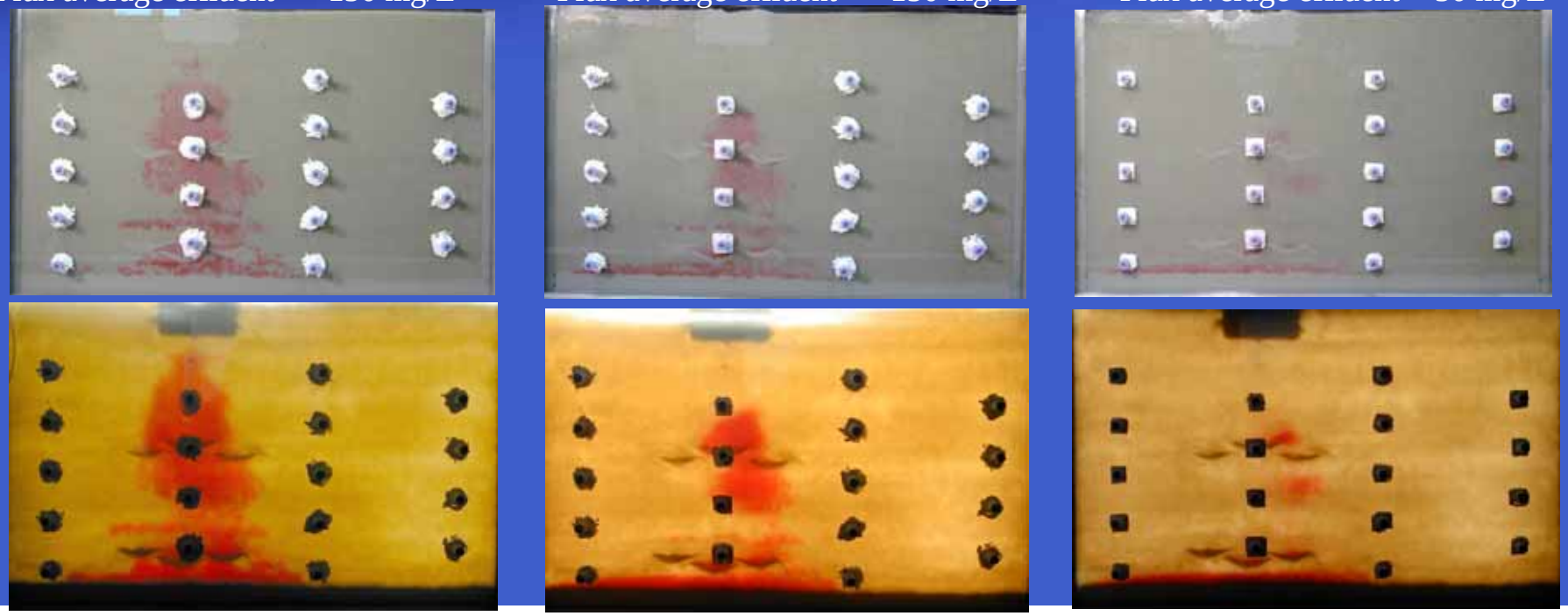
Pre-Surfactant Flood I
GTP=1.6
Flux average effluent = >150 mg/L

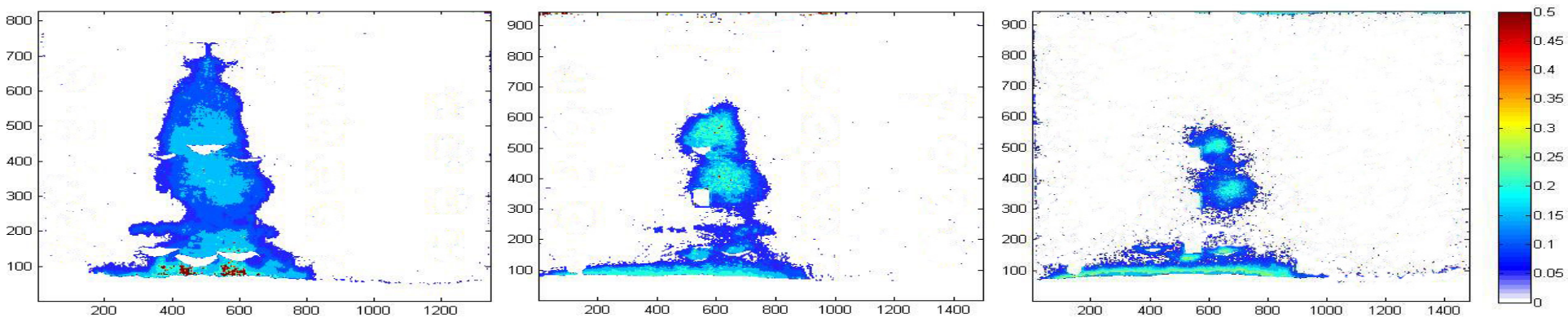
1.3 PV Tween 80 → 21 PV H_2O →

Pre-Surfactant Flood II
GTP=1.37; 28% mass removal
Flux average effluent = >150 mg/L

1.0 PV Tween 80 → 30 PV H_2O →

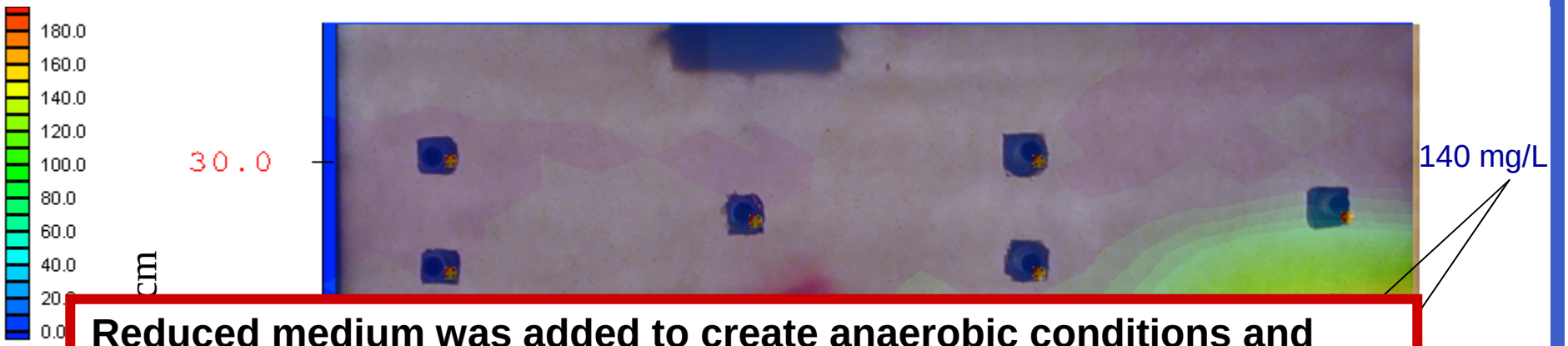
Post-Surfactant Flood II
GTP=1.06; 55% mass removal
Flux average effluent = 50 mg/L





Localized PCE Concentrations (0-200 mg/L) Prior to Reduced Medium Introduction

March 20, 2007; conditions prior to medium intro

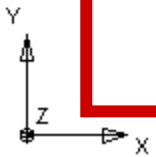


Reduced medium was added to create anaerobic conditions and provide electron donor (10mM lactate)

Nine side ports upstream of the source zone were manually bioaugmented via syringe with 20 mL per side port with an augmented Bio-Dechlor INOCULUM (BDI-SZ), a PCE-to-ethene dechlorinating consortium containing:

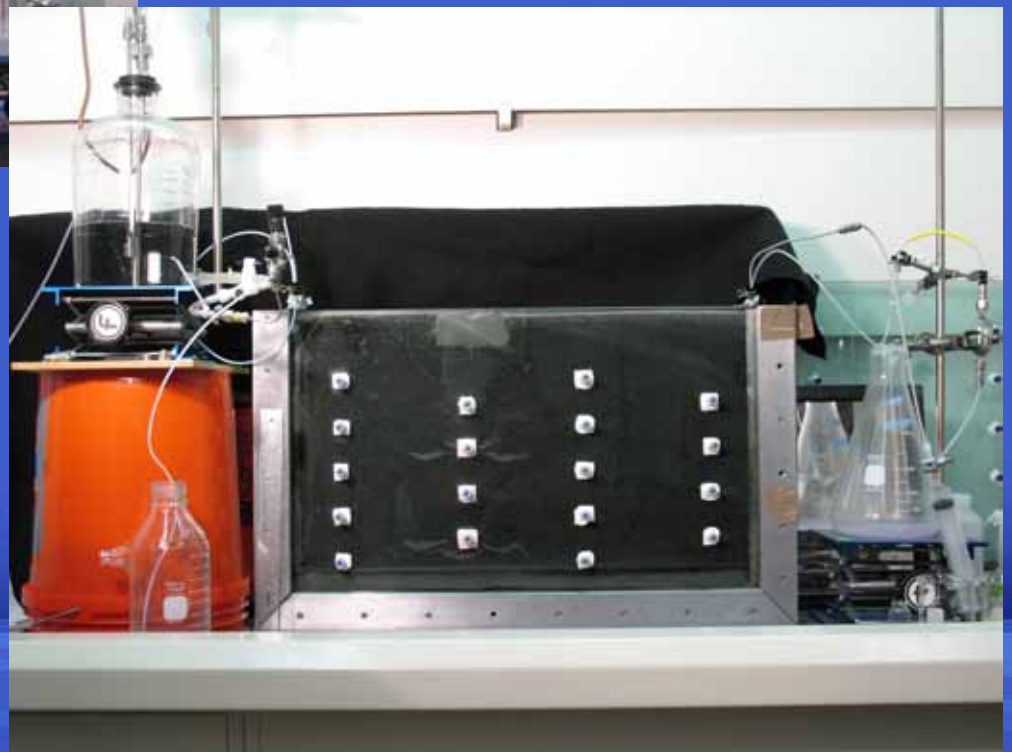
- ***Geobacter lovleyi* strain SZ**
- ***Dehalobacter* spp.**
- ***Dehalococcoides* spp.**

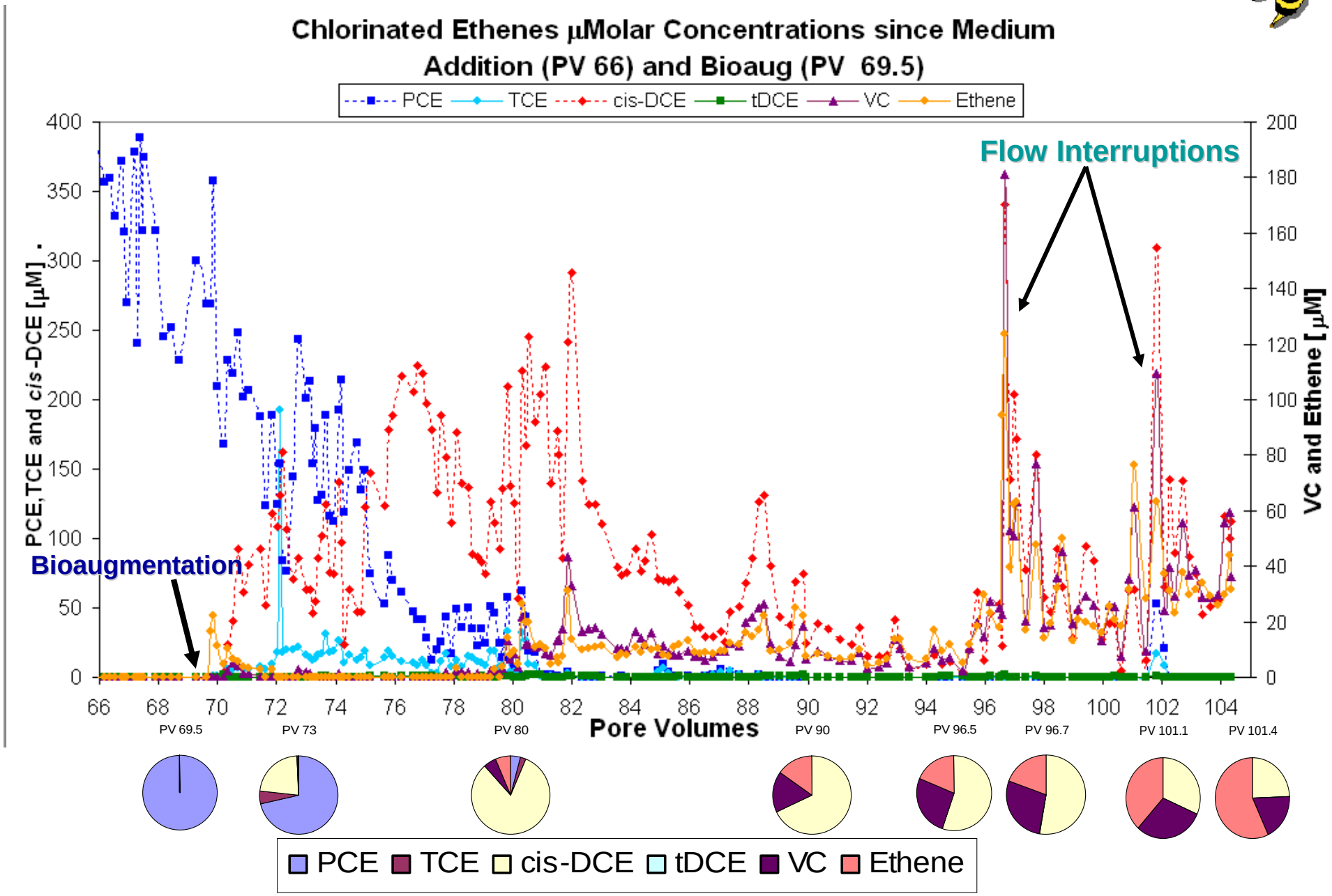
Bio-Dechlor INOCULUM™ (Dechlorinating Microbes)



Prior to Bioaugmentation

< 4 PVs following bioaugmentation




Chlorinated Ethenes µMolar Concentrations since Medium Addition (PV 66) and Bioaug (PV 69.5)
PCE
TCE
cis-DCE
tDCE
VC
Ethene
Flow Interruptions
Bioaugmentation
PCE,TCE and cis-DCE [µM]
VC and Ethene [µM]
Pore Volumes
PV 69.5
PV 73
PV 80
PV 90
PV 96.5
PV 96.7
PV 101.1
PV 101.4
PCE
TCE
cis-DCE
tDCE
VC
Ethene

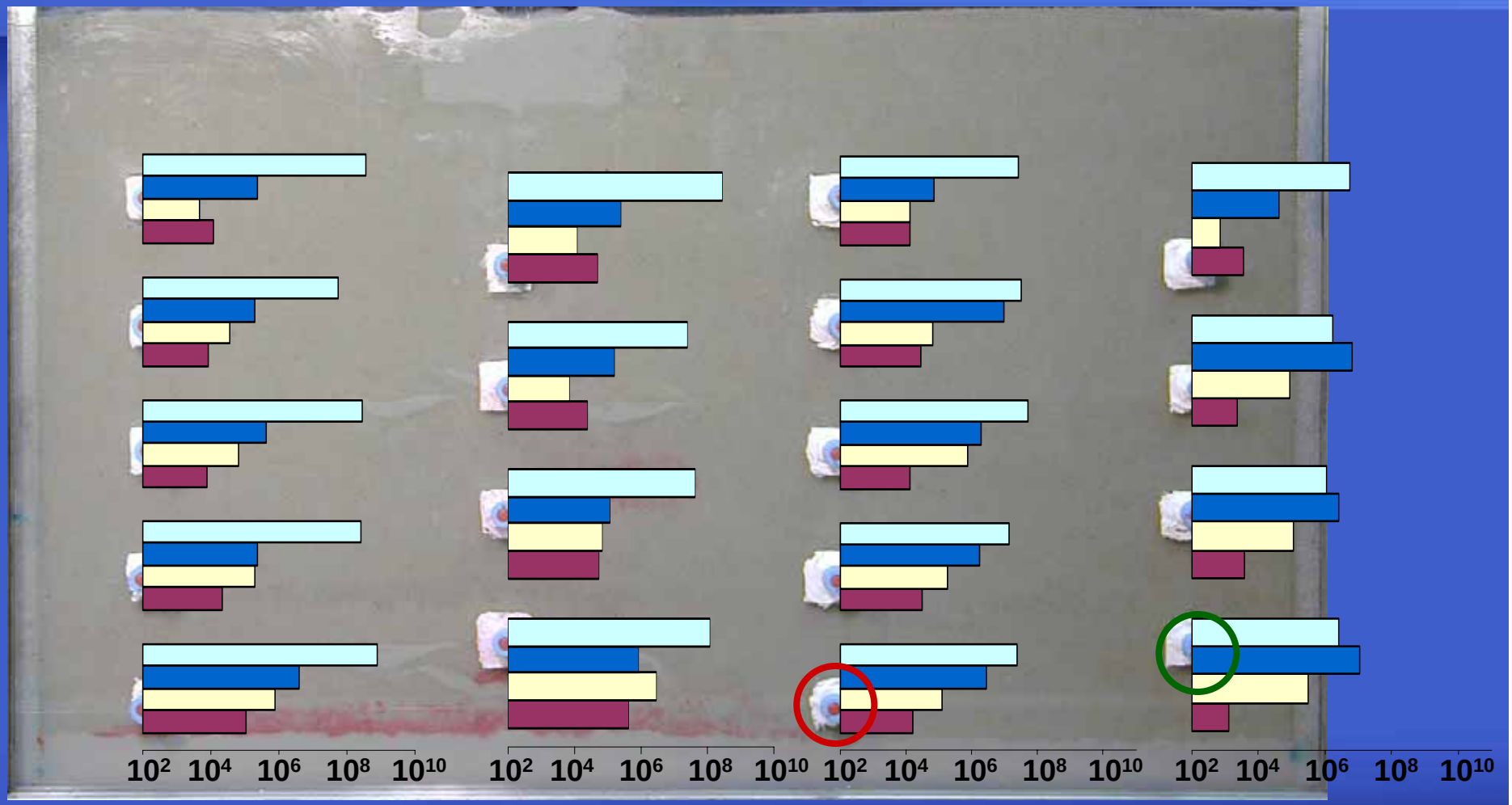
Localized Chlorinated Ethenes

- Just down gradient from the original PCE-DNAPL source zone and near the bottom ("hot spot"):
  - Prior to flow interruption, 90 mg/L PCE (540 µM) and 110 mg/L cDCE (1135 µM)
  - Immediately following the flow interruption, 38 mg/L PCE (230 µM) and 147 mg/L cDCE (1500 µM)
  - 3PVs following the flow interruption, 5 mg/L PCE (31 µM) and 95 mg/L cDCE (985 µM)

- Locations on the perimeter of the "hot spots":
  - VC before 8.5 mg/L (135 µM) and after 8.3 mg/L (130 µM)
  - Ethene before 2.5 mg/L (100 µM) and after 5.3 mg/L (185 µM)

Spatial Distribution of Total Dehalococcoides

(Measured with qPCR; log scale = 10^2-10^{10} gene copies per mL)



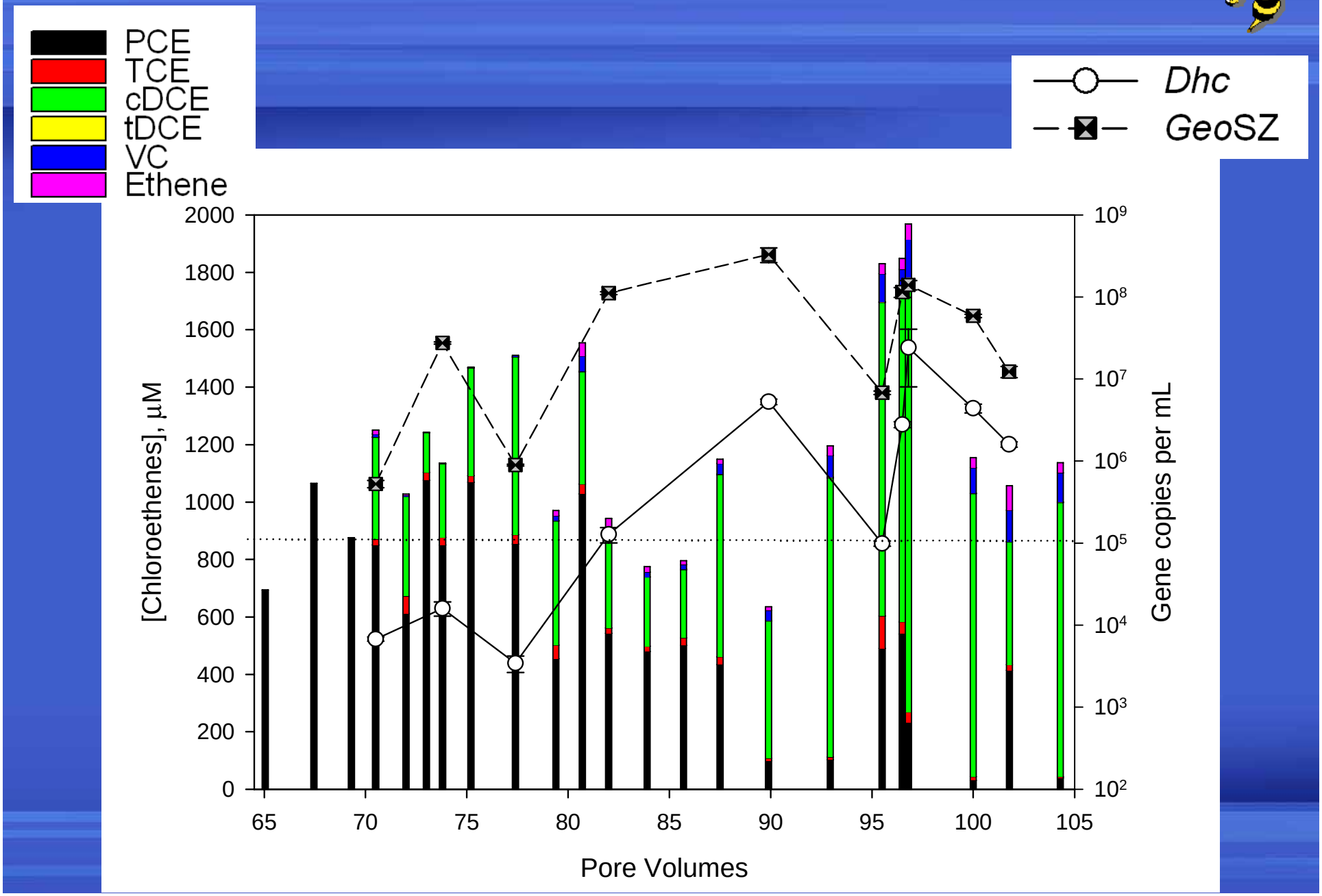
PV 73.8 (4.5 PV post inoculation)

PV 82.0 (13.5 PV post inoculation)

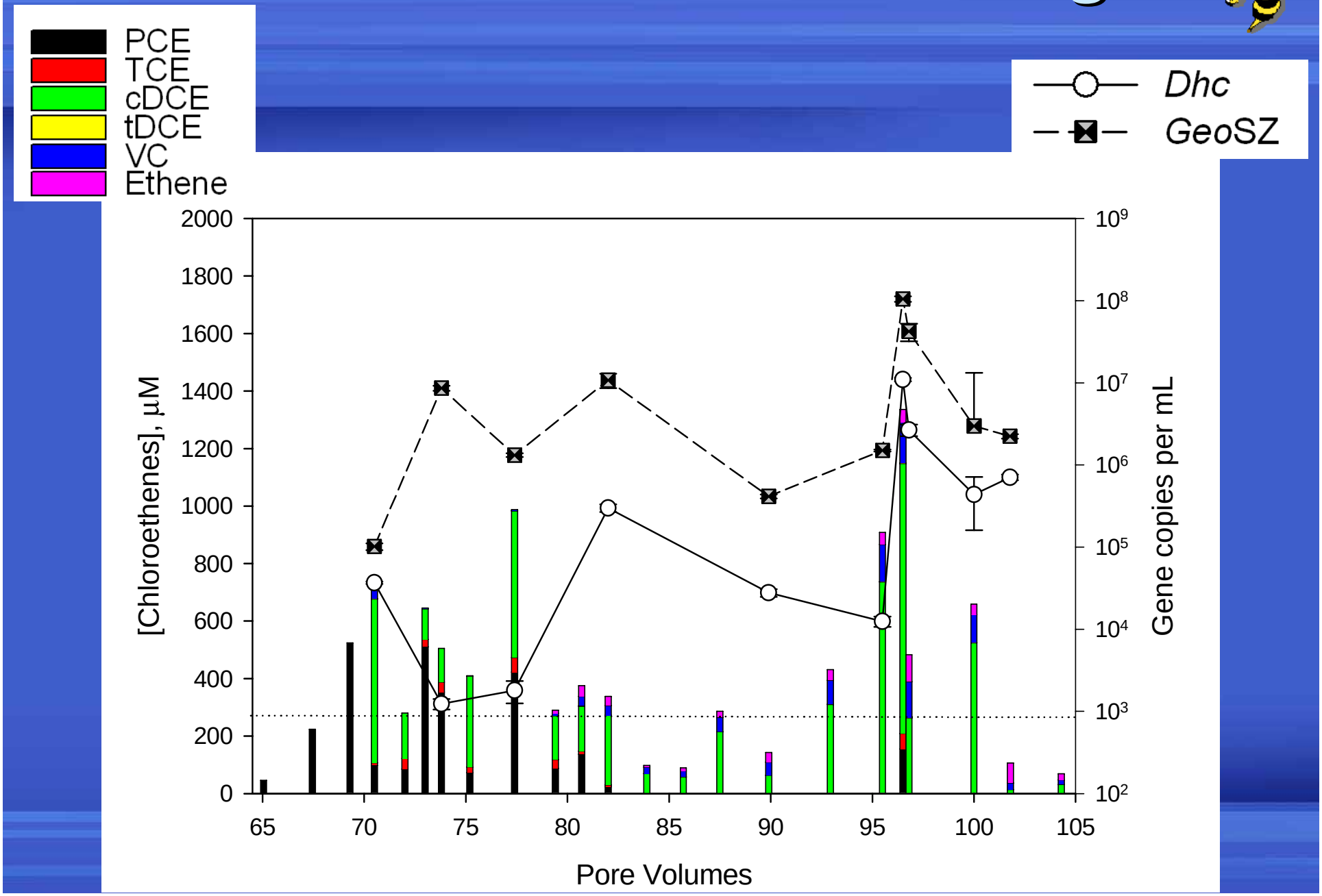
PV 96.5 (27 PV post inoculation)

PV 96.7 (27.3 PV post inoculation and post flow interruption)

Dechlorinators in the Source Zone



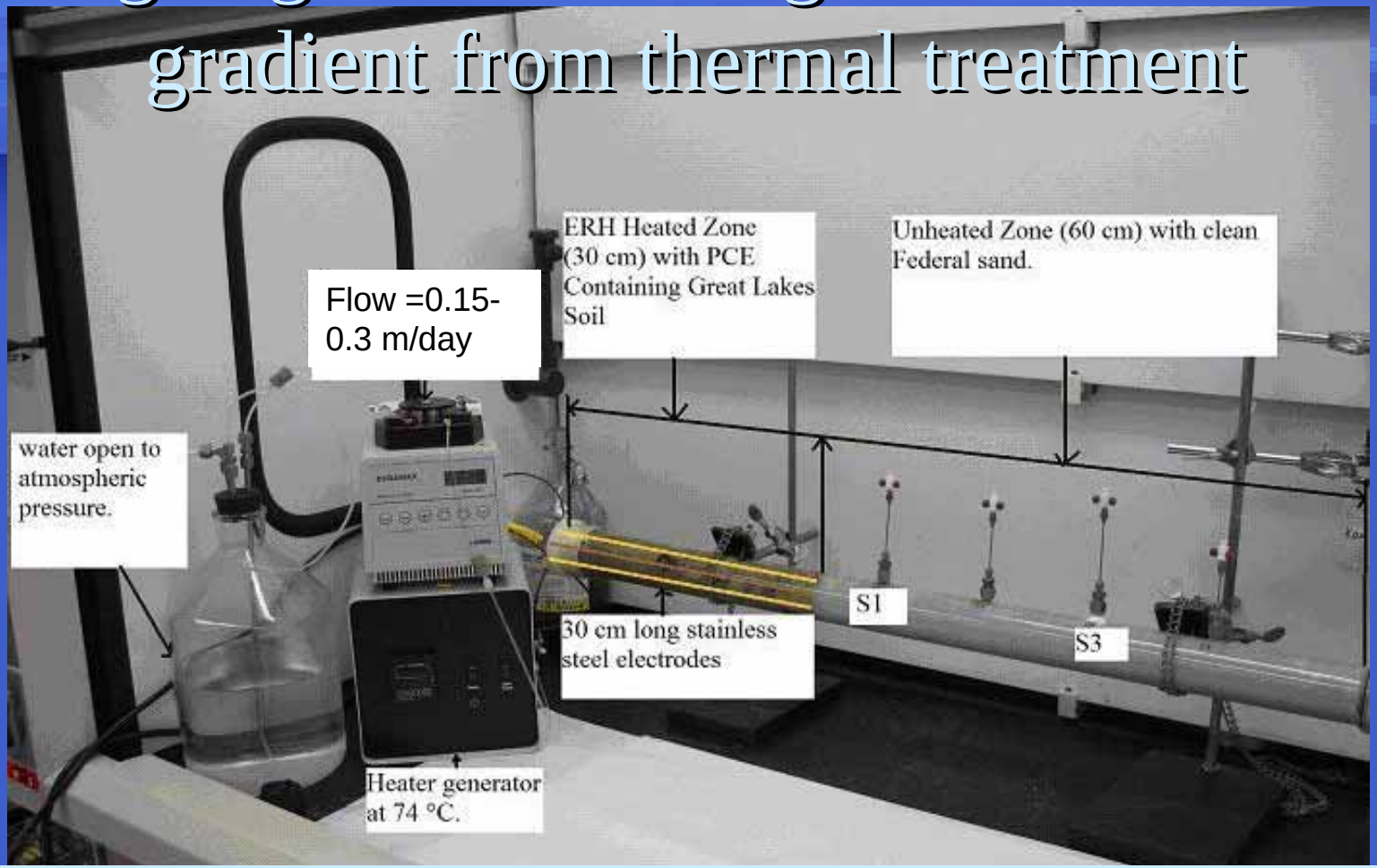
Dechlorinators in the Plume Region



Bio-Box Conclusions

- Bioaugmentation following surfactant (Tween 80) flushing appears to be a feasible treatment train
- Conversion of PCE to *cis*-DCE was achieved with minimal lag time
- *Dehalococcoides* concentrations are linked to proximity to source zone with growth of more than an order of magnitude
- *Geobacter lovleyi* SZ concentrations were consistently higher than *Dehalococcoides*, especially in the presence of remaining PCE-DNAPL, consistent with dominant *cis*-DCE byproduct
- Flow interruptions increased dechlorinator concentrations, and thus, source zone dissolution
- Bioenhanced dissolution near source zone (2 to 3-fold)
- Ethene was formed in the presence of PCE-DNAPL and *cis*-DCE above 6µM
- Accumulation of *cis*-DCE may have limited complete detoxification of PCE to ethene
  - System residence times was insufficiently long for sequential conversion of *cis*-DCE to VC before VC conversion to ethene.

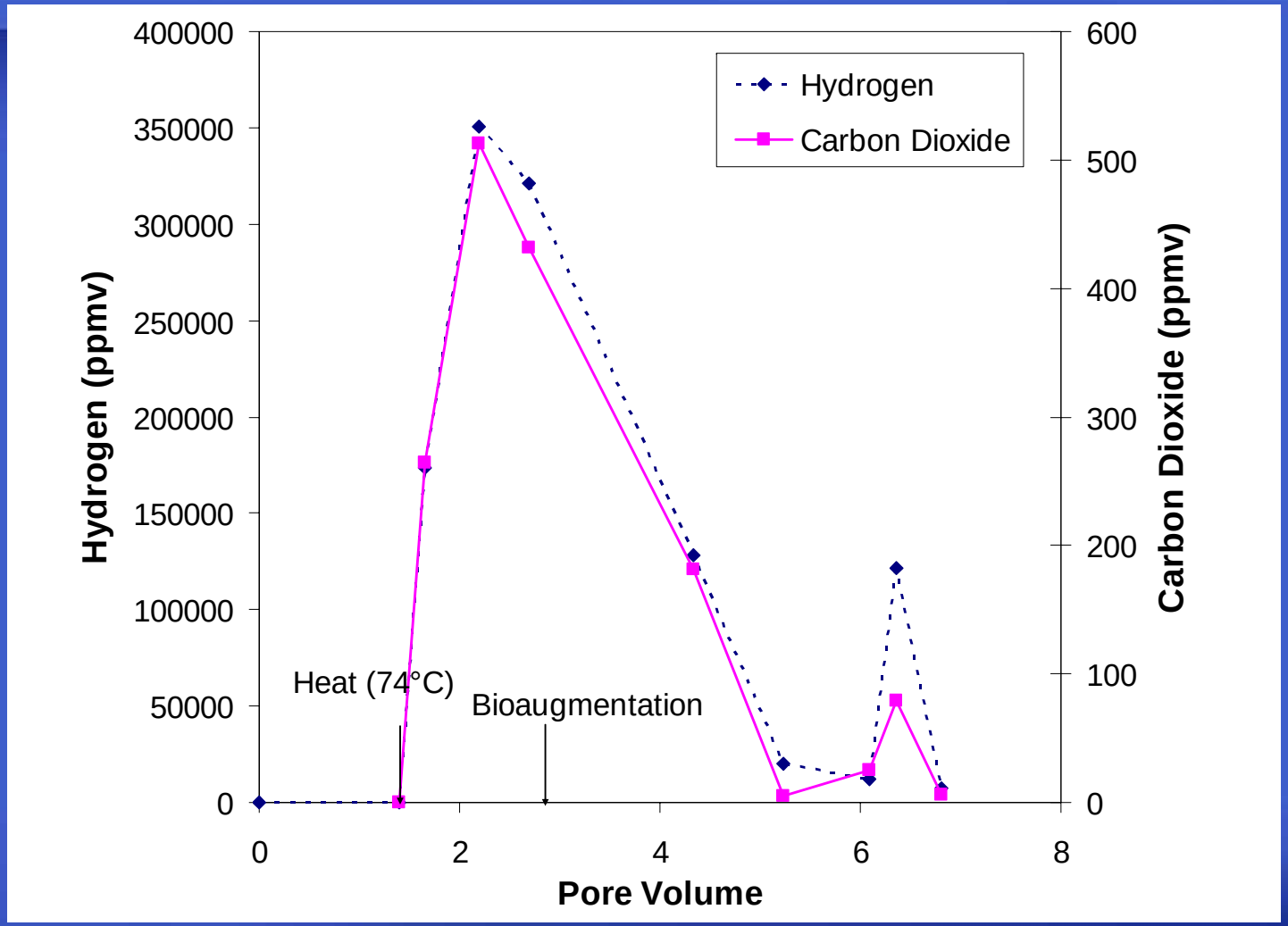
Ongoing work : Bioaugmentation down gradient from thermal treatment



Evaluate two PCE to ethene dechlorinating inoculums, both containing *Dehalococcoides* spp. and *Dehalobacter* spp.:

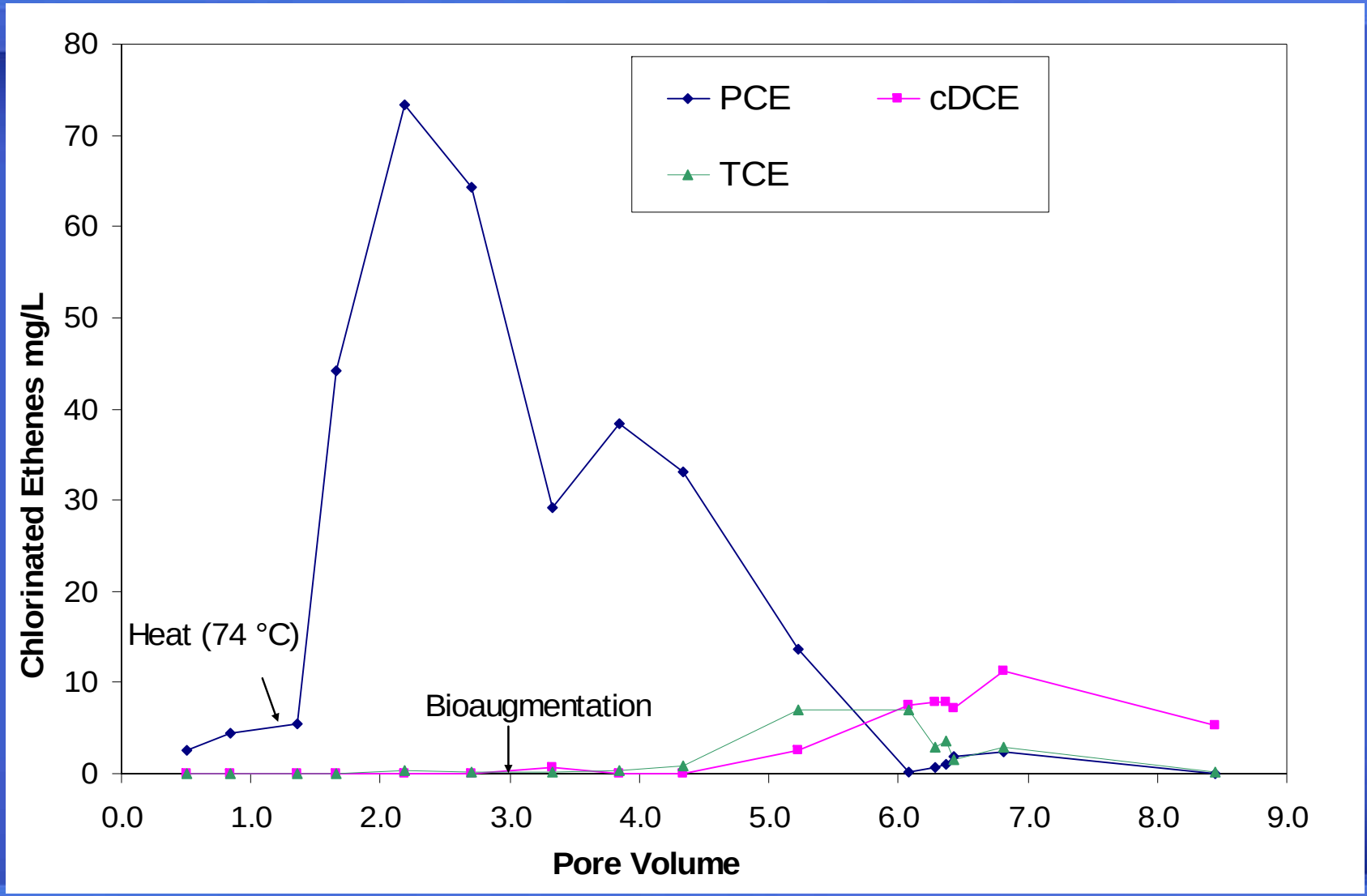
1. A methanogenic consortium obtained from Rice University (work completed by Jed Costanza)
2. A non-methanogenic consortium, Bio-Dechlor Inoculum (BDI) with *the Geobactor lovleyi* strain SZ obtained from the Löffler lab at GT

H_2 and CO_2 Concentrations



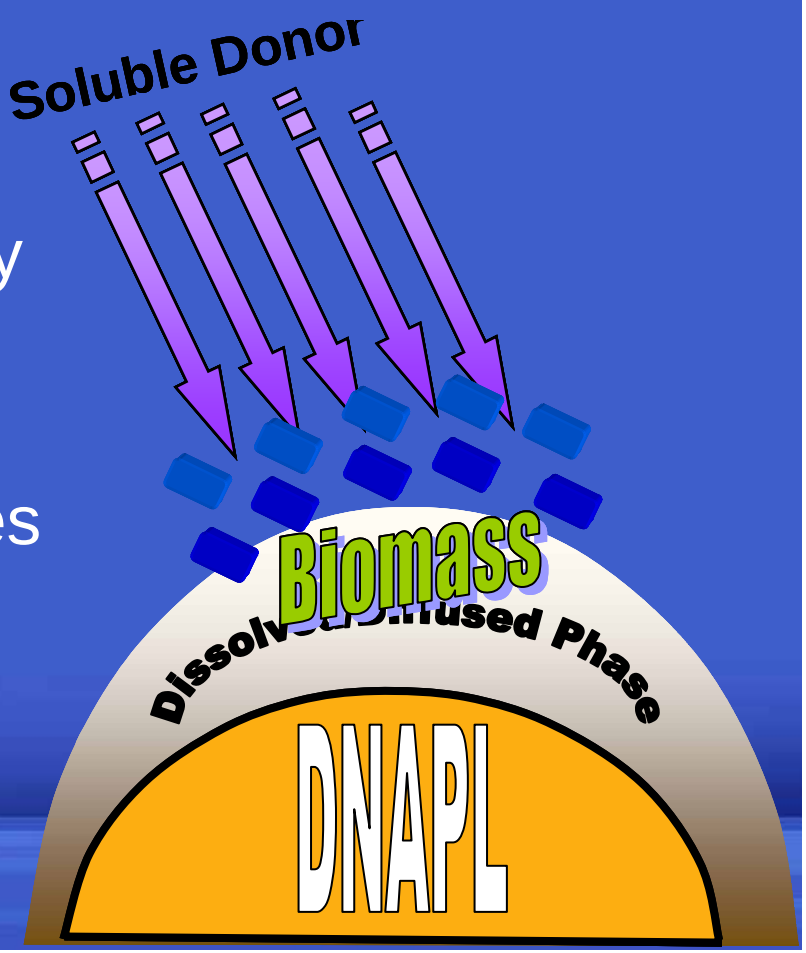
Hydrogen and carbon dioxide produced from heating the Great Lakes soil at 74 °C.

Effluent VOC concentrations



Growth at the DNAPL:Water Interface

- Studies have shown that soluble electron donor injection achieves dissolution rate increases of 2- to 3-fold
  - Limited by the difficulty of maintaining a constant supply at the DNAPL:water interface
  - Donor is consumed in competing microbial processes
    - 5 to 10 time ED equivalent safety factor is often applied in the field



Technical Motivation

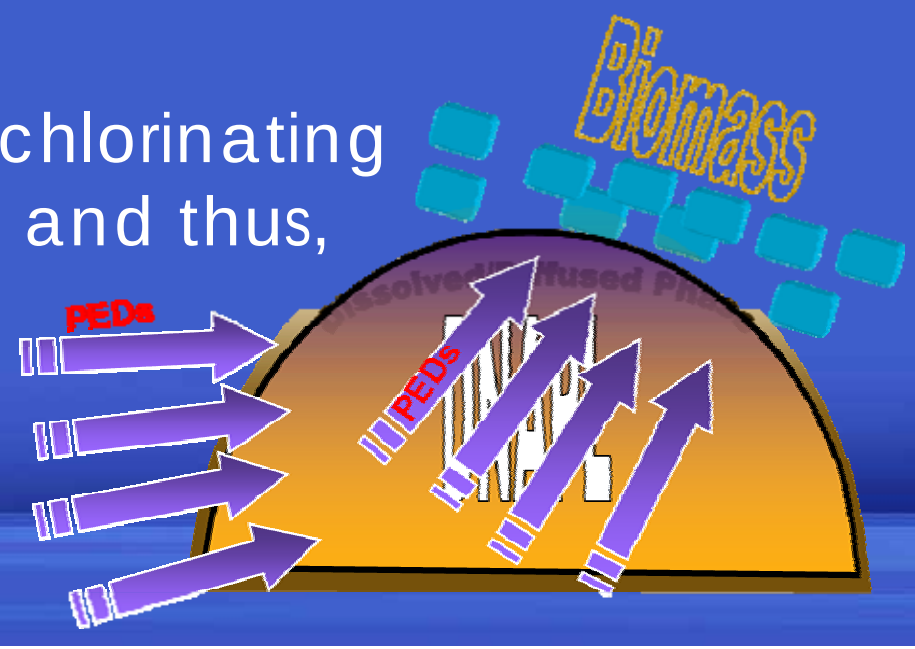
NO CONTACT = NO ENHANCED DISSOLUTION

- Bacteria responsible for enhanced dissolution typically grow at the intersection of the DNAPL:water interface and the electron donor
- Adding extra ED will move the bacteria closer to the DNAPL, but this requires higher amounts of ED ($$$)
- Shift towards mixing donor substrate with DNAPL
  - growth of dechlorinators is favored, and conditions suitable for methanogens are minimized [*Yang and McCarty*, 2002]

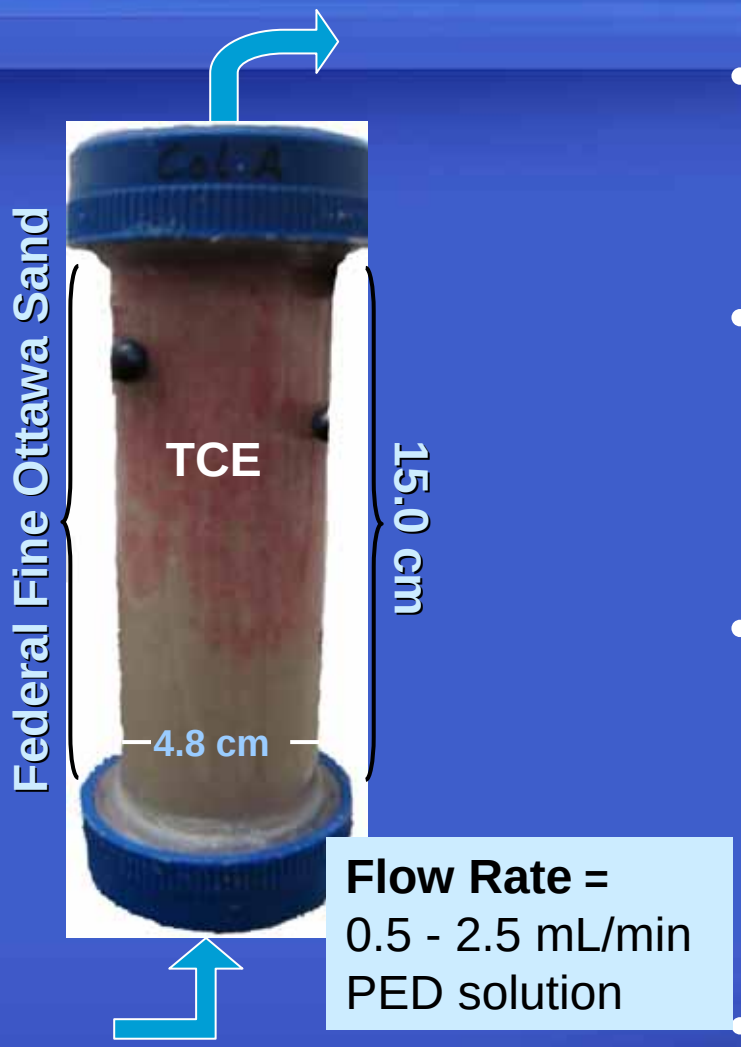
Technology Description

- Partitioning electron donors (PEDs) are water soluble, relatively inexpensive substrates that:
  - dissolve into DNAPLs,
  - slowly released, and
  - readily fermented at the organic: aqueous interface to yield electron donors, including acetate and hydrogen

- Promote the growth of dechlorinating biomass close to the DNAPL and thus, enhance dissolution rates.

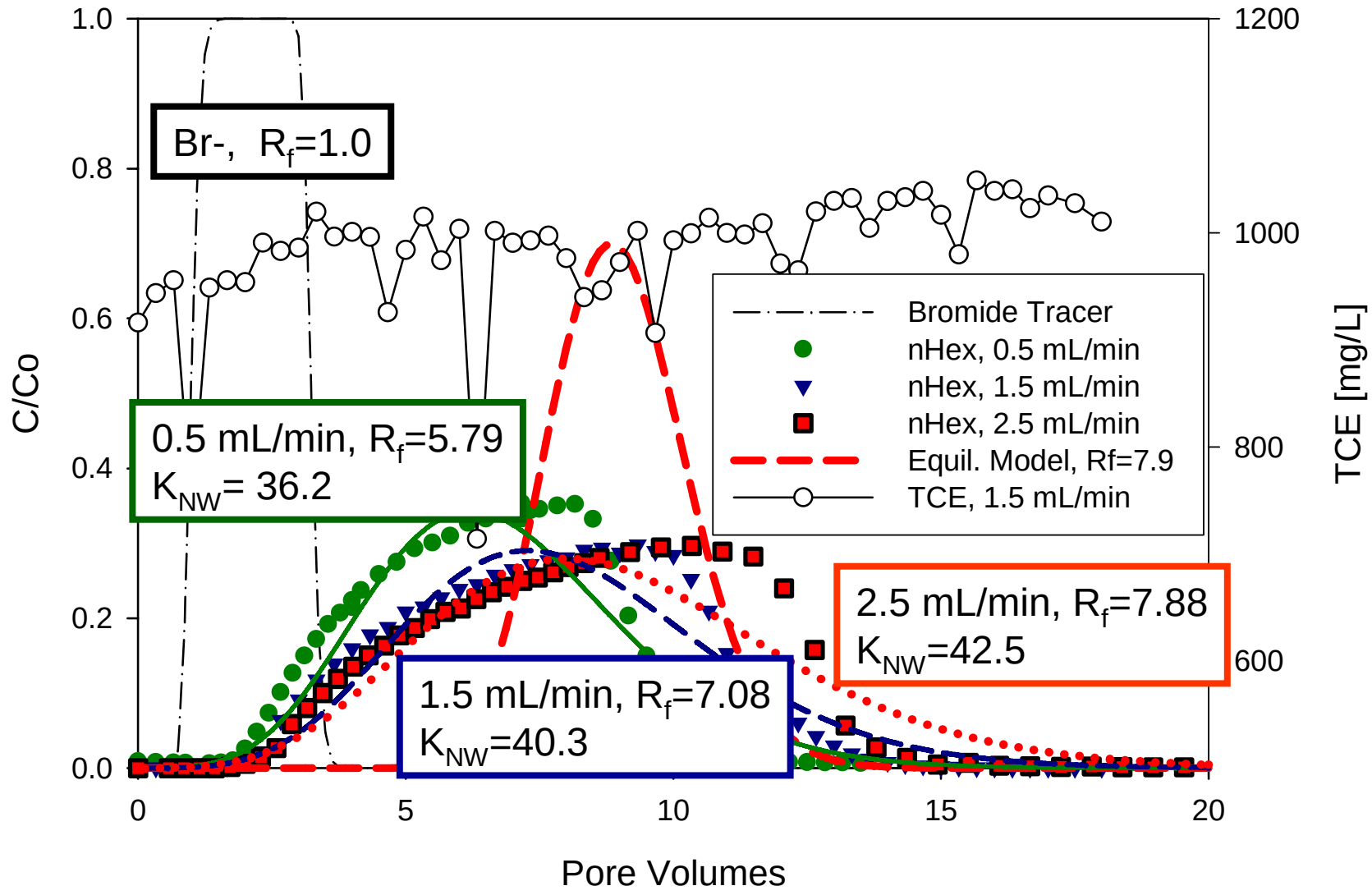


Column Studies

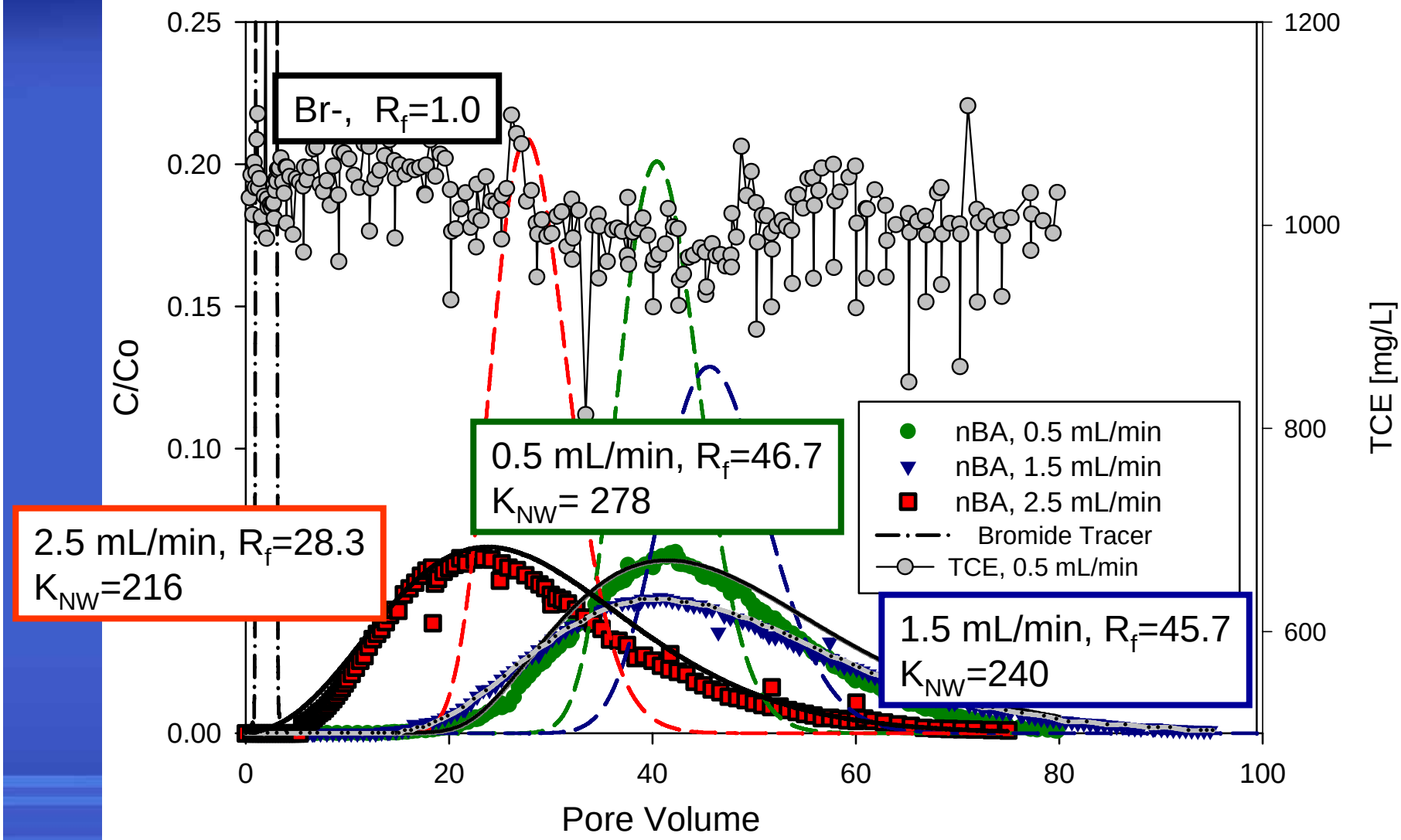


- Quantify n-Butyl Acetate and n-Hexanol mass transfer in a dynamic system
- Packed with well-characterized aquifer material (Federal Fine Ottawa Sand) with a uniform distribution of TCE (sat. ~ 15%)
- Approx. 2 PVs of concentrated (4-5 g/L) PED solution with bromide as a non-reactive tracer were introduced into separate columns
  - pore-water velocities of 1.2 -6.0 m/day.
- Collected effluent samples analyzed for PED and TCE using a GC with FID

n-Hexanol Breakthrough



n-Butyl Acetate Breakthrough

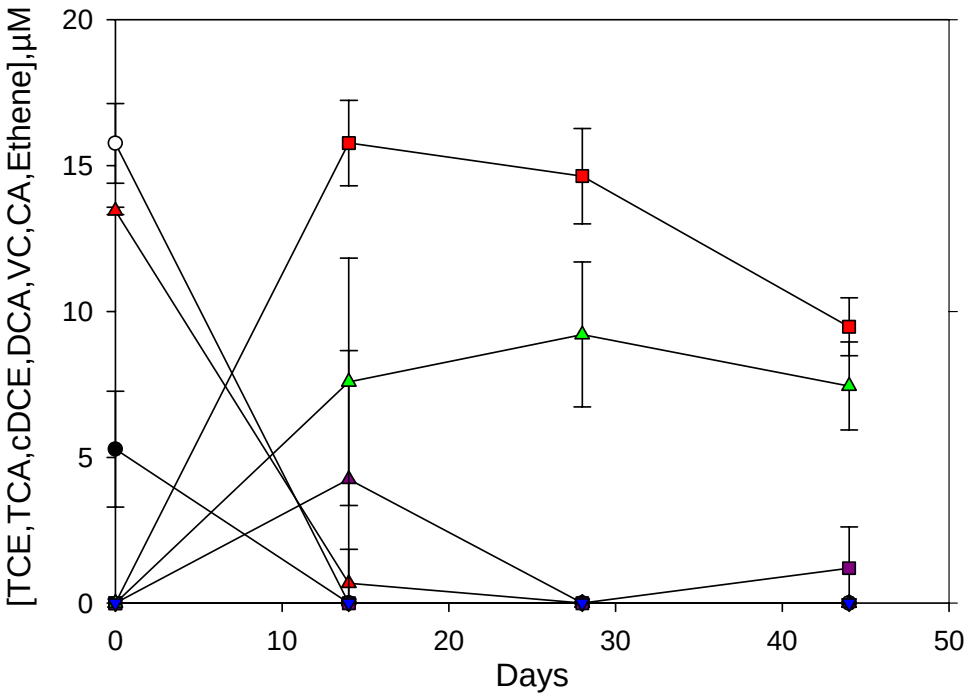


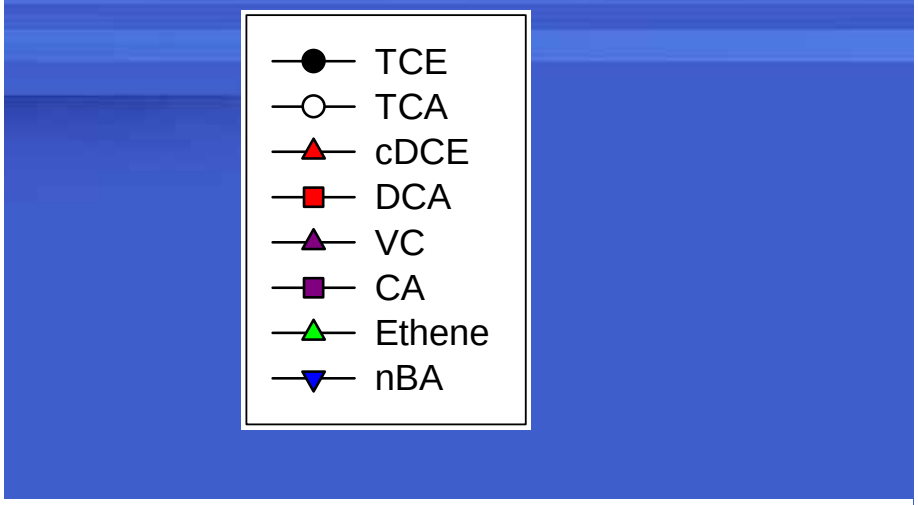
Biotic Batch Study

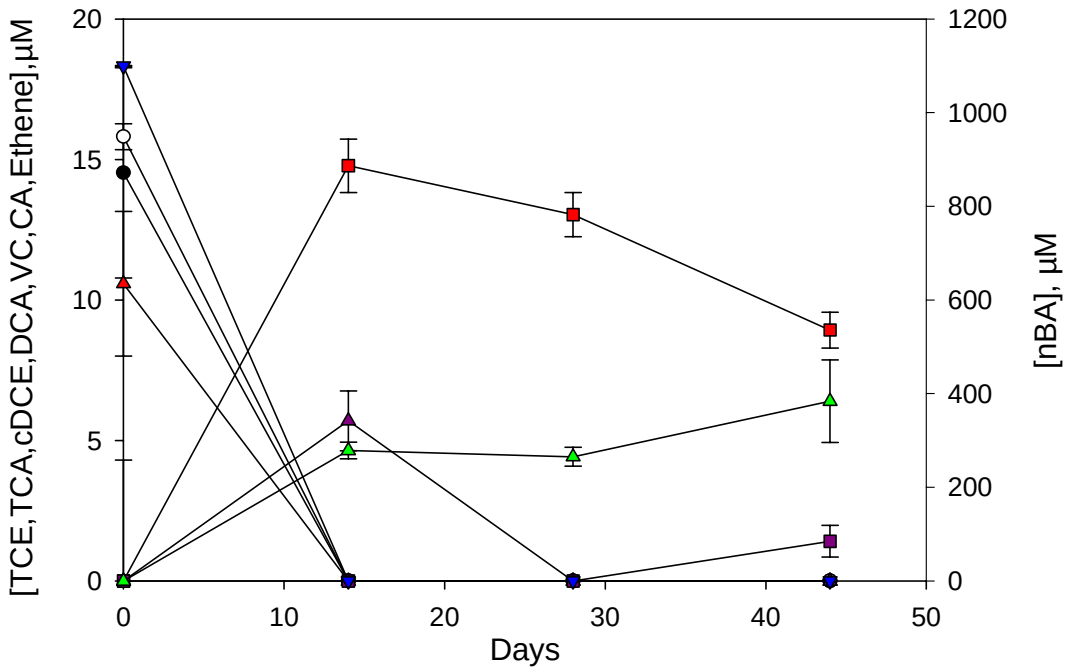
- Evaluate the ability of KB-1 Plus to dechlorinate a contaminant mixture composed of TCE and 1,1,1-TCA with MEL (methanol, ethanol and lactate) and nBA as the electron donor

Abiotic Control x3 | **nBA donor +NAPL x3** | **nBA donor+ Low TCE/TCA x3** | **MEL donor +NAPL x3** | **MEL donor + Low TCE/TCA x3**

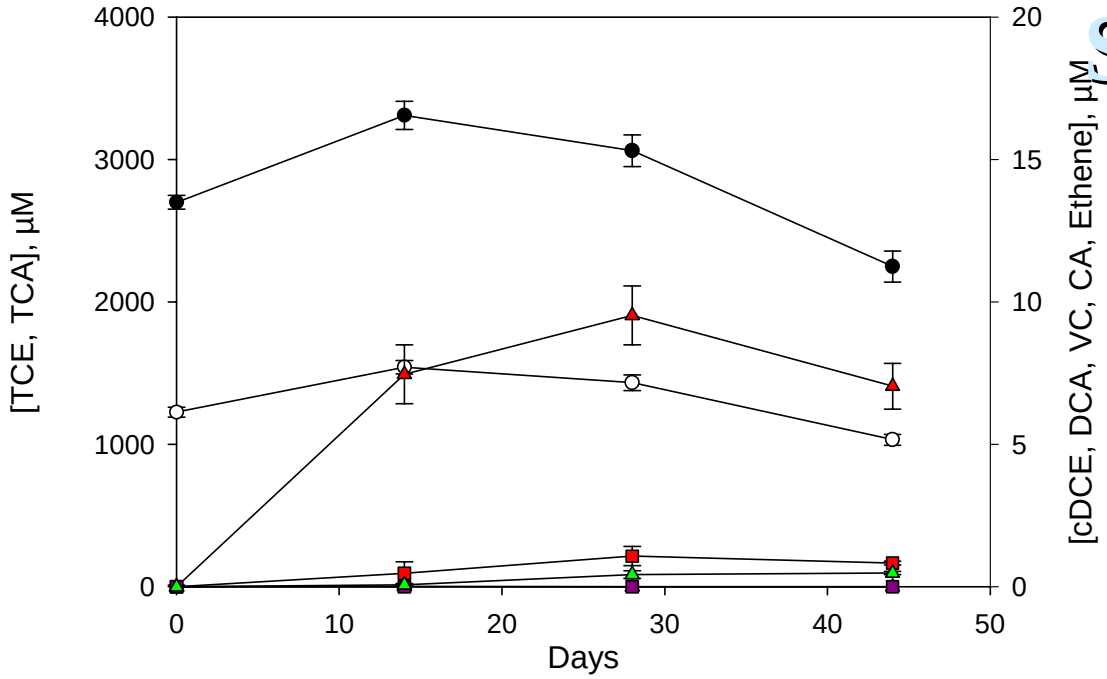
Low TCE/TCA

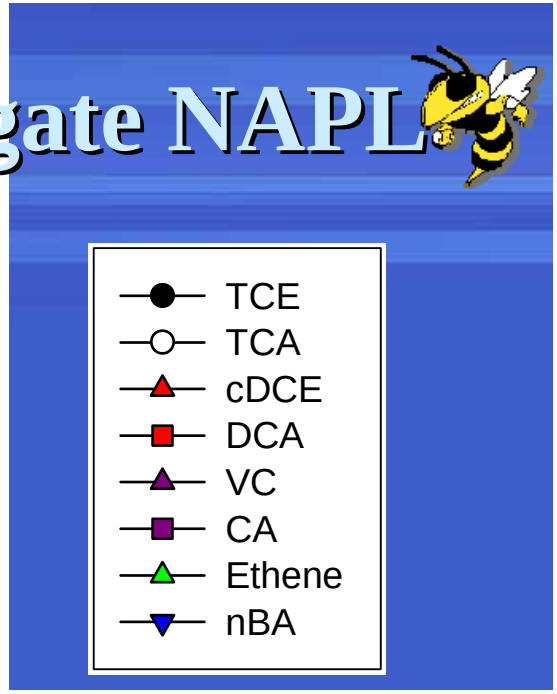

[TCE,TCA,cDCE,DCA,VC,CA,Ethene],µM
20
15
10
5
0
0
10
20
30
40
50
Days

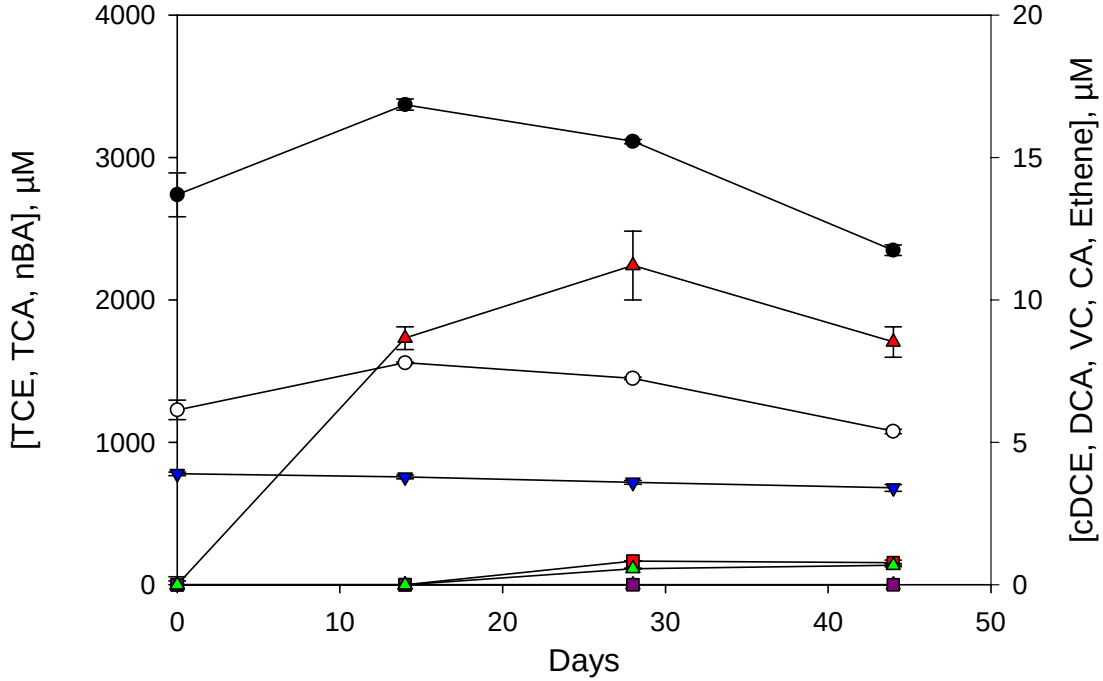

TCE
TCA
cDCE
DCA
VC
CA
Ethene
nBA


[TCE,TCA,cDCE,DCA,VC,CA,Ethene],µM
20
15
10
5
0
1200
1000
800
600
400
200
0
[nBA], µM
0
10
20
30
40
50
Days

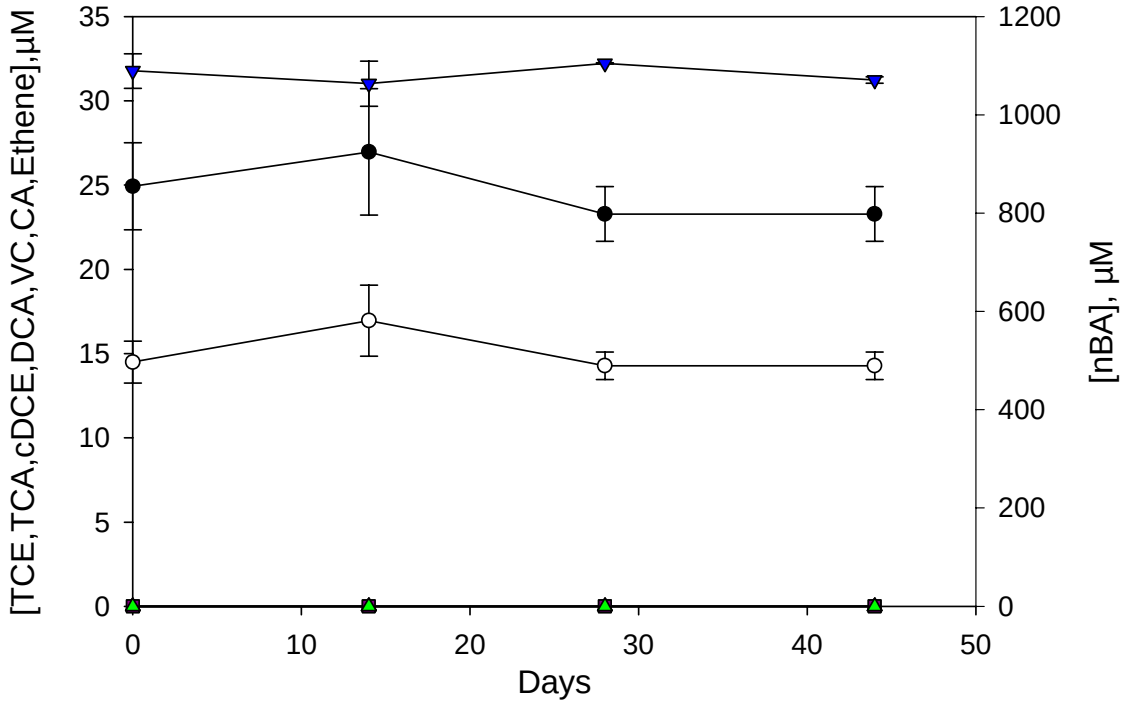
Surrogate NAPL

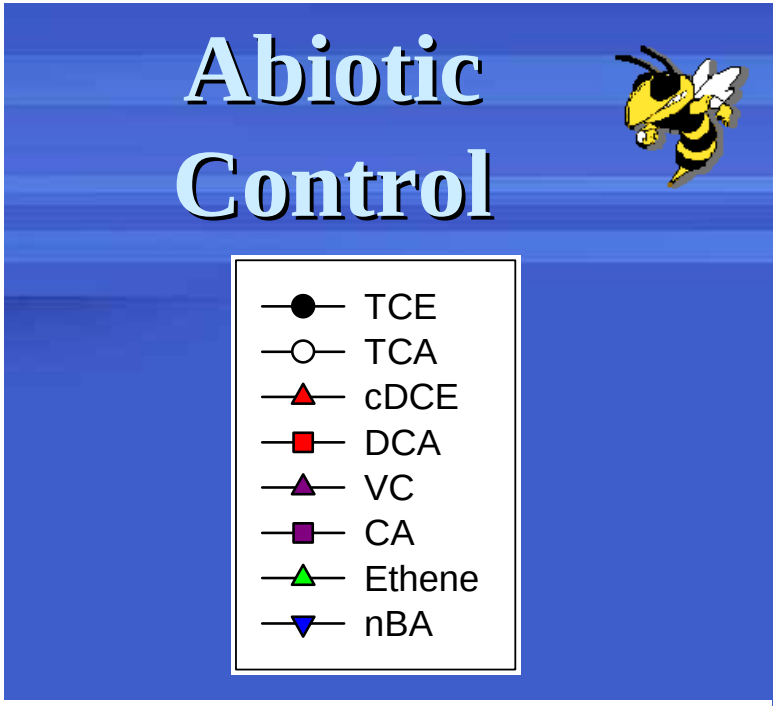


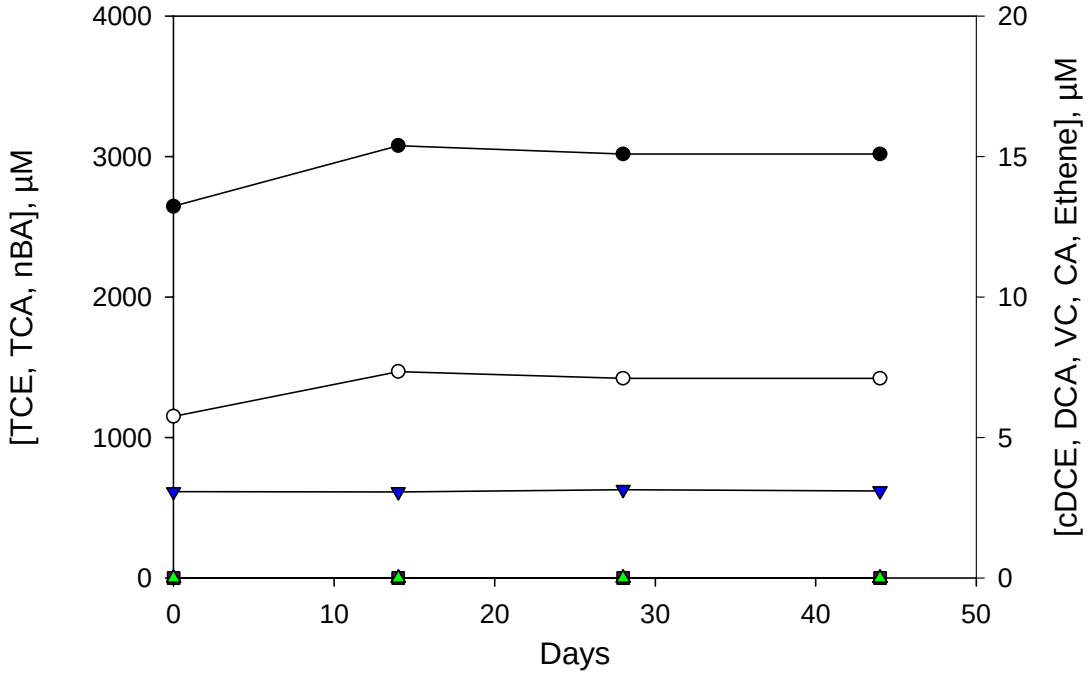




Abiotic Control







Biotic Batch Summary

BIOTIC (KB-1 PLUS) TREATMENT	*% TCE and TCA DECHLORINATED*	*% nBA DEGRADED*
nBA + Surrogate NAPL* (TCE and TCA >200 mg/L)	31	13
nBA + Low (5 mg/L) TCE and TCA	100	100
Methanol, Ethanol and Lactate (MEL) + Surrogate NAPL*	33	n/a
MEL + Low (5 mg/L) TCE and TCA	100	n/a
Negative Control with All Amendments	<10	0

** Surrogate NAPL = mixture of 1,1,1-TCA and TCE in hexadecane*

PED Conclusions

- PEDs have the potential to offer a lasting source of reducing equivalents to support microbial reductive dechlorination
- The strong partitioning behavior will be advantageous for field-based applications since:
  - A single PED injection could persist for approximately *6-times (n-hexanol) and 100-times (nBA)* the number of delivered pore volumes
- nBA addition can support dechlorination and reduce the need for frequent or repeated electron donor injections

Acknowledgements

This work was supported by:

- **SERDP Project ER-1293:** Development of Assessment Tools for Evaluation of the Benefits of DNAPL Source Zone Treatment
- **SERDP Project ER-1419** : Investigation of Chemical Reactivity, Mass Recovery and Biological Activity During In Situ Thermal Treatment of DNAPL Source Zones
- **ESTCP Project ER-0716:** Improving Effectiveness of Bioremediation at DNAPL Source Zone Sites by Applying Partitioning Electron Donors (PEDs)