

# **Reactive Barriers for the Passive Remediation of Chlorinated Solvents in Sediments and Groundwater Discharge**

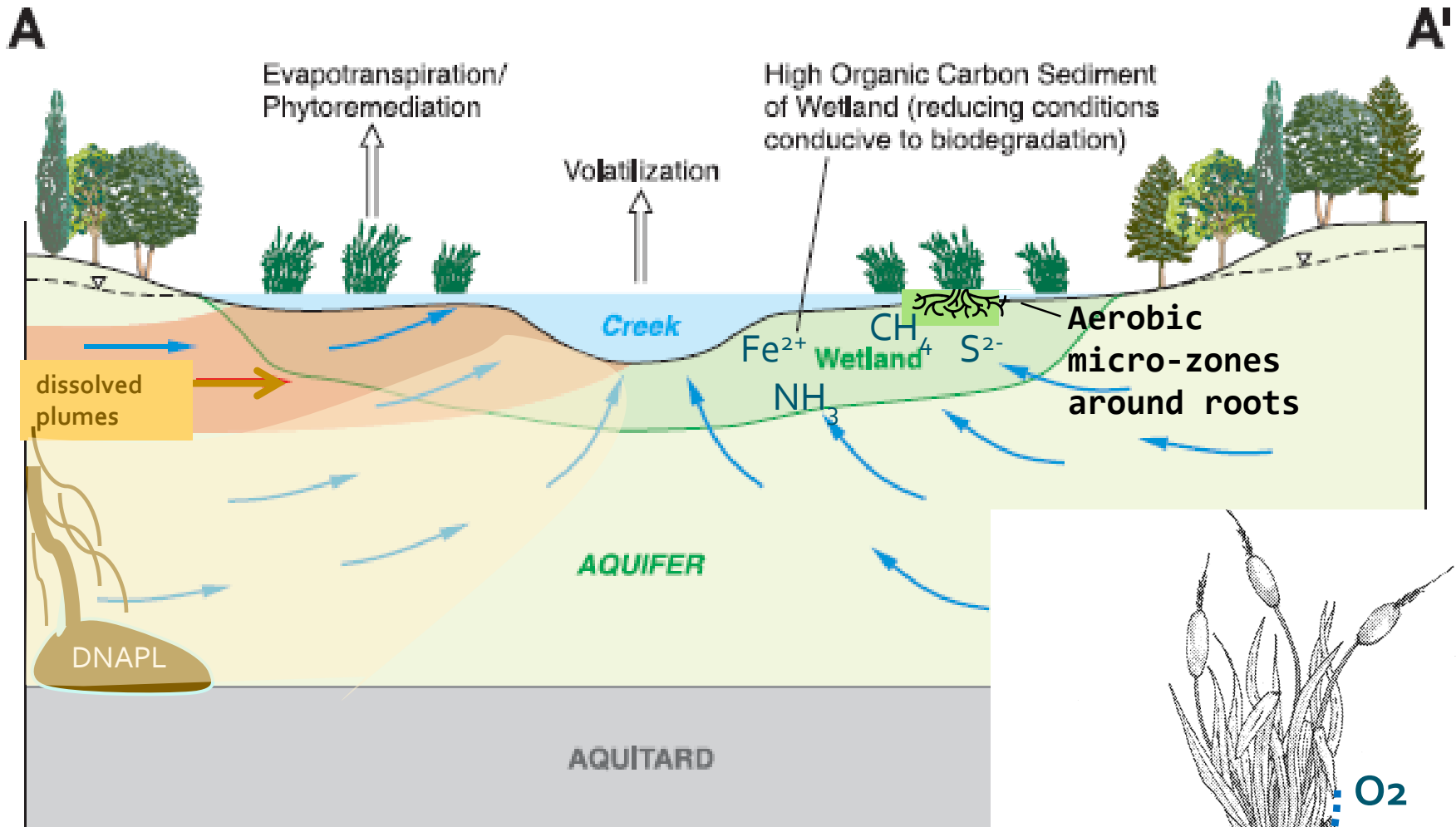
**Michelle M. Lorah**  
USGS, Baltimore, Maryland

*in cooperation with*

***DoD, Aberdeen Proving Ground***

***USEPA, Region III***

***NIEHS, Superfund Research Program***



Conceptual model for chlorinated solvent contamination in wetland (modified from Lorah et al., 2005)

# Chlorinated VOCs at West Branch Canal Creek and their anaerobic degradation pathways

Parent VOCs in orange

Chlorinated ethanes:

HCA= hexachloroethane

PtCA= pentachloroethane

1122TeCA= 1,1,2,2-tetrachloroethane

Chlorinated ethenes:

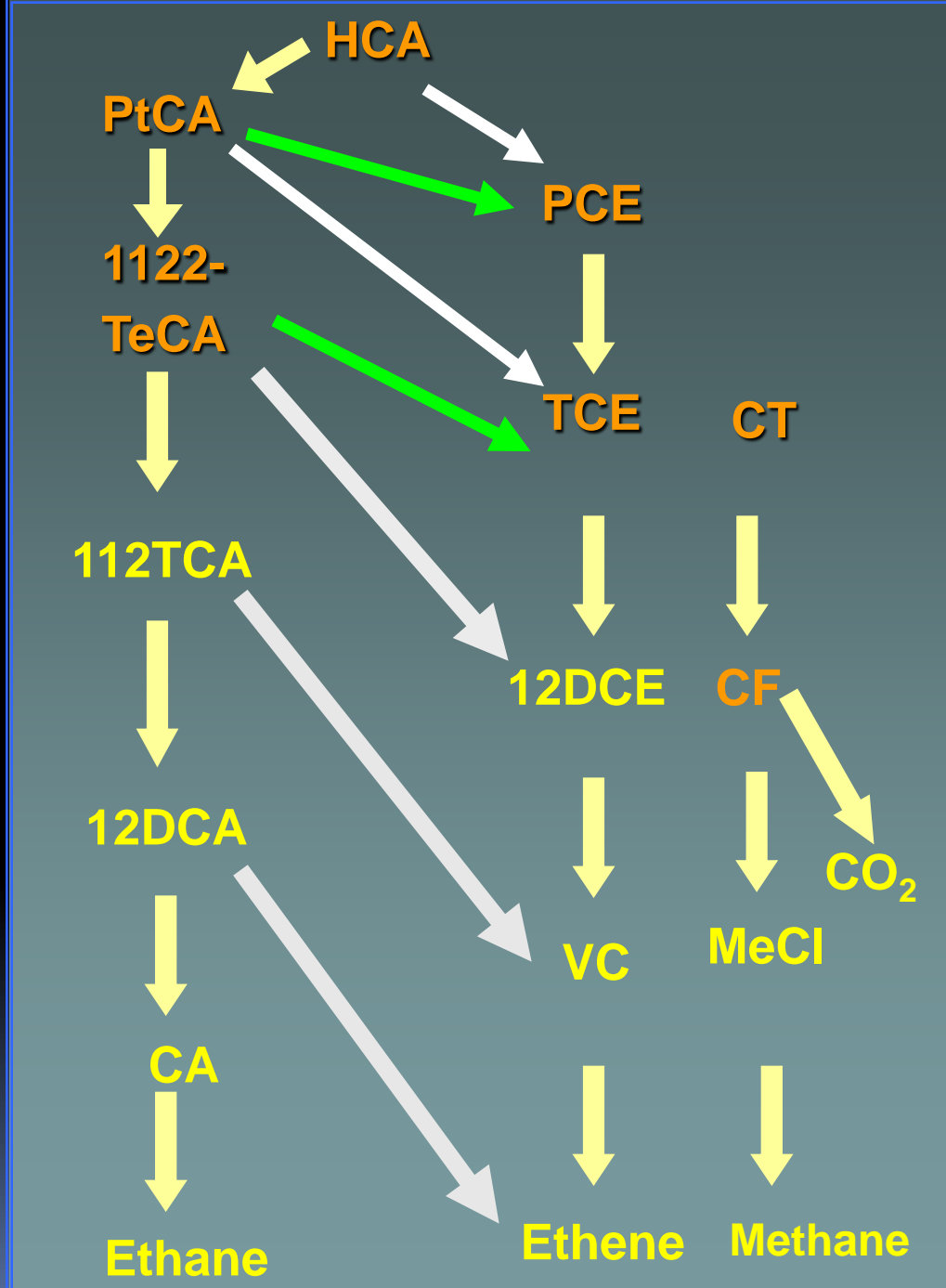
PCE= tetrachloroethene

TCE= trichloroethene

Chlorinated methanes:

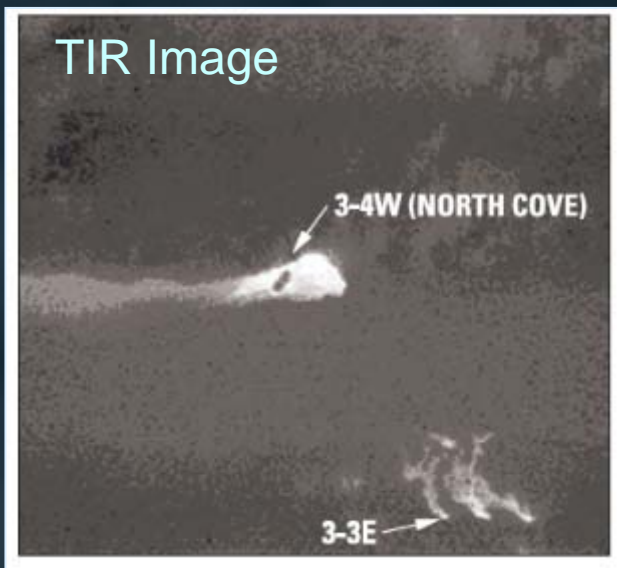
CT= carbon tetrachloride

CF= chloroform



# Site Characterization

TIR Image



## Chloroform



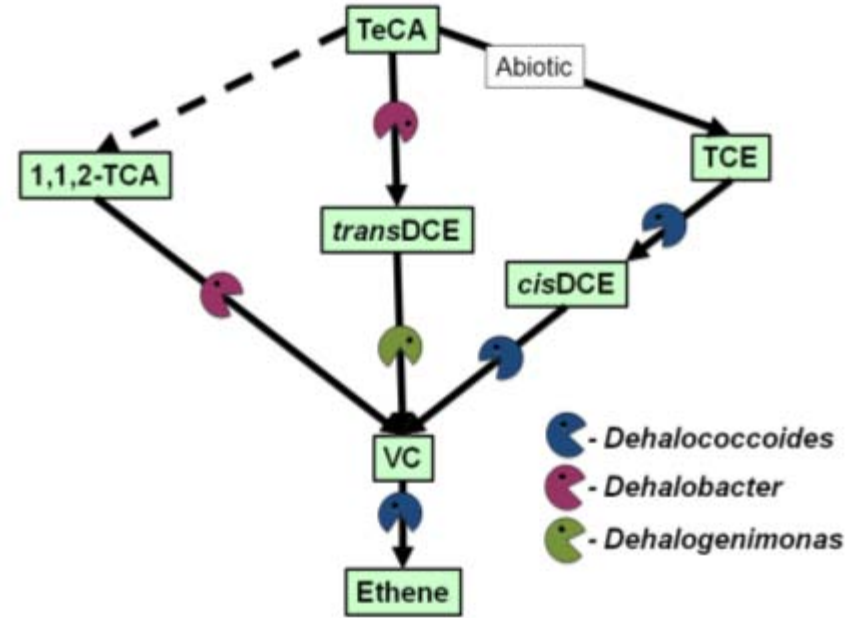
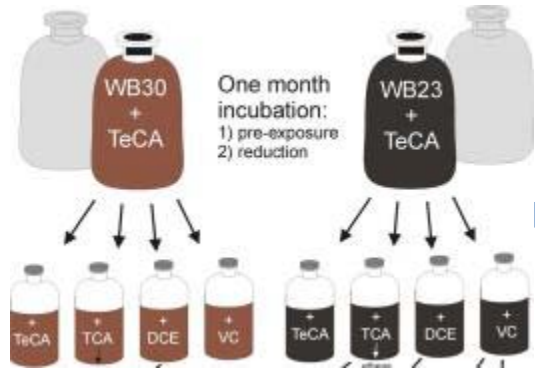
## Tetrachloroethene



West Branch Canal Creek, APG

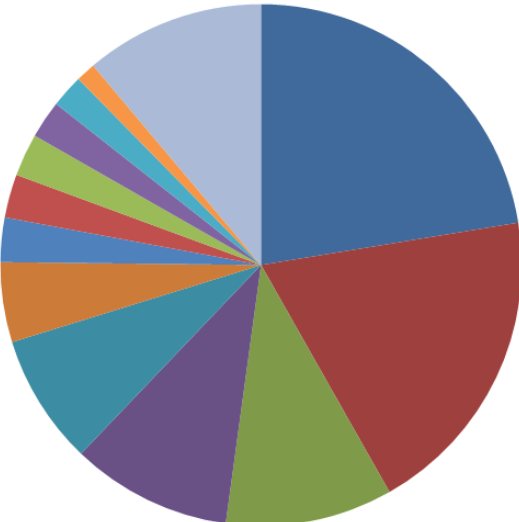


# WBC-2 Dechlorinating Culture



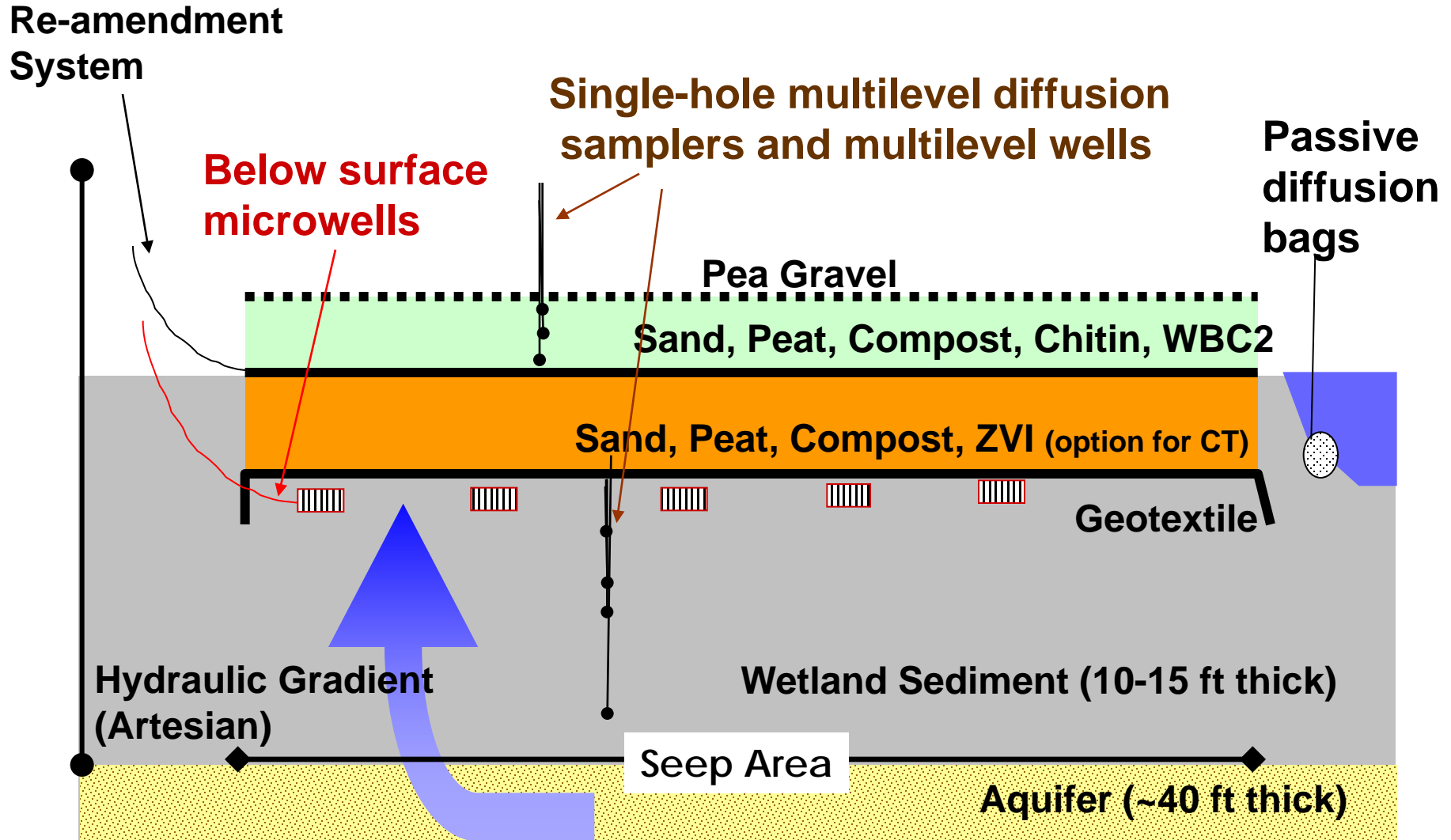
WBC-2 #1

Relative Abundances above 1%



- Otu00014 - Bacteria; Bacteroidetes; unclassified; unclassified; unclassified; unclassified; unclassified
- Otu00008 - Bacteria; Proteobacteria; Deltaproteobacteria; Desulfuromonadales; Geobacteraceae; Geobacter; unclassified
- Otu00013 - Bacteria; WWE1; [Cloacamonae]; [Cloacamonales]; [Cloacamonaceae]; WV22; unclassified
- Otu00023 - Bacteria; Proteobacteria; Deltaproteobacteria; Desulfobacterales; Desulfobulbaceae; Desulfobulbus; unclassified
- Otu00004 - Bacteria; Tenericutes; Mollicutes; Acholeplasmatales; Acholeplasmataceae; Acholeplasma; unclassified
- Otu00040 - Bacteria; Chloroflexi; Anaerolineae; Anaerolineales; Anaerolineaceae; C1\_B004; unclassified
- Otu00029 - Bacteria; Firmicutes; Clostridia; Clostridiales; Eubacteriaceae; Acetobacterium; unclassified
- Otu00002 - Bacteria; Proteobacteria; Gammaproteobacteria; Pseudomonadales; Pseudomonadaceae; Pseudomonas; stutzeri
- Otu00031 - Bacteria; Firmicutes; Clostridia; Clostridiales; [Mogibacteriaceae]; unclassified; unclassified
- Otu00017 - Bacteria; Chloroflexi; Dehalococcoidetes; Dehalococcoidales; Dehalococcoidaceae; Dehalogenimonas; unclassified
- Otu00003 - Bacteria; Proteobacteria; Epsilonproteobacteria; Campylobacteriales; Campylobacteraceae; Sulfurospirillum; unclassified
- Otu00036 - Bacteria; Bacteroidetes; unclassified; unclassified; unclassified; unclassified; unclassified
- Other

# Reactive Barrier Design and Monitoring



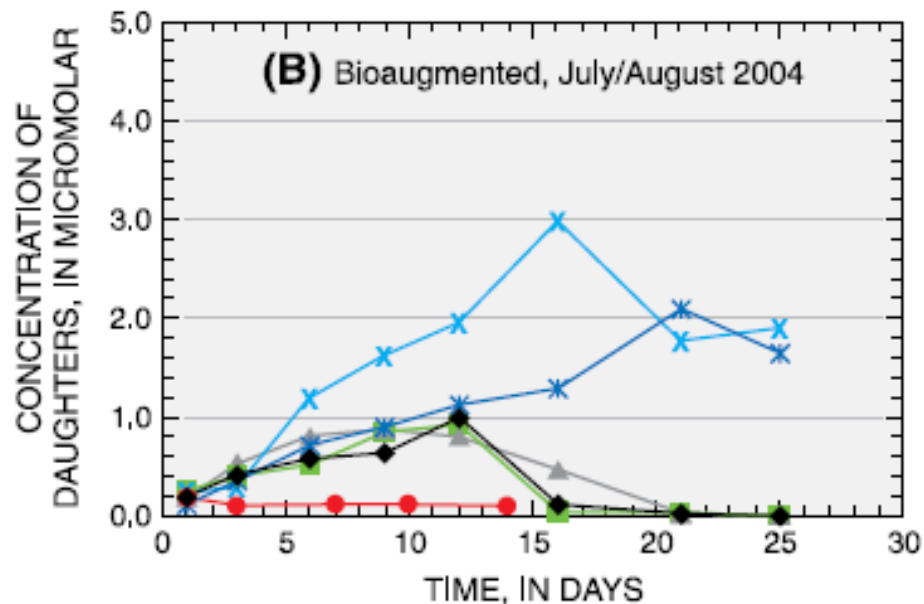
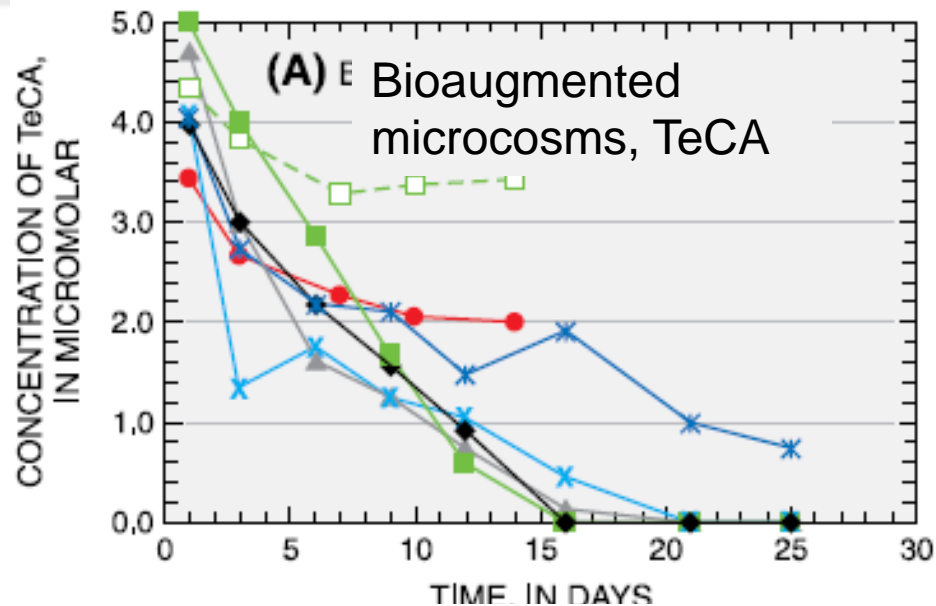
NOT TO SCALE

# Microcosms: Wetland Sediment- Compost Mixtures

- Different composts tested for support of WBC-2 activity and VOC degradation
- Variable results with different composts for degradation of both parent and daughter compounds

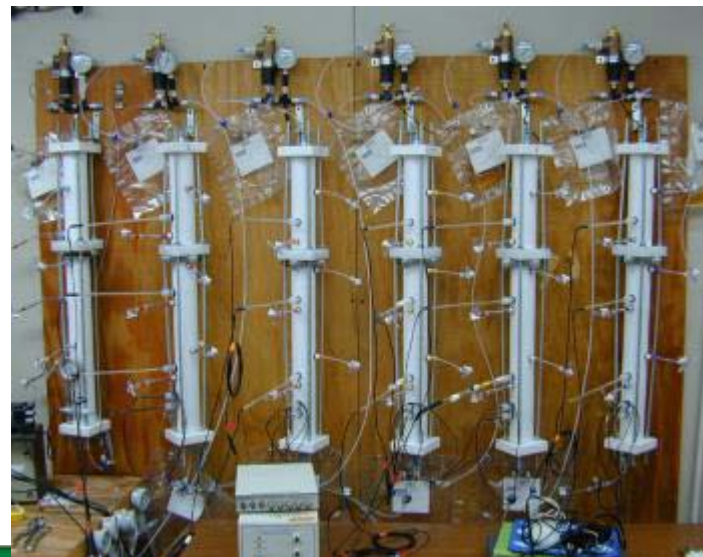
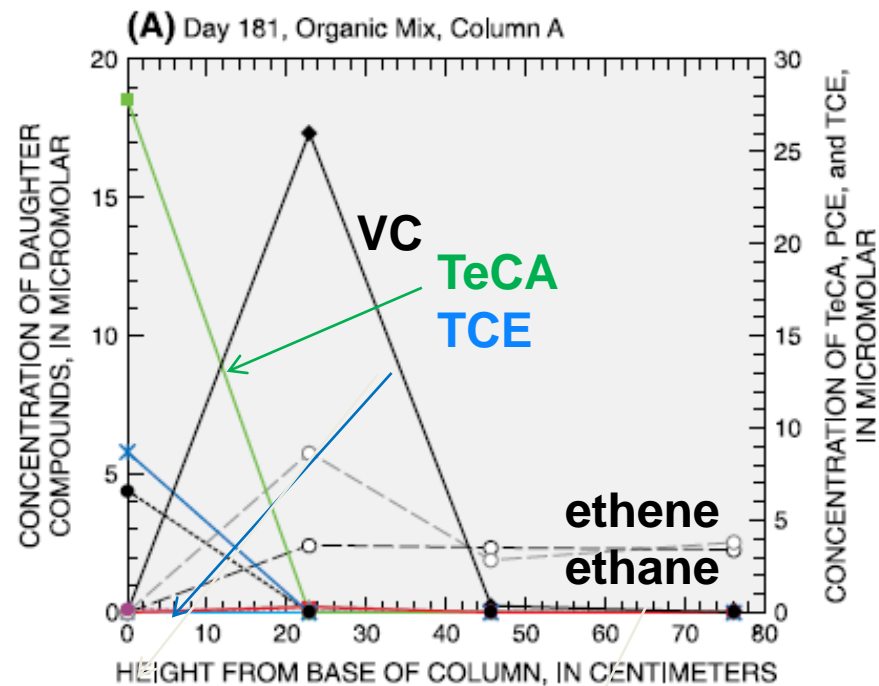
## EXPLANATION

- |              |                           |
|--------------|---------------------------|
| ◆—◆ BionSoil | ■—■ Crab                  |
| ▲—▲ Leafgro  | ×—× Poultry               |
| ×—× Paygro   | ●—● Tender Loving Compost |



# APG Reactive Barrier: Upward Flow Columns

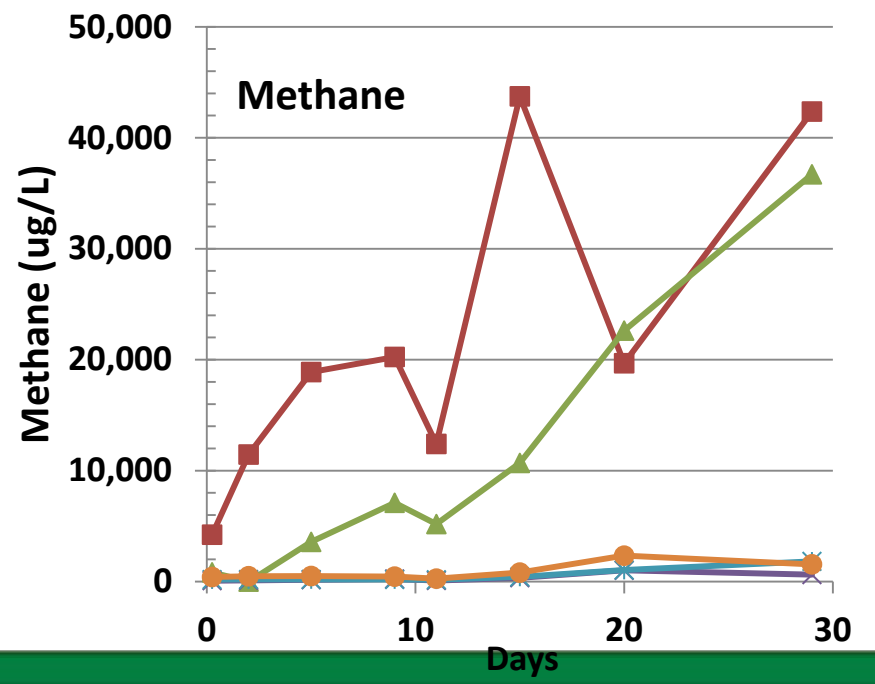
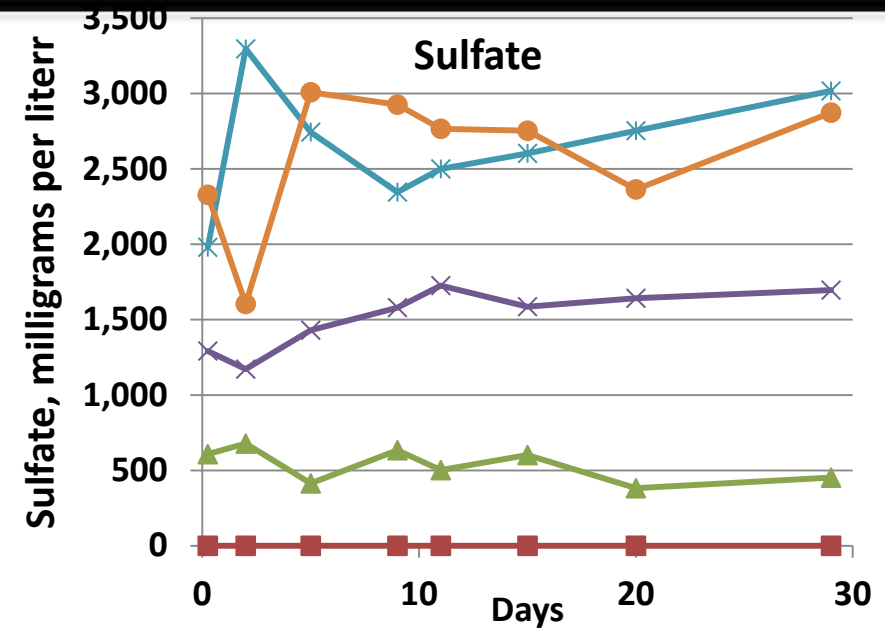
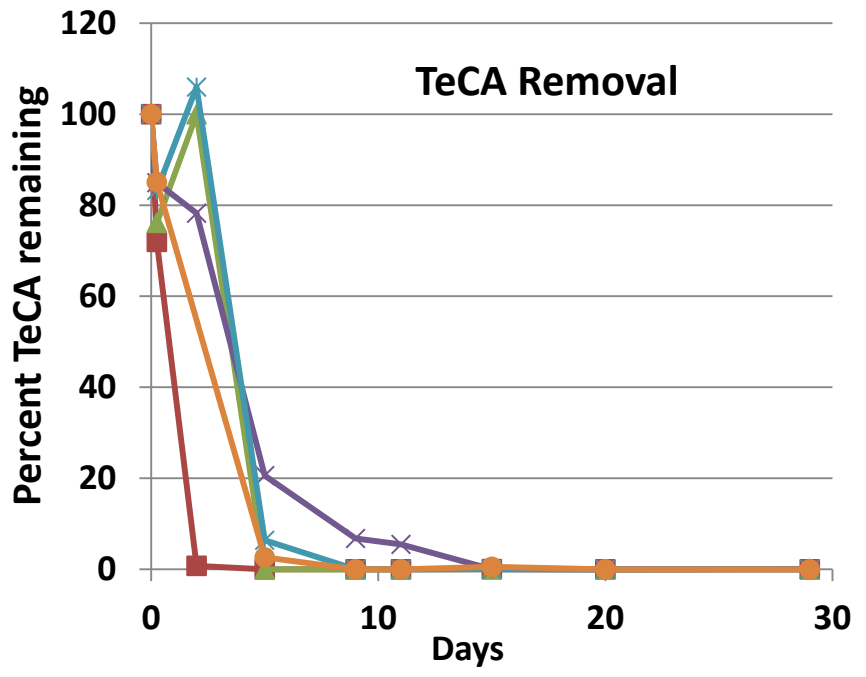
Contaminant	$k$ ( $\text{day}^{-1}$ )	$t_{1/2}$ (hrs)
1122TeCA	3.4	4.8
Chloroform	2.3	7.2
Carbon tetrachloride	2.8	5.9
Tetrachloroethene	1.4	12
Trichloroethene	3.0	5.5



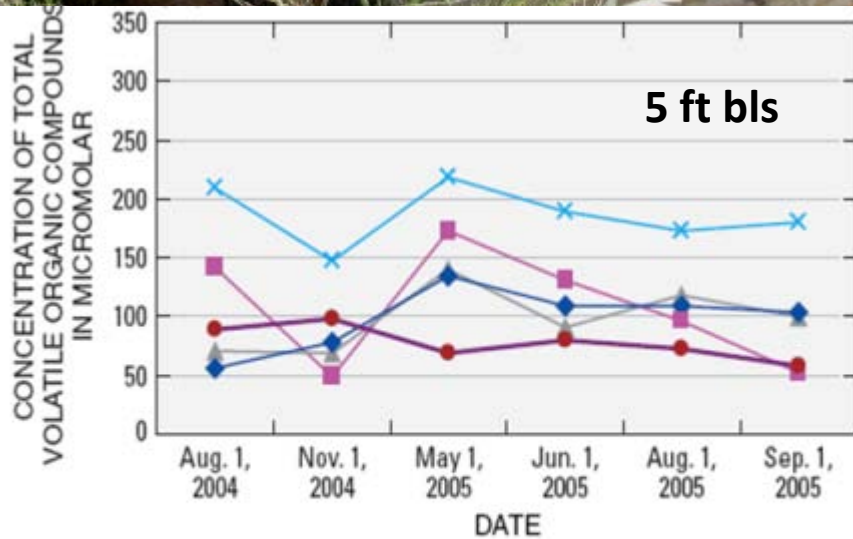
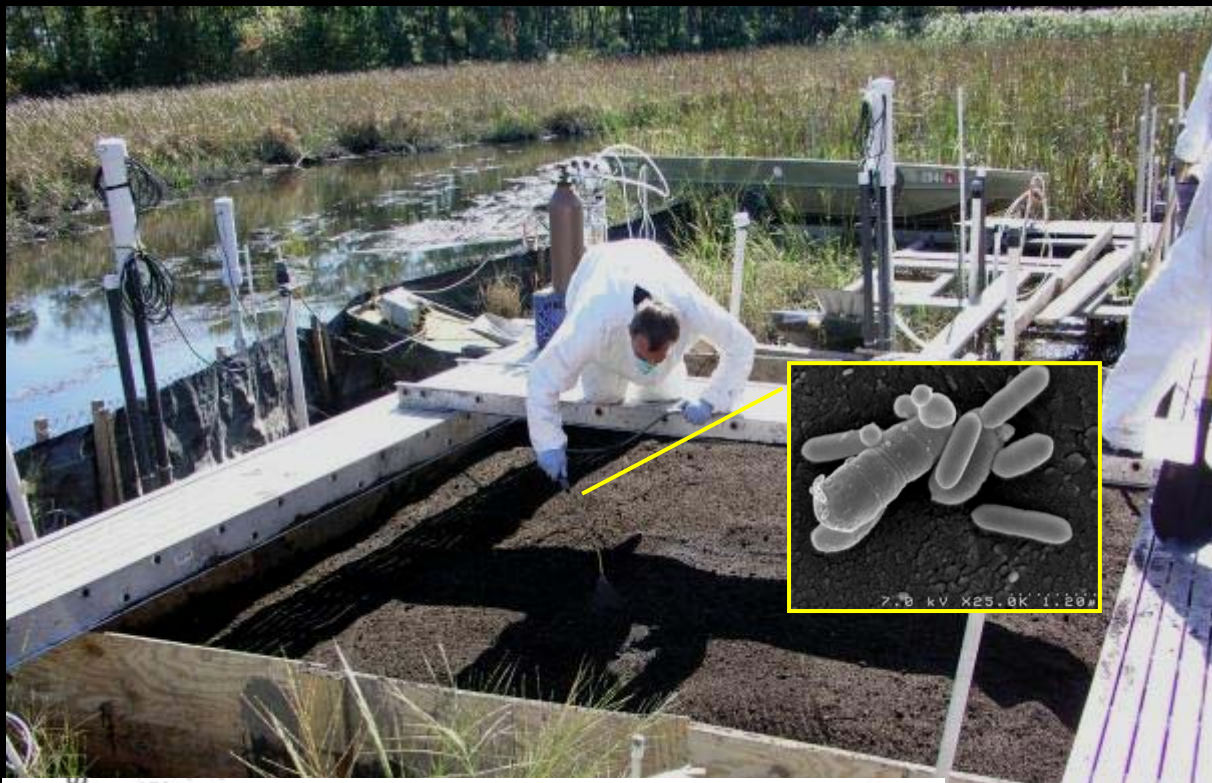


# Salinity microcosms

- WBC2, 4 ppt
- ▲ WBC2, 10 ppt
- × WBC2, 20 ppt
- \* WBC2, 30 ppt
- WBC2, 35 ppt

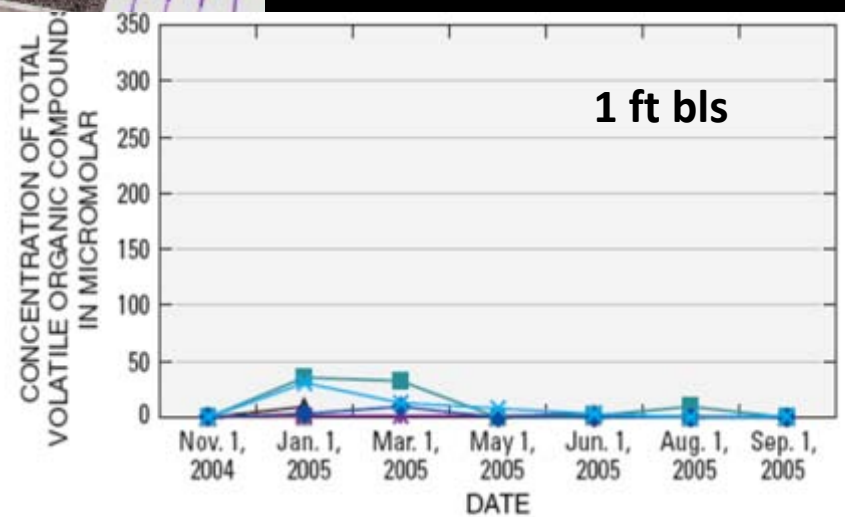


# Reactive Barrier- West Branch Canal Creek, APG



**EXPLANATION**

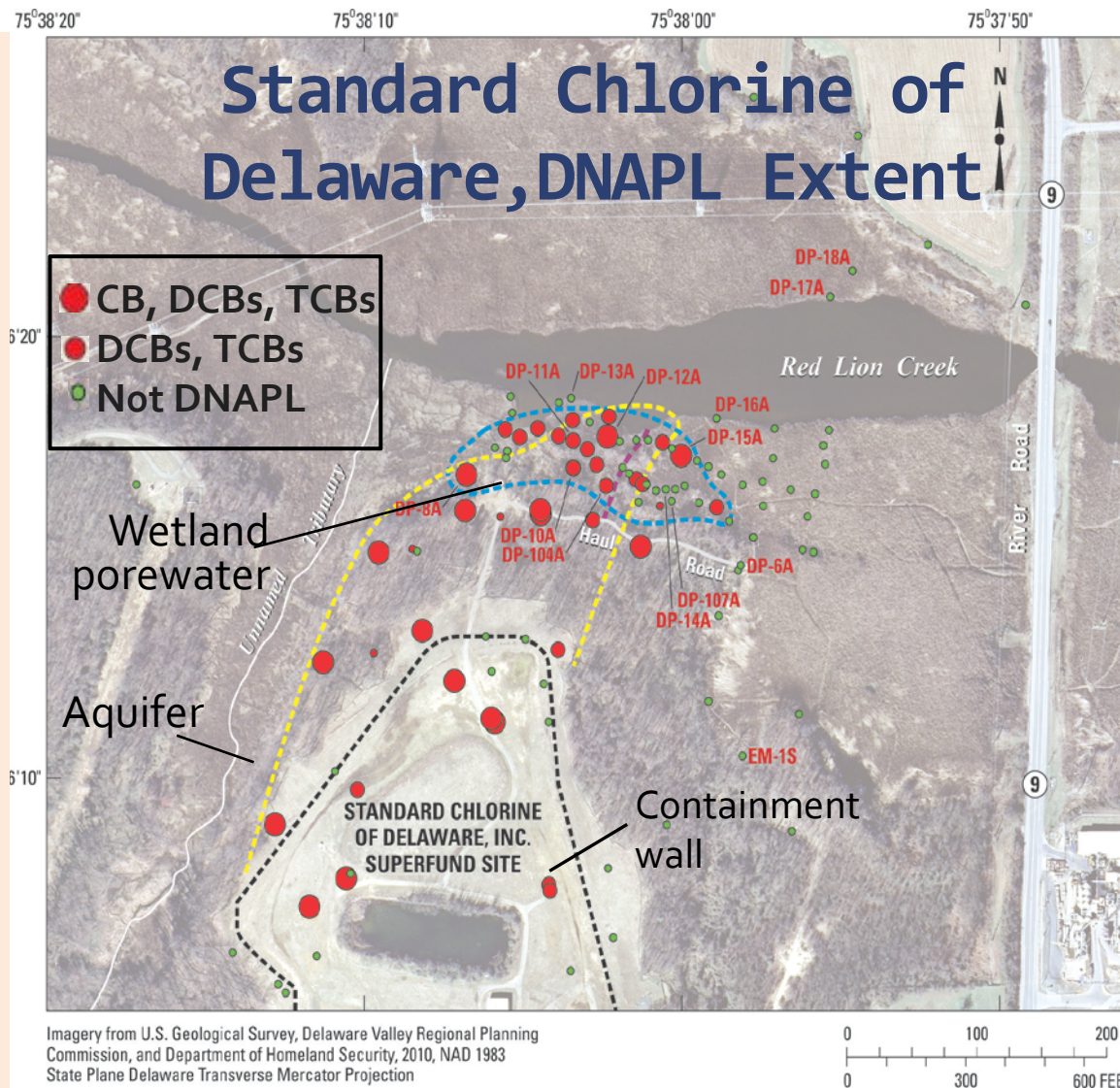
♦ PTC1-5 ft    ■ PTC2-5 ft    ▲ PTC3-5 ft  
 × PTC4-5 ft    ● PTC5-5 ft



**EXPLANATION**

♦ PTB1B    ■ PTB2B    ▲ PTB3B    × PTB4B    ✱ PTB5B  
 ● PTB6B    ■ PTB7B    ● PTB8B    ▲ PTB9B

- Chemical plant 1966-2002; EPA Superfund 2002
  - 1981- 5,000 gal CB
  - 1986 storage tanks- 579,000 gal 14DCB and TCBs
- Abuts Red Lion Creek, part of Delaware River watershed
- Treatment in uplands, but not in wetlands
- Half of water flow to Red Lion Creek is from Columbia Aquifer



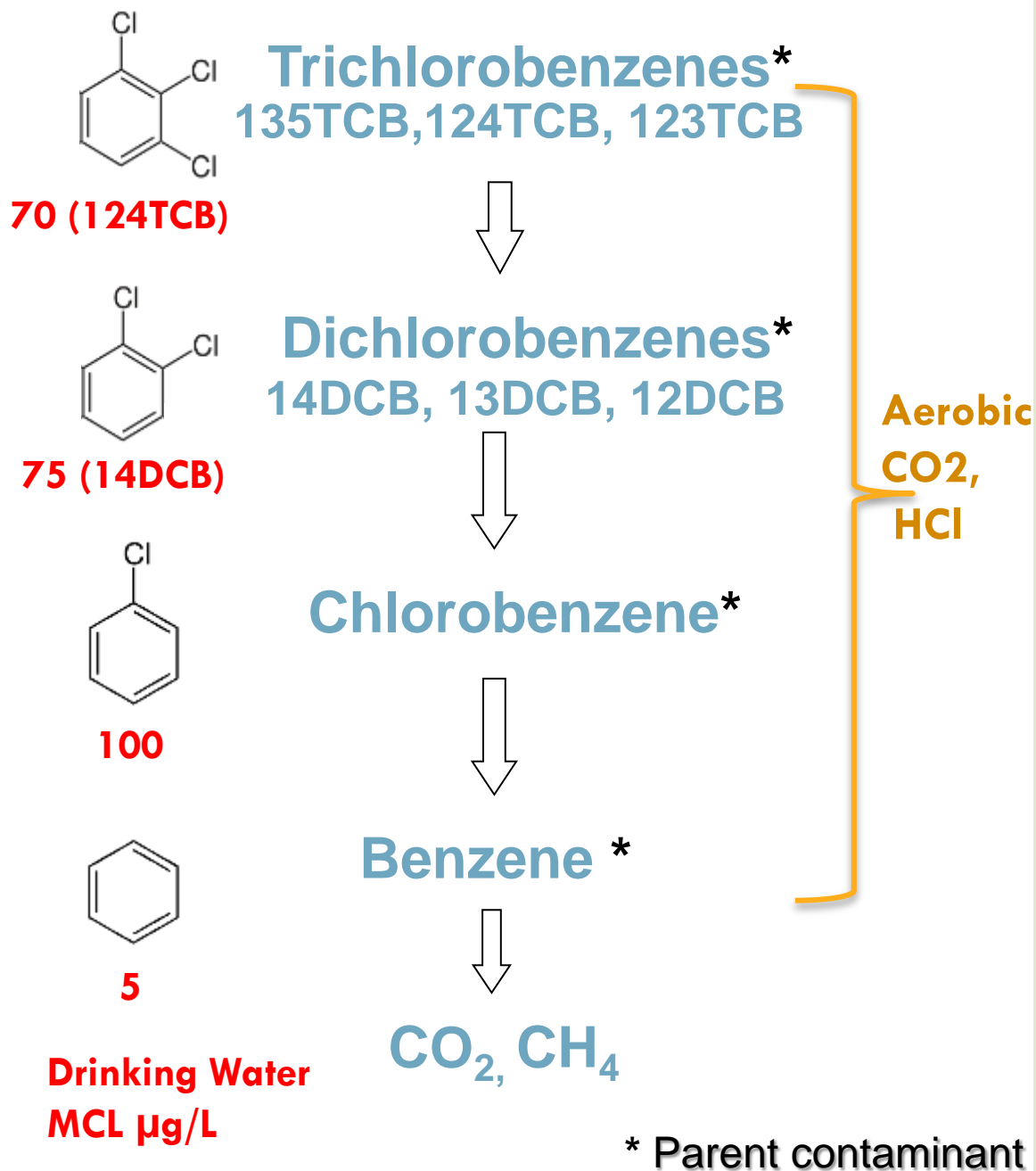
# Biodegradation Pathways

## Anaerobic (reductive dechlorination)

- CB serves as terminal electron acceptor
- Separate e<sup>-</sup> donor required
- rate decreases with decreasing number Cl

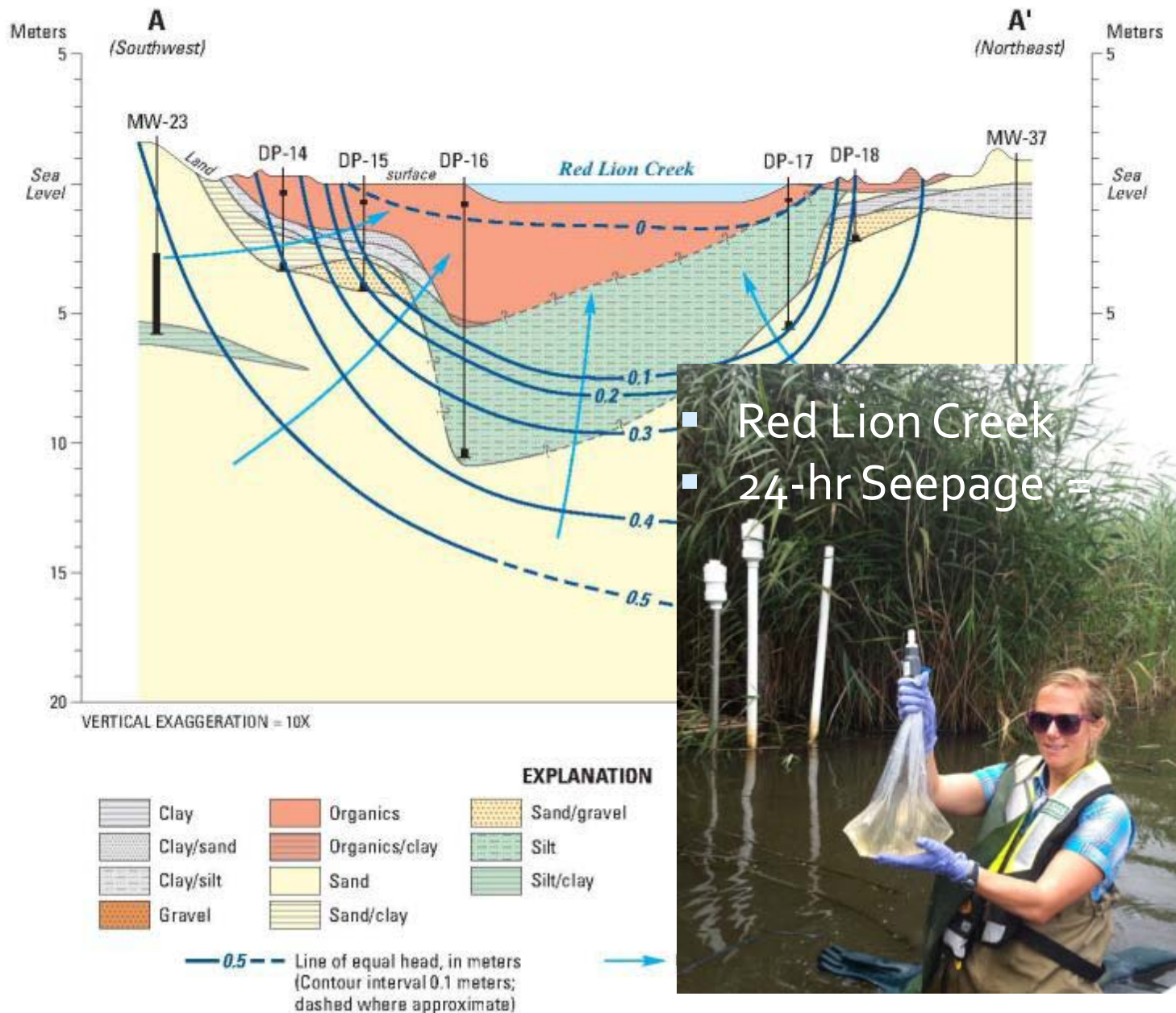
## Aerobic (oxidation)

- O<sub>2</sub> required as electron acceptor
- CBs utilized as C and e<sup>-</sup> donor
- rate increases with decreasing number Cl
- Short-lived intermediates



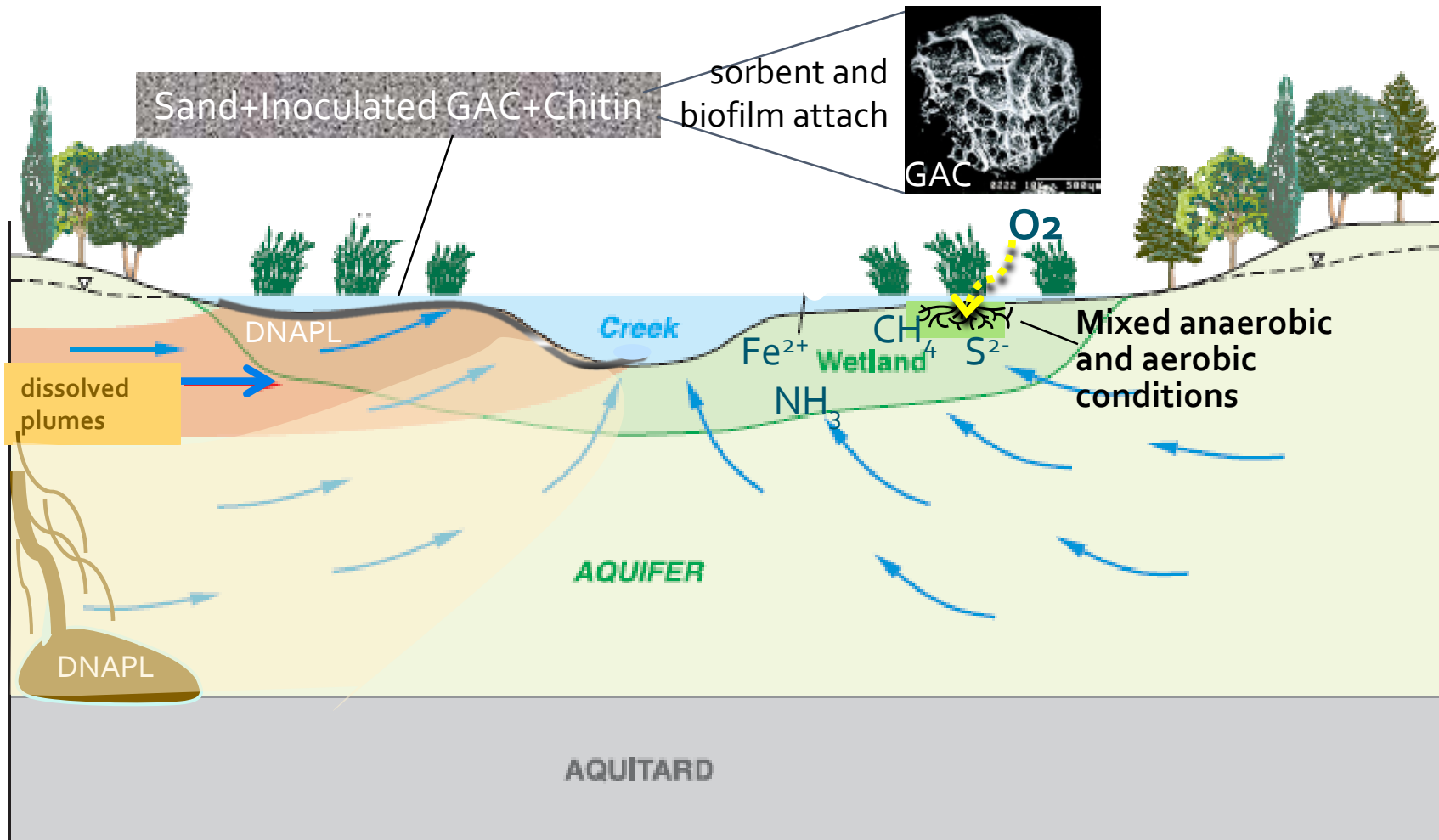
# Wetland Study Area, SCD

- Upward flow at all sites
- Seepage measured on wetland surface and creek bottom



- Red Lion Creek
- 24-hr Seepage =



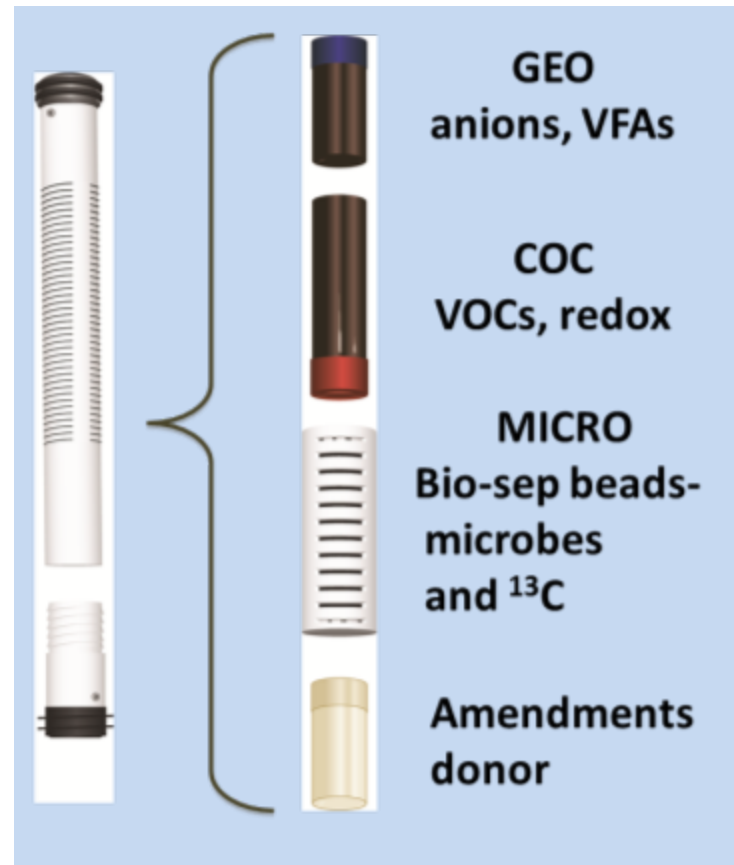


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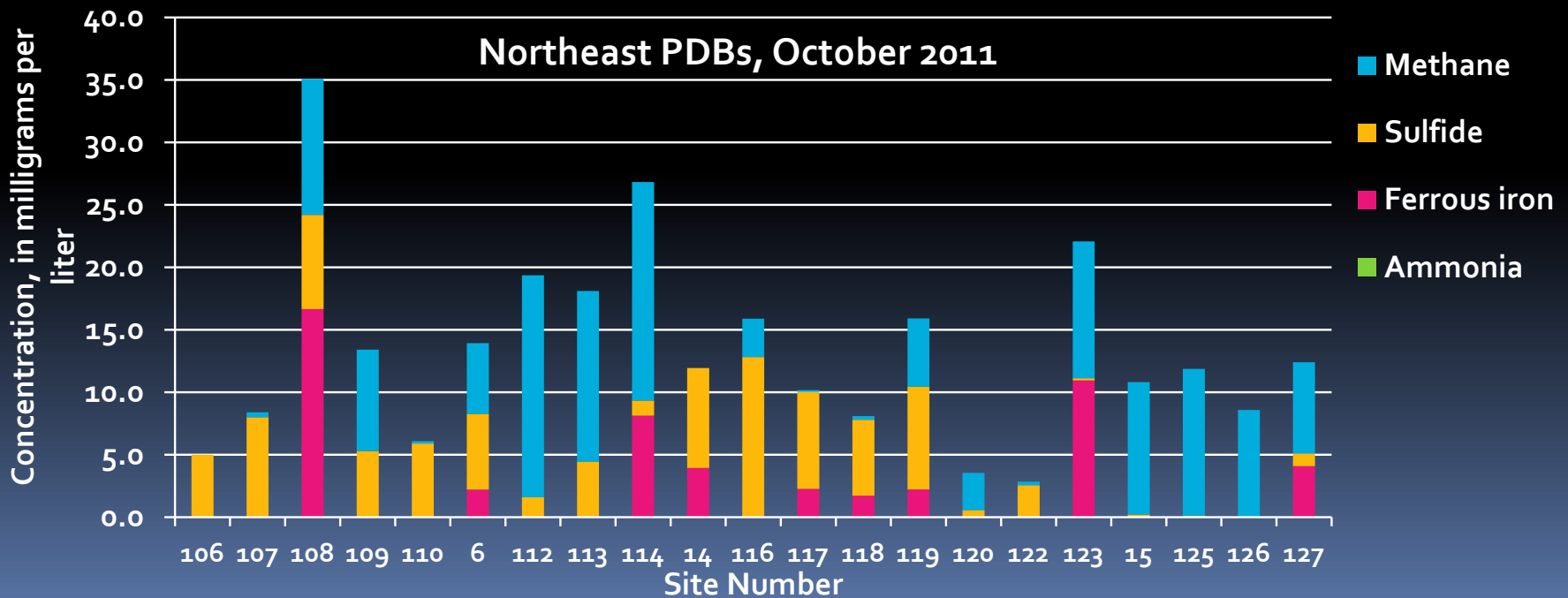
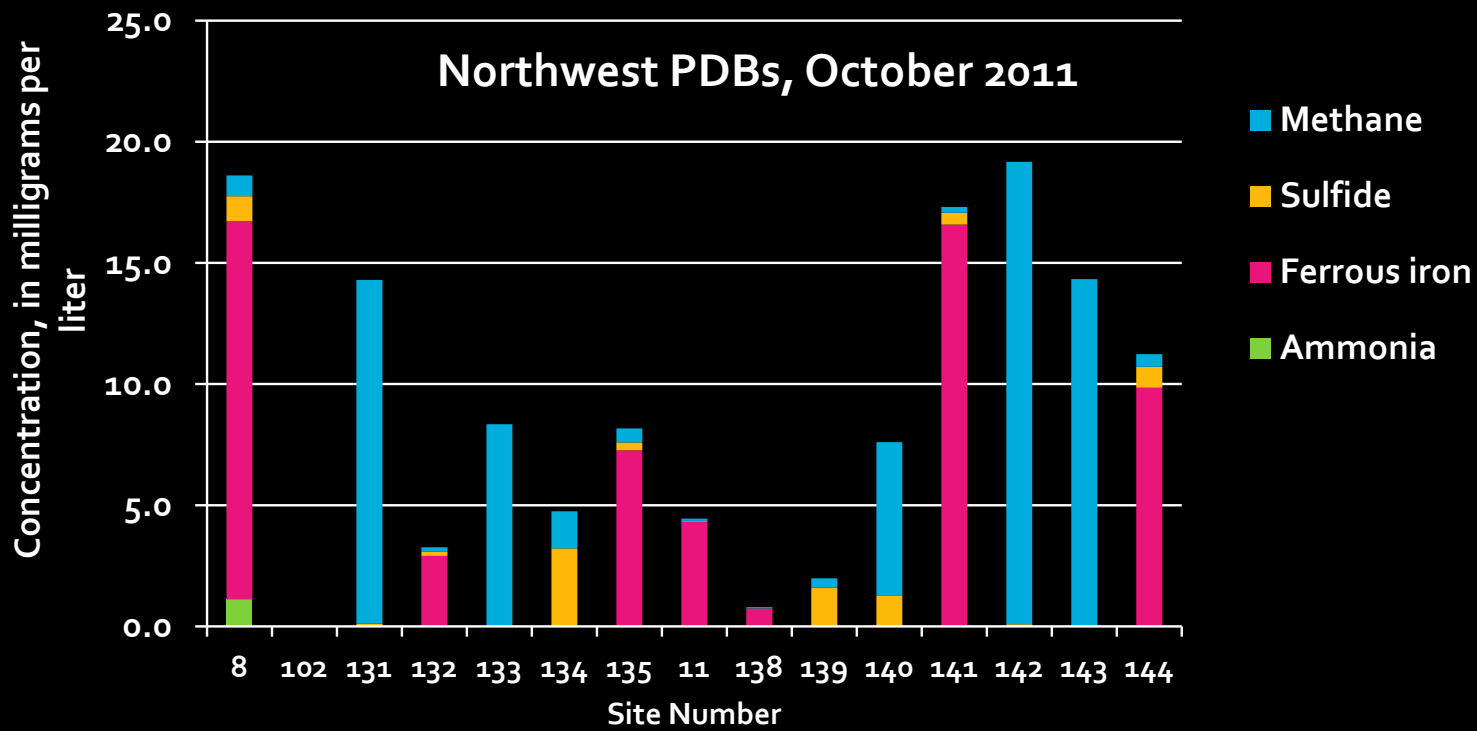
Conceptual model for contamination and dual-biofilm reactive barrier in wetland

# Approach to evaluate natural and enhanced biodegradation

- *In situ* microcosms with Bio-Traps (Microbial Insights)
  - Stable isotope probing ( $^{13}\text{C}$ -labeled 14DCB, CB, B)
  - Microbial species and functional genes for biodegradation
- Evaluate biodegradation processes in flow-through bioreactors
  - Upflow fixed film bioreactors
  - Mimic growth in subsurface
  - Allows changing conditions

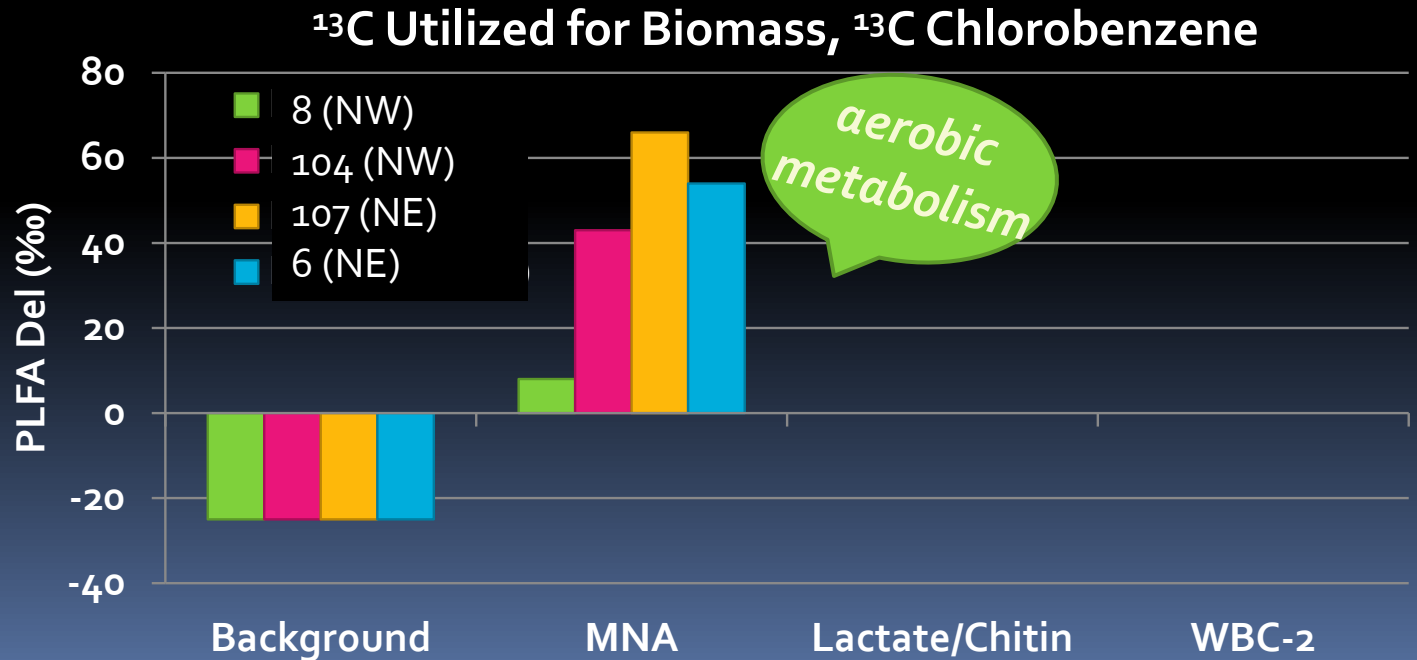
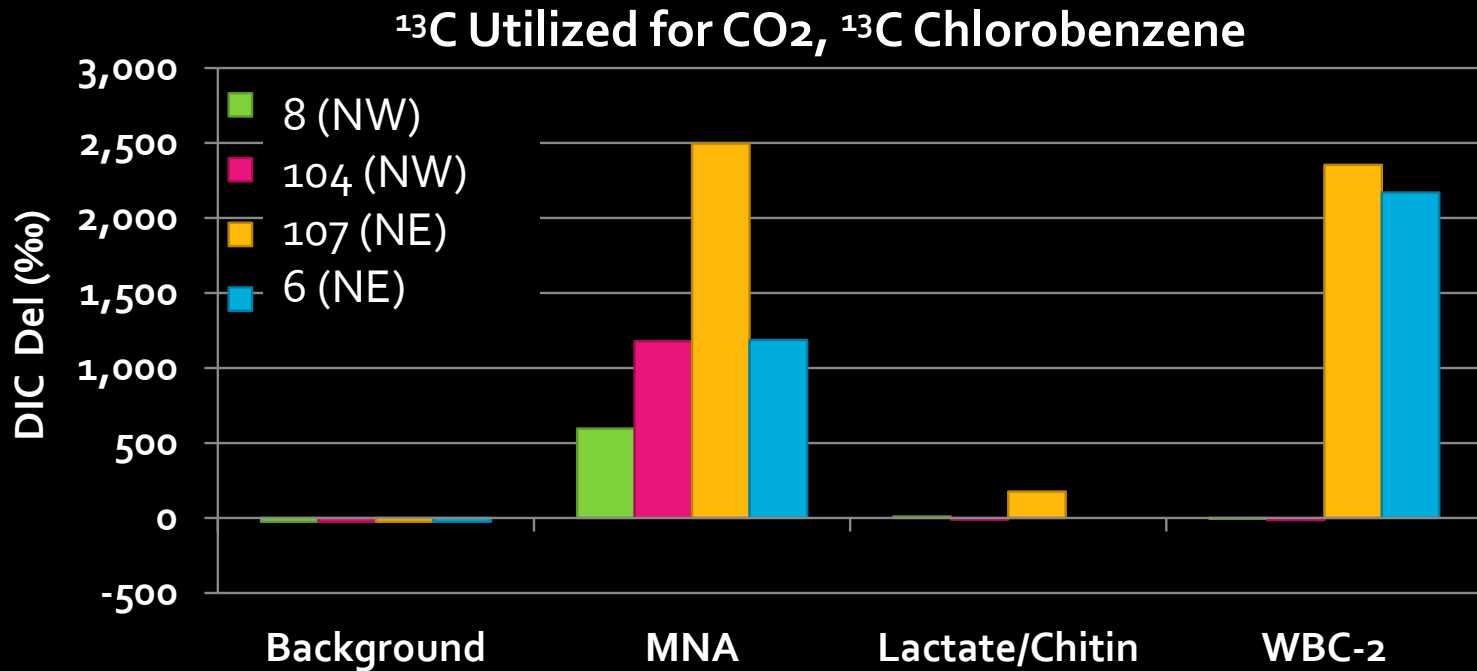


**Bioreactor  
polypropylene  
support matrix  
for biofilms**

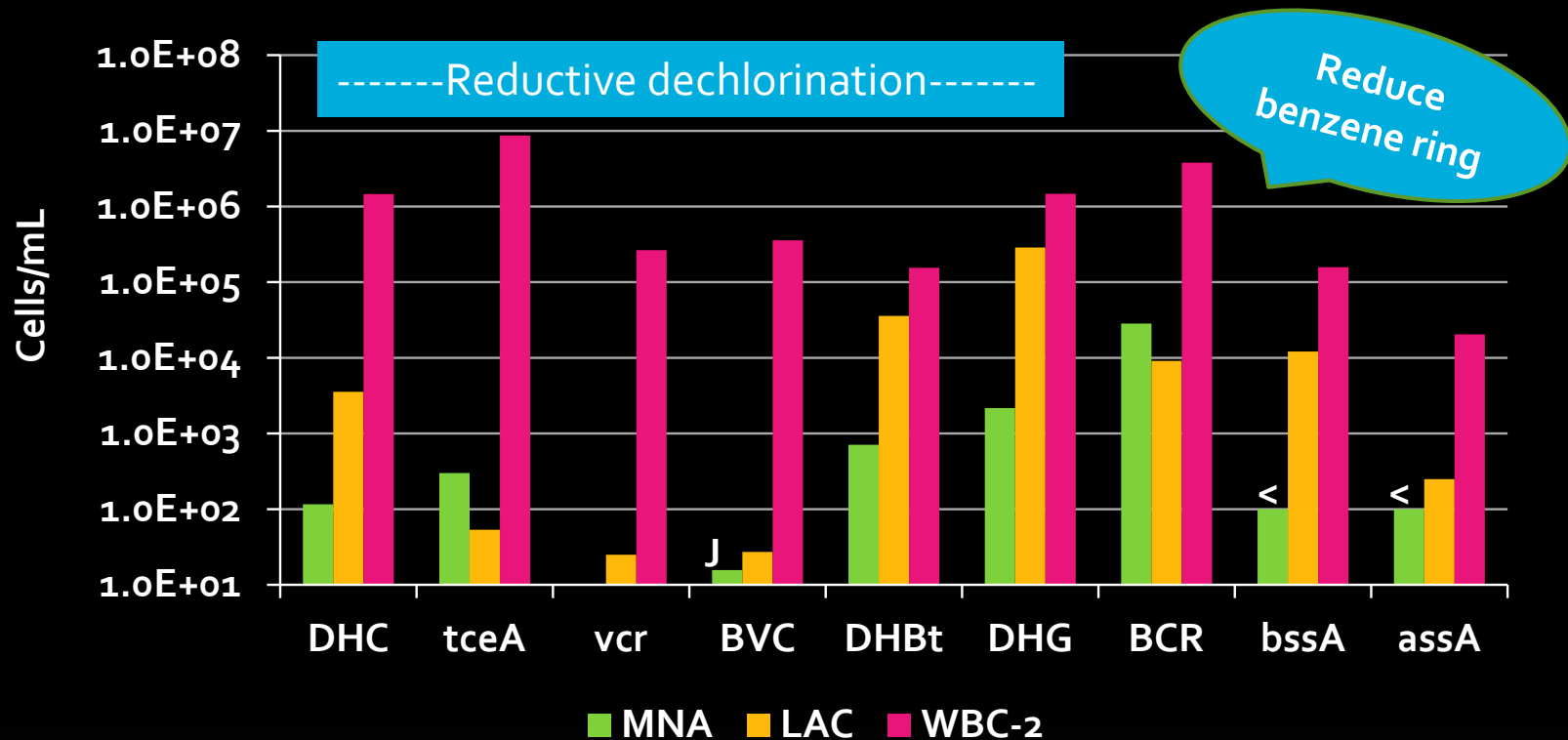




Bio-Traps:  
<sup>13</sup>C-labeled  
Chloro-  
benzene



# QuantArray Microbial Analysis- Anaerobic



## Reductive dechlorination:

DHC, Dehalococcoides spp.

TCE, tceA reductase

VCR, vinyl chloride reductase

BV<sub>1</sub>, vinyl chloride reductase

DHBt, Dehalobacter spp.

DHG, Dehalogenimonas spp.

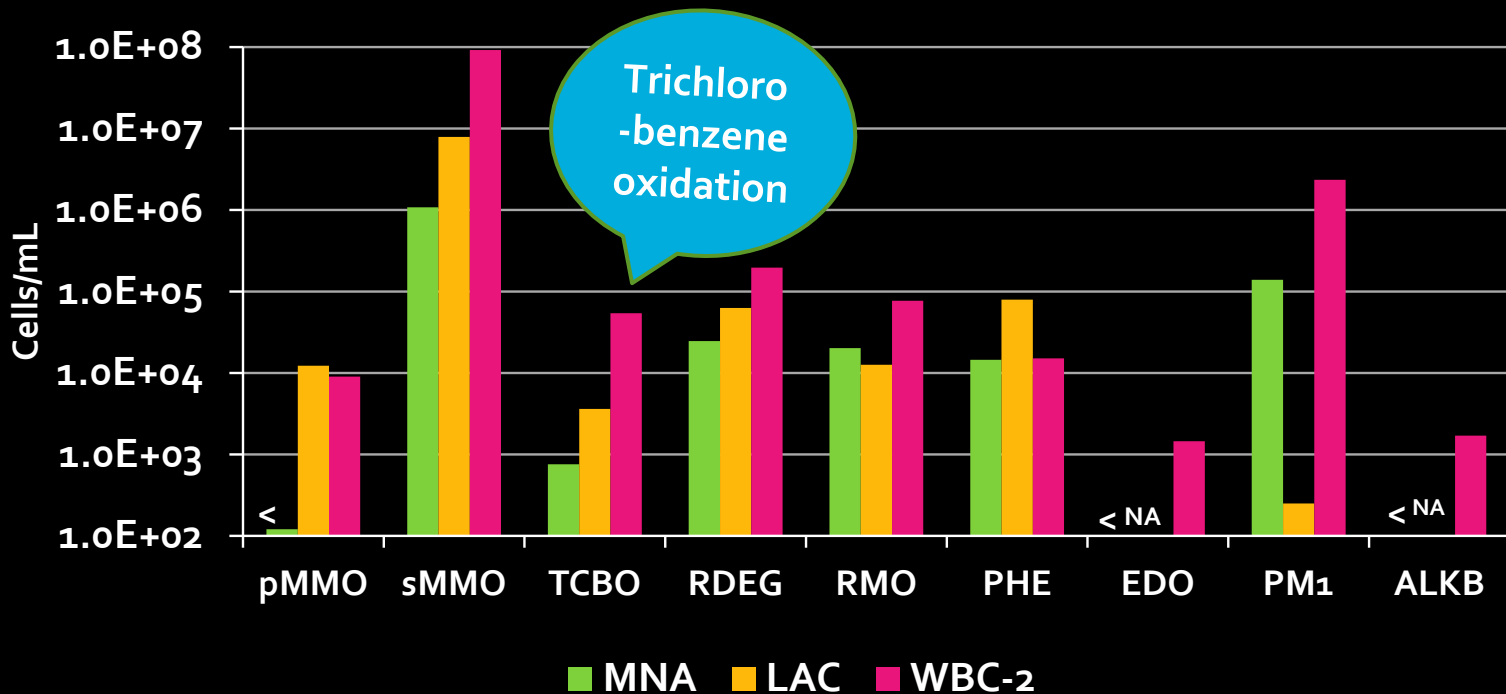
## BTEX, PAHs and alkanes:

BCR, Benzoyl coenzyme A reductase

bssA, benzylsuccinate synthase

assA, alkylsuccinate synthase

# QuantArray Microbial Analysis- Aerobic



pMMO, particulate methane monooxygenase

sMMO, soluble methane monooxygenase

TCBO, trichlorobenzene dioxygenase

RDEG, toluene monooxygenase 2

RMO, toluene monooxygenase

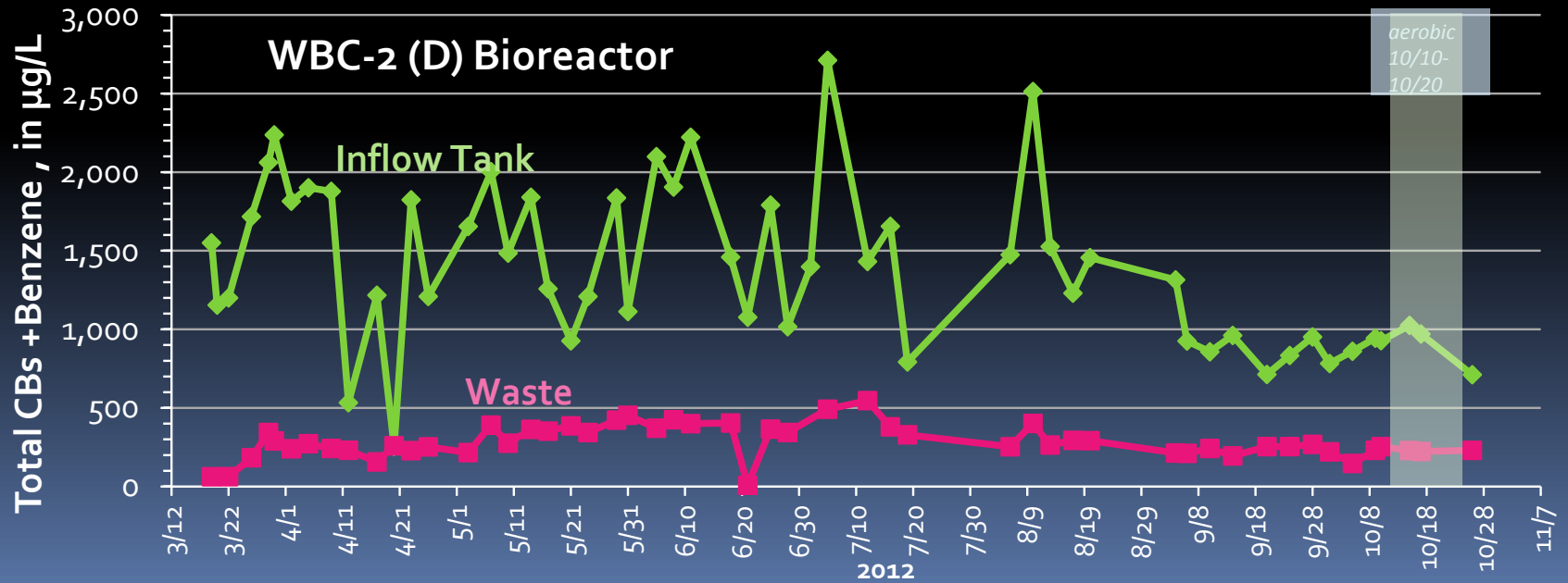
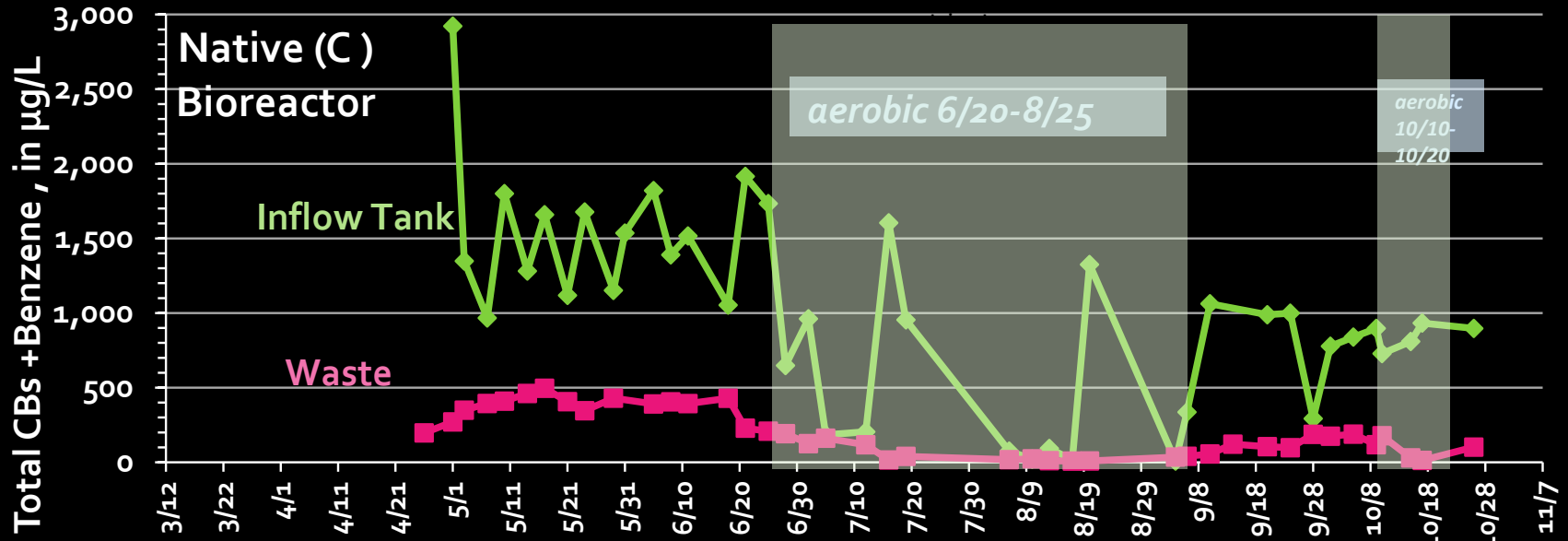
PHE, phenol hydroxylase

EDO, ethylbenzene/isopropylbenzene dioxygenase

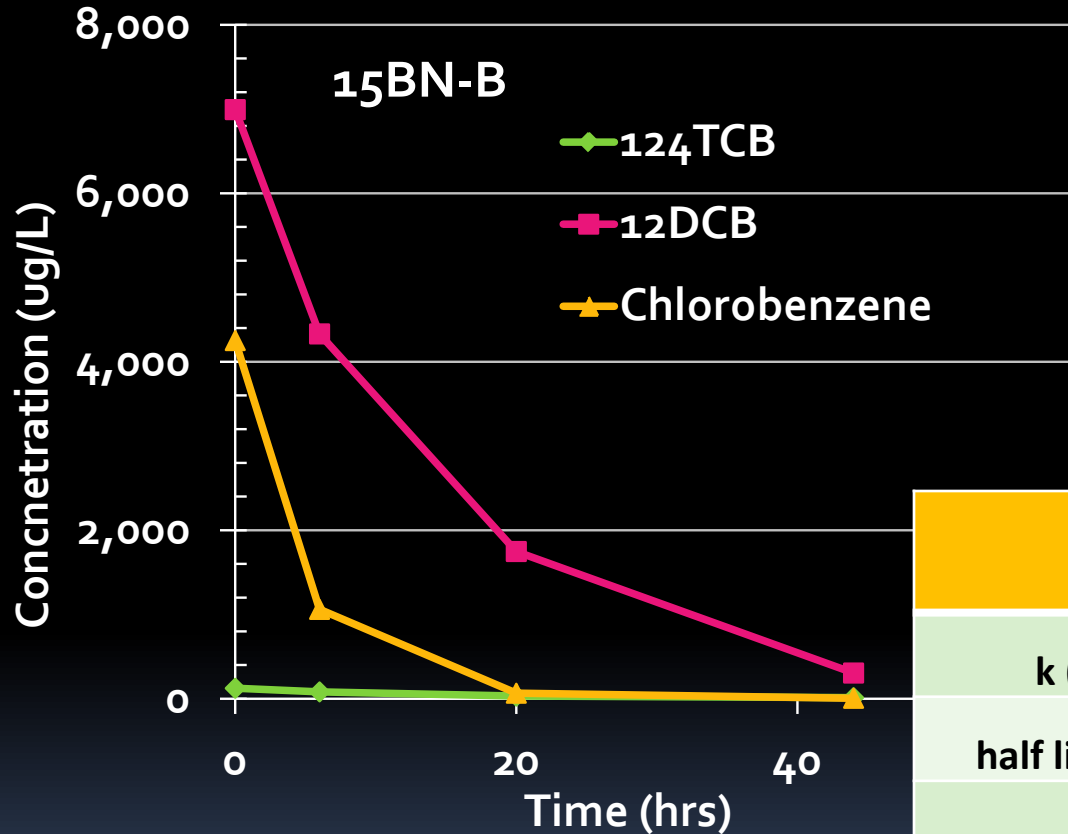
PM<sub>1</sub>, Methylibium petroliphilum PM<sub>1</sub>

ALKB, alkane monooxygenase

# SCD Bioreactors



# Aerobic Native Culture (15B)



	124TCB	12DCB	CB
k (per hr)	0.051	0.071	0.15
half life (hrs)	13.6	9.8	4.6
r <sup>2</sup>	.972	.999	.968

# Reactive Barrier Concept

## Aerobic Zone

$O_2$  diffusion from surface and dispersed throughout from plant roots



Sand Grains



GAC – sorbent and biofilm support



Anaerobic Biofilm Predominant

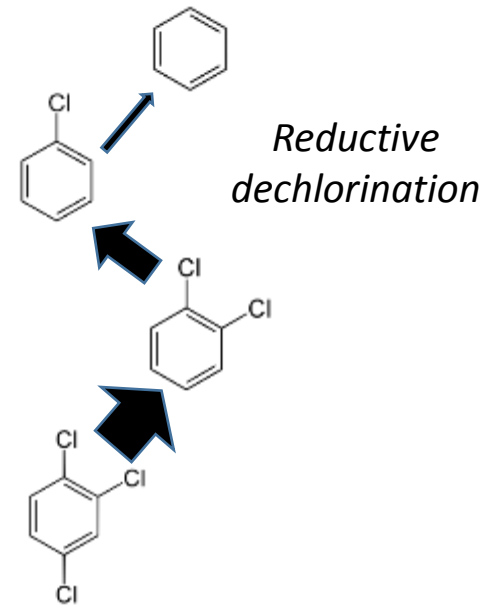
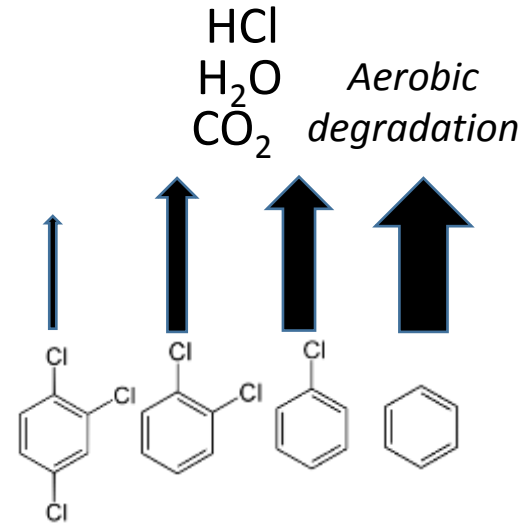
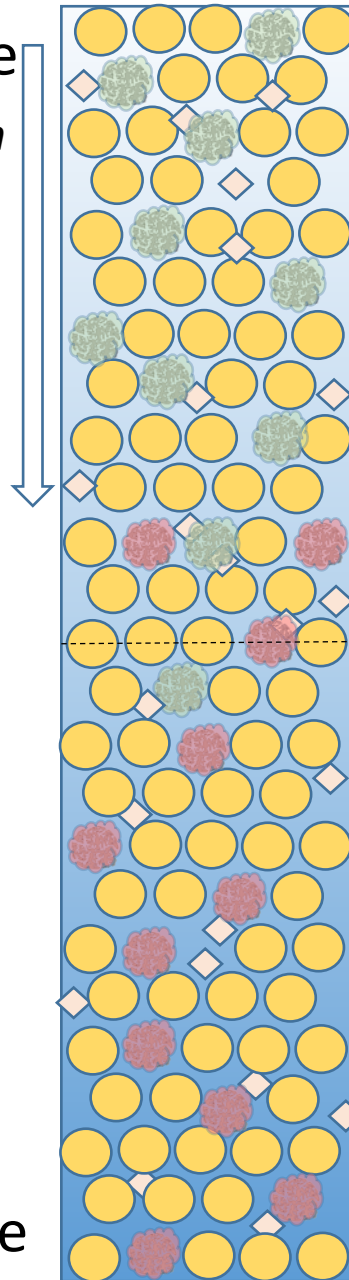


Aerobic Biofilm Predominant



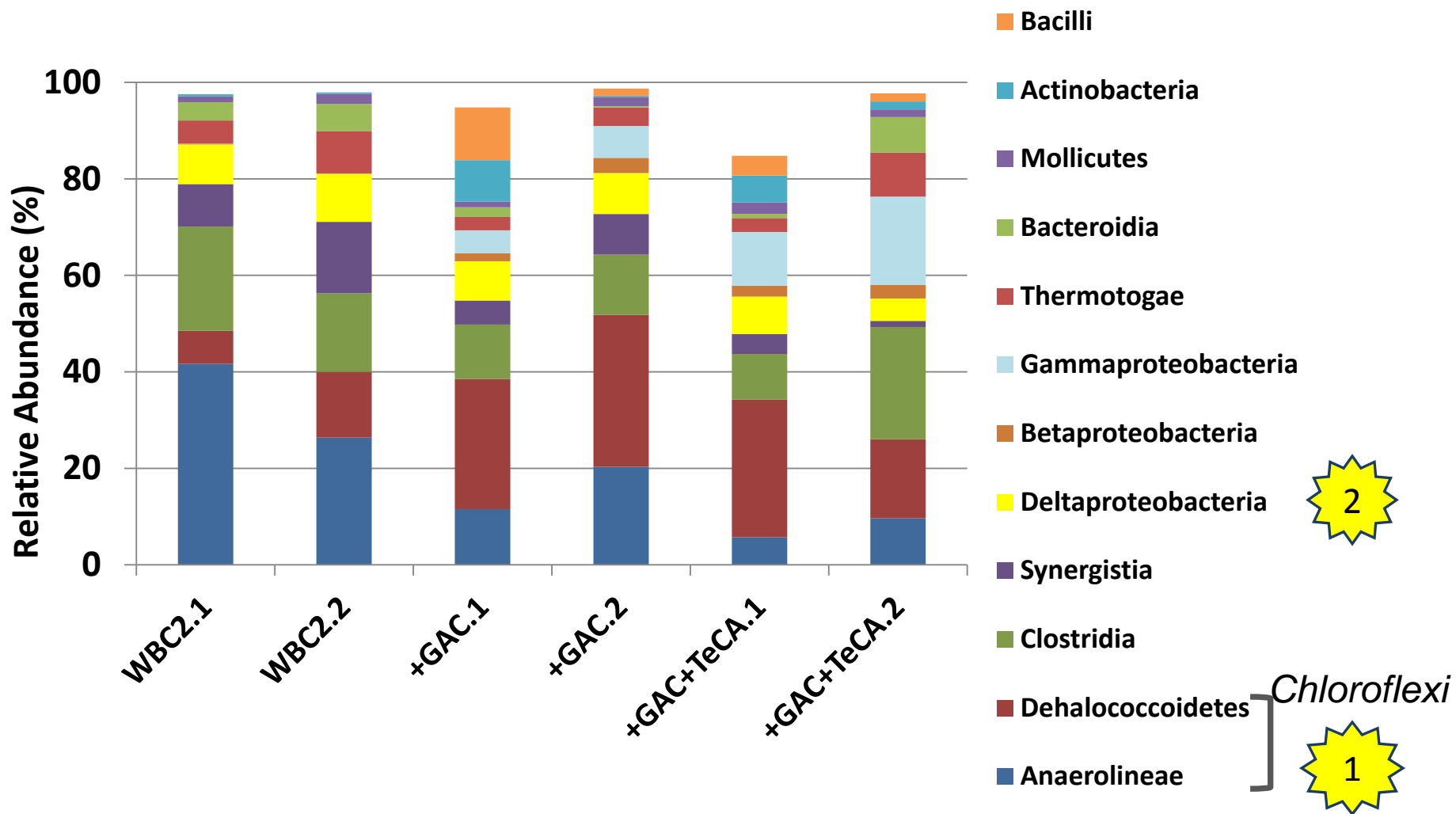
Chitin – Slowly dissolving C source

## Anaerobic zone

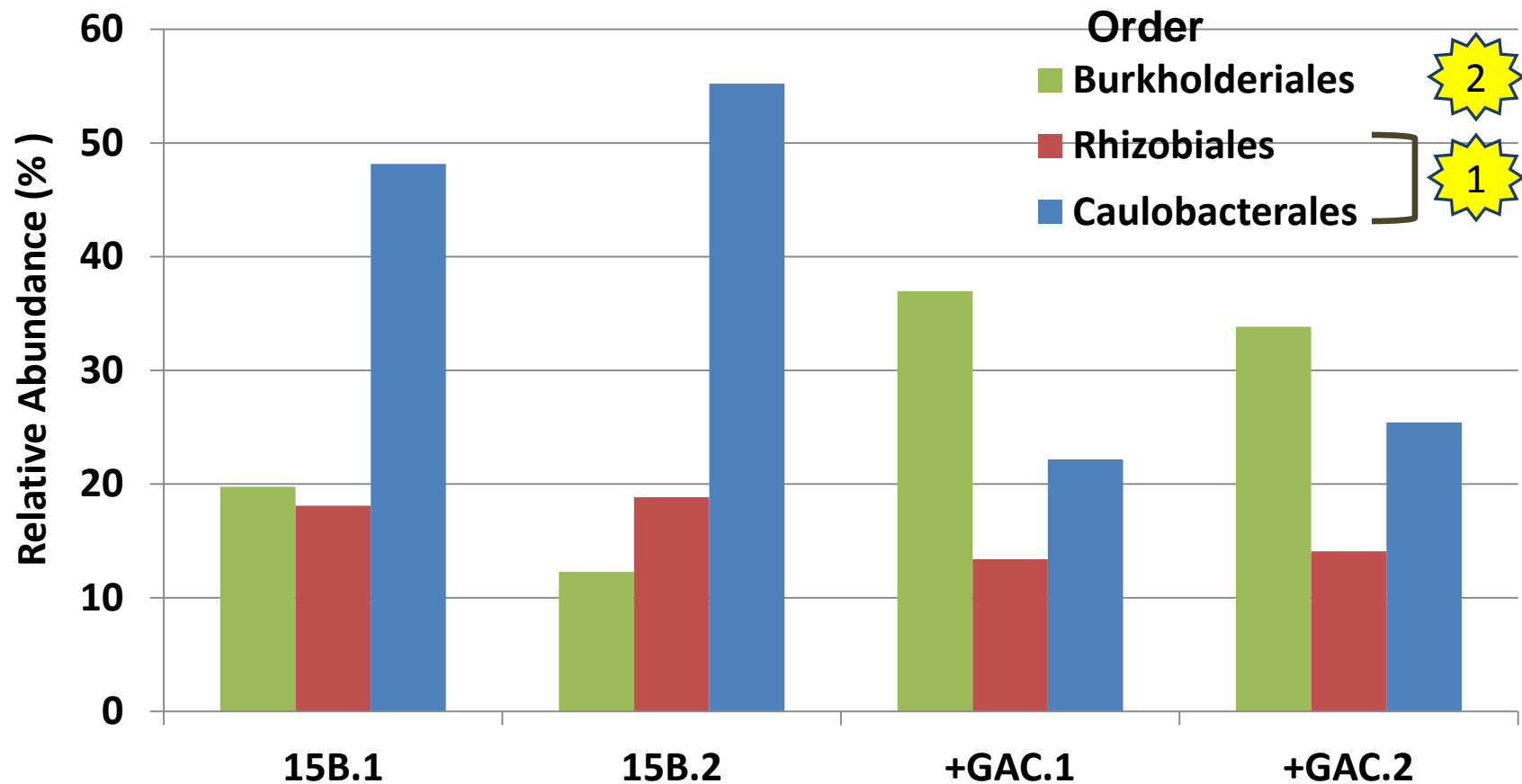


GW flow

# GAC with WBC-2: Classes >1% Abundance



## GAC with 15B: Proteobacteria, Order

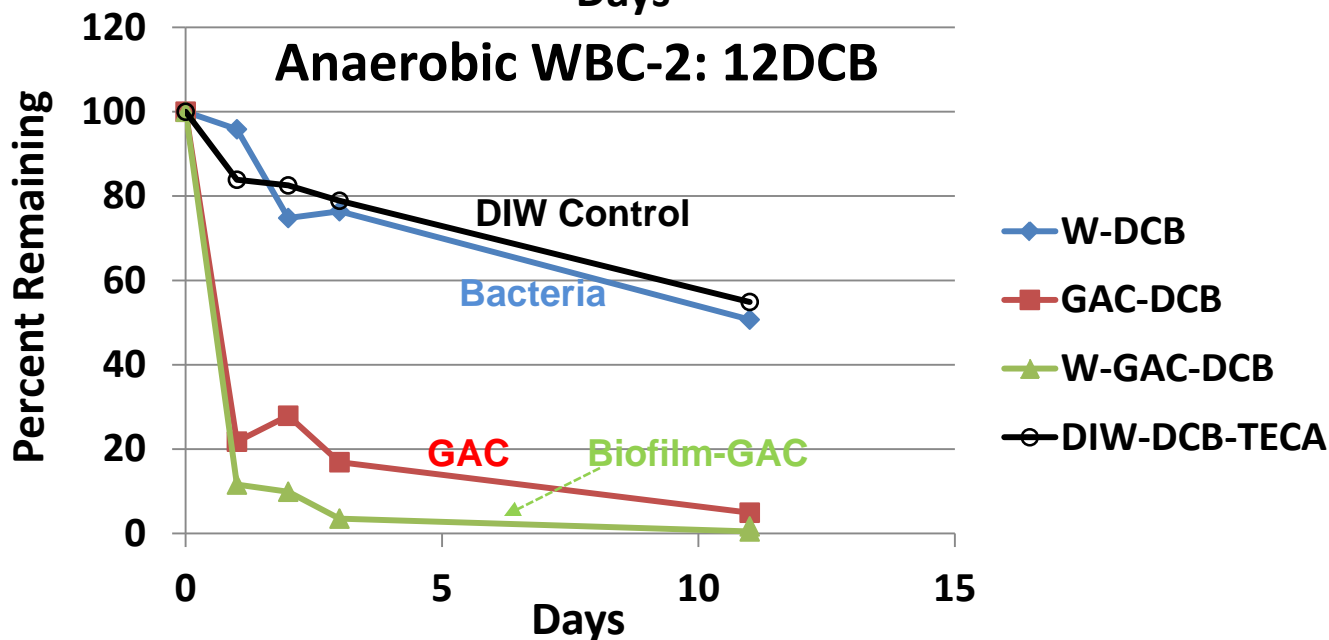
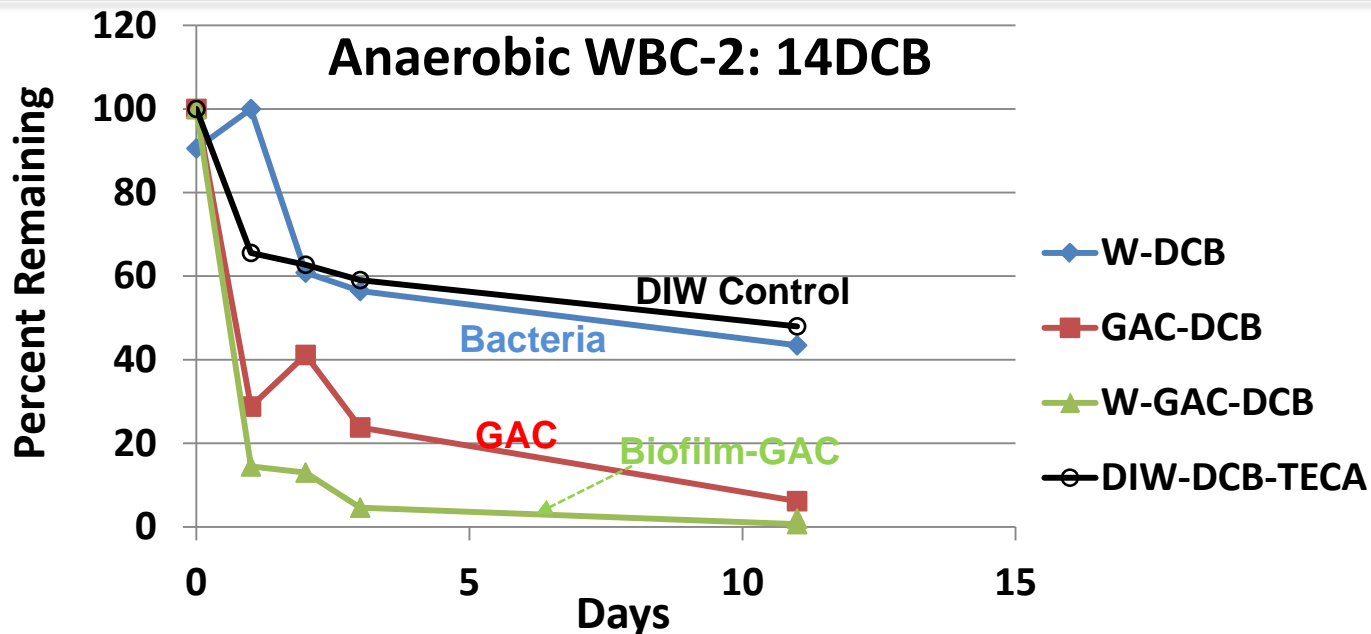


- *Significant increase in the Betaproteobacteria group Burkholderiales on GAC.*



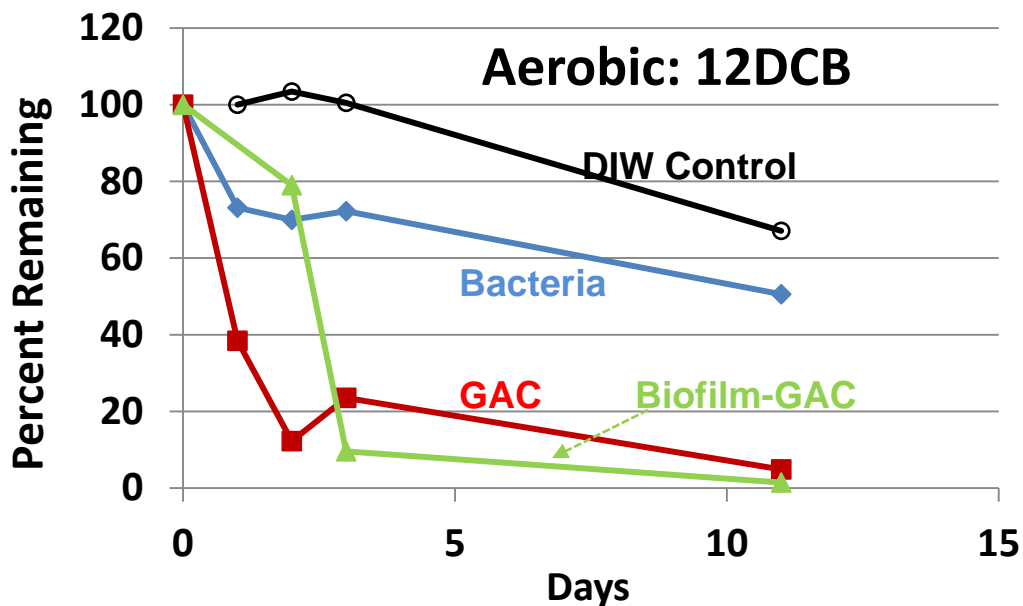
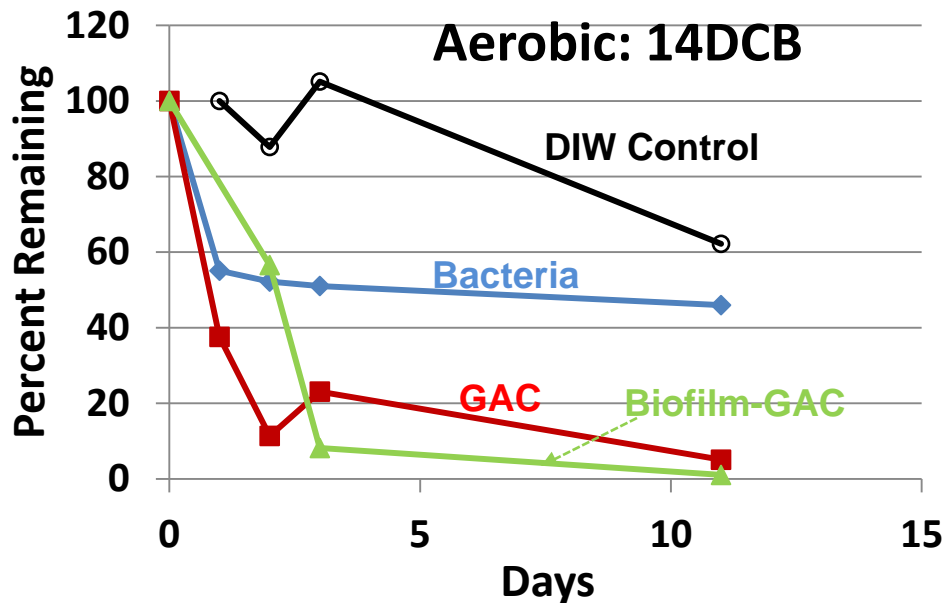
# Microcosm Results: Anaerobic WBC-2 Biofilm on GAC

- Slight decrease in CBs with culture in mineral media compared to DIW
- Rapid sorption to GAC with and without anaerobic biofilm
- Distinctly faster overall CB removal in biofilm-GAC



# Microcosm Results: Aerobic 15B Seeded on GAC

- *Delay in sorption to GAC with aerobic biofilm*
- *Slightly faster overall CB removal in biofilm-GAC*



# Column Testing

**Sand Columns:  
Medium Sand+  
5 % GAC +  
3 % Chitin**



**Sediment Columns:  
in progress- no data yet  
5 % GAC +  
3 % Chitin**

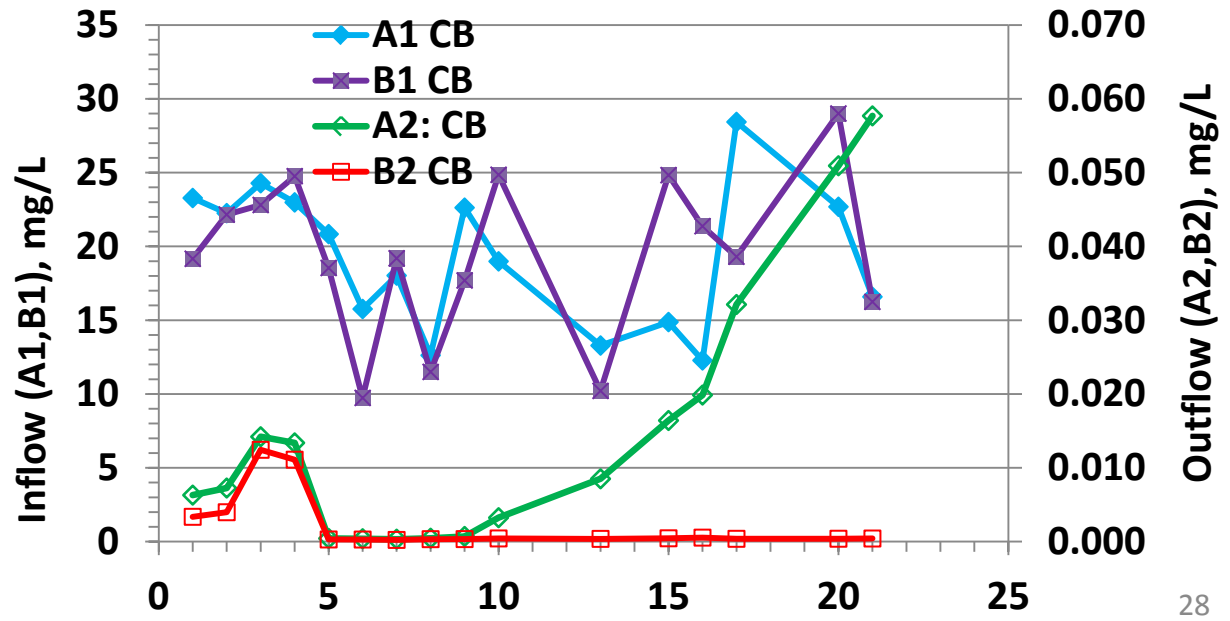
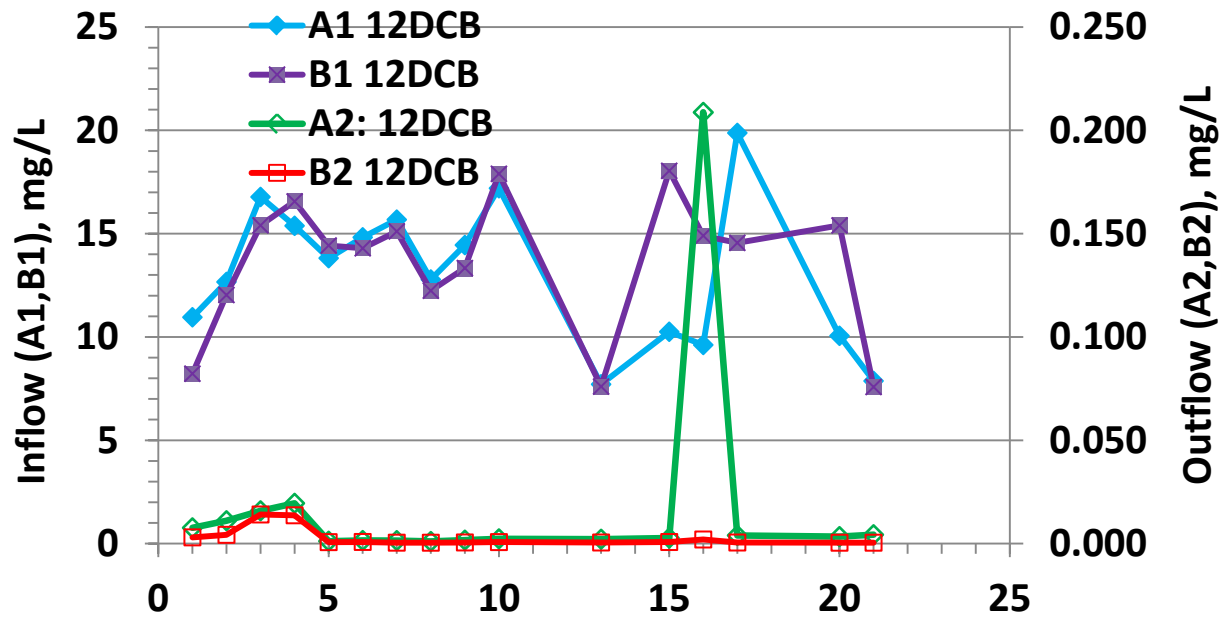


# Sand Columns:

Medium Sand+  
HRT= 0.45 day

A= WBC2-GAC  
B= WBC2+15B-GAC

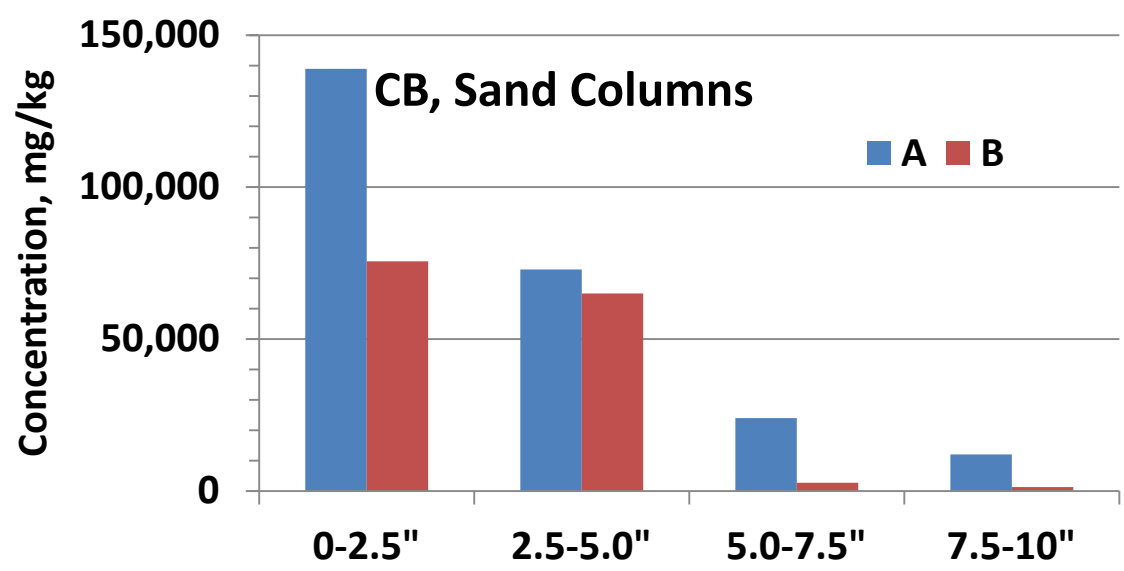
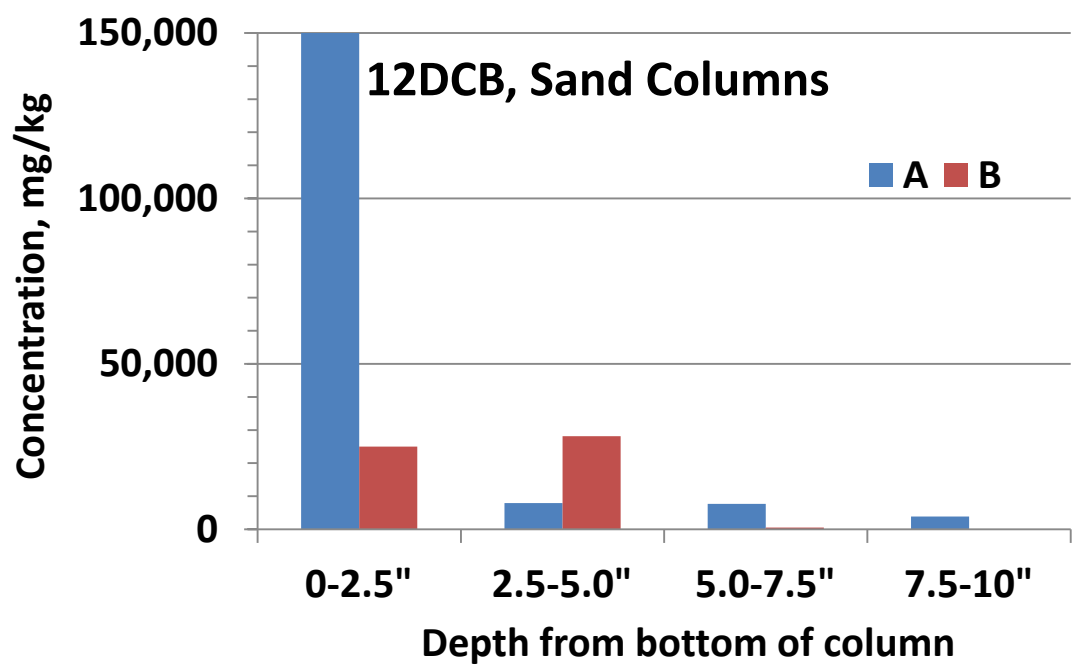
- Outflow VOC concentrations very low in both columns
- Greater CB removal column with both the anaerobic and aerobic culture



# Sand Columns: Sediment methanol extract analysis

**A= WBC2-GAC**  
**B= WBC2+15B-GAC**

*Generally, less VOCs  
remaining in the columns  
that contained both the  
WBC-2 and 15B cultures*

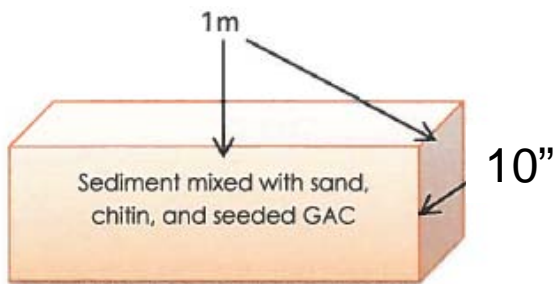




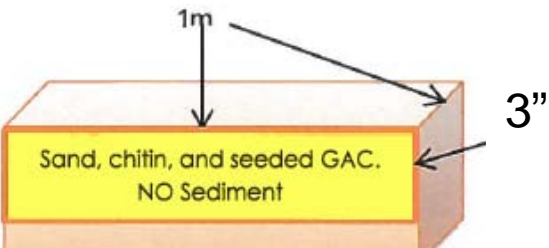
*.....lab testing ongoing but also  
started small-scale field pilot tests*

# Barrier Reactive Pilot Test Plots

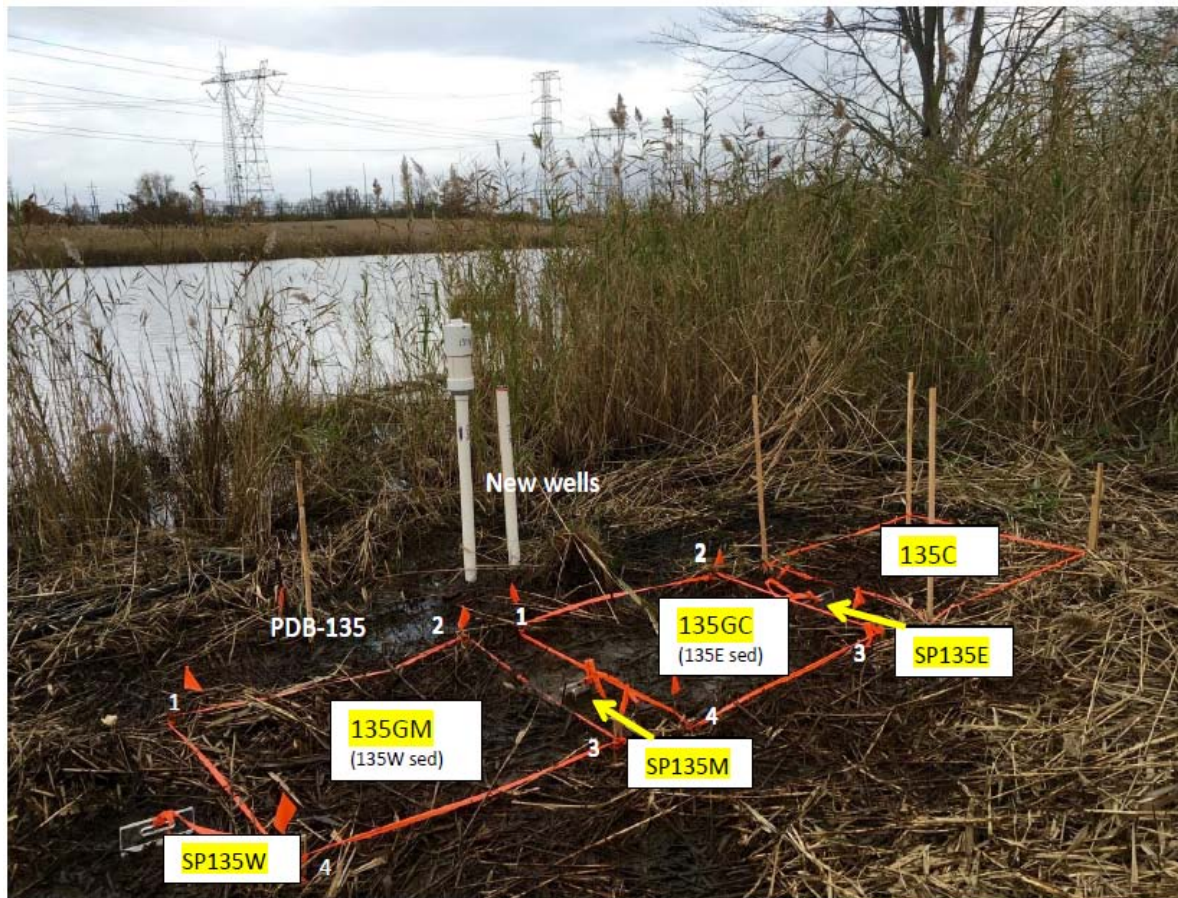
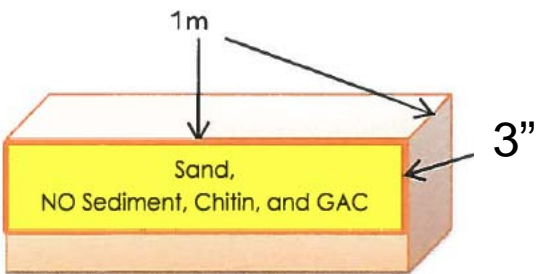
**GM**



**GC**



**C**



TOTAL	Sand	Chitin	GAC
pounds	783	30	43

Site 135 test area with 3 plots and pre-installation sampling.

40 L of each culture



15B aerobes grown in lab in 5 days



WBC-2 in anaerobic cylinder from Sirem Lab  
(20L mixed with DI-H<sub>2</sub>O for GAC seeding)





Buckets of pre-measured sand-chitin-seeded GAC dumped in plot and mixed into sediment to depth of 10 inches with small auger or “egg-beater” attachments on drill.

# Acknowledgements

Site characterization



Feasibility evaluation



Technology development



Pilot test remediation

## USGS MD-DE-DC

### Fate and Bioremediation Team

Dr. Michelle Lorah

Jessica Teunis

Mastin Mount

Michael Brayton

Dr. Charles Walker

Roberto Cruz

Emily Majcher

Anna Baker

Luke Myers

### NRP Collaborators:

Dr. Isabelle Cozzarelli

Dr. Denise Akob

## Johns Hopkins University

Dr. Ed Bouwer

Steven Chow, PhD student



## Geosyntec Consultants

Dr. Neal Durant

Dr. Amar Wadhawan

