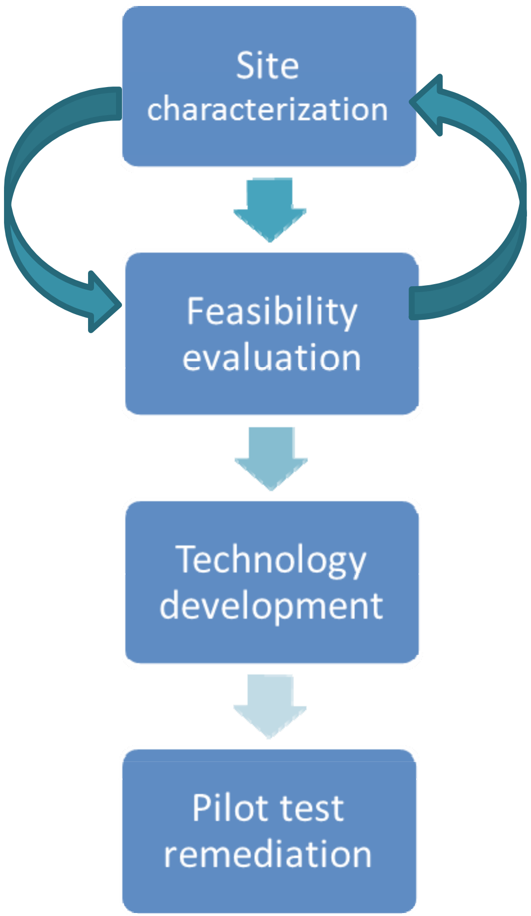
Technologies for Biogeochemical and Hydrogeologic Characterization and Their Integration for Site Remediation



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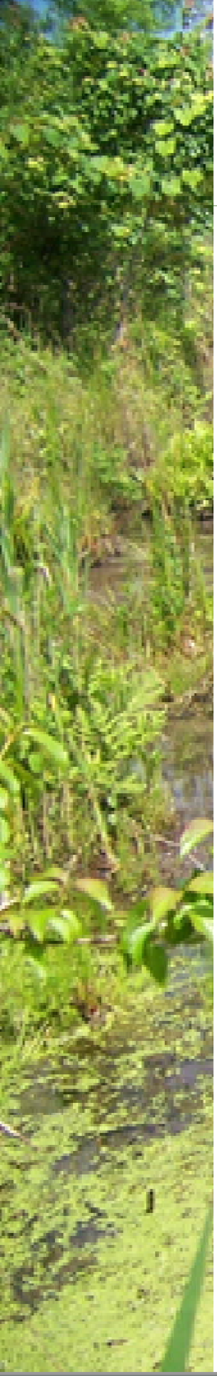
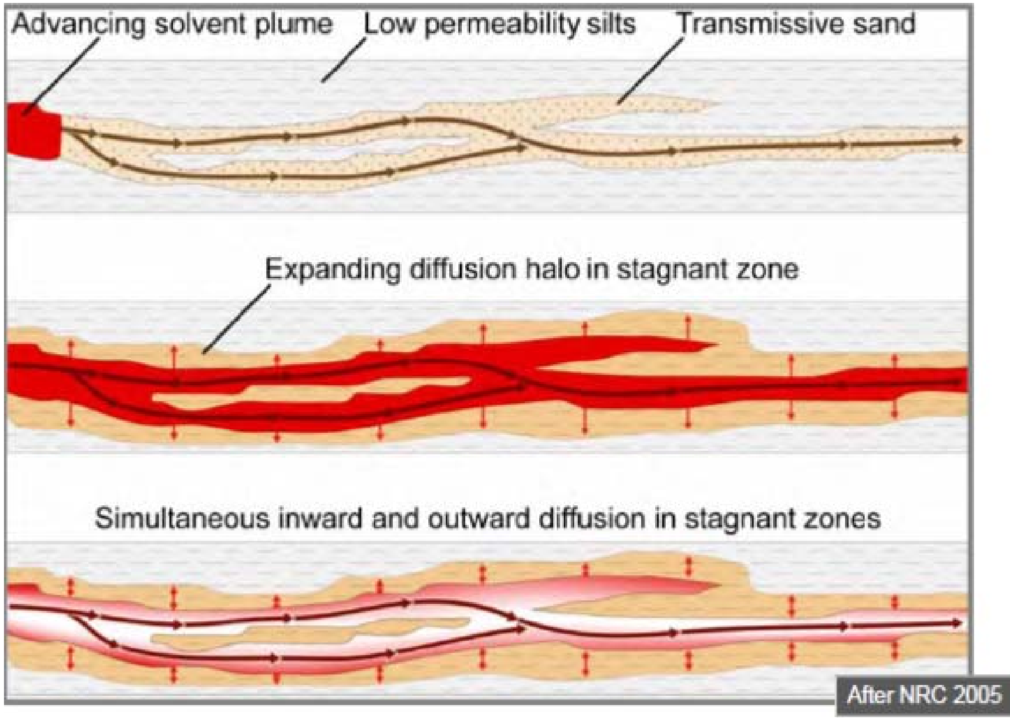


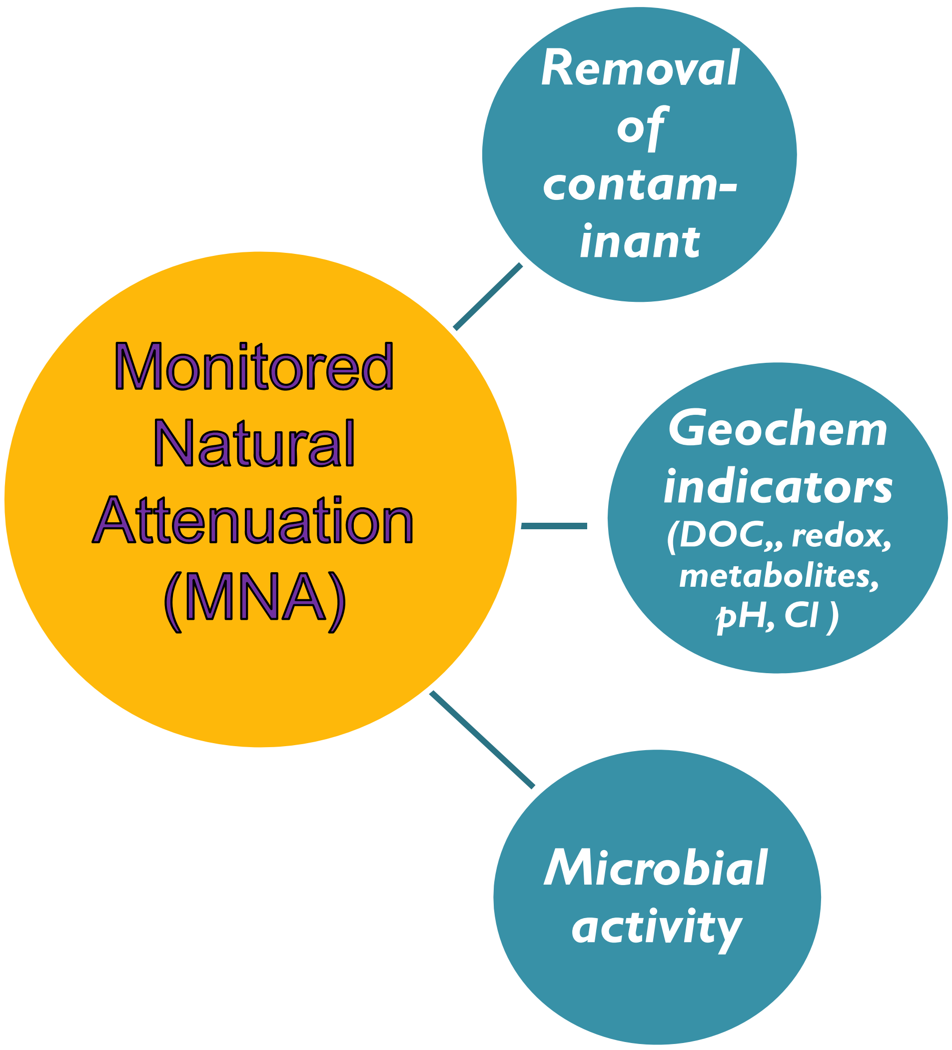
- Complex hydrogeology
  - fractured rocks
  - low permeability layers; rock matrix
- Difficult contaminant mix
  - DNAPL
  - dissolved and highly sorbed mix
  - emerging contaminants
- Sensitive habitat or location
  - wetlands
  - bottom sediments

Biogeochemical Characterization- Why?

- Provide the remedy- MNA, bioremediation, biogeochemical reduction
- Secondary effects- alteration of natural biogeochemical conditions, or from presence of secondary contaminants
- Long-term efficiency
  - changes in transmissive plume with remediation
  - low permeability zones
  - "slow" processes key (back diffusion, sorption and desorption, abiotic and biotic degradation reactions)

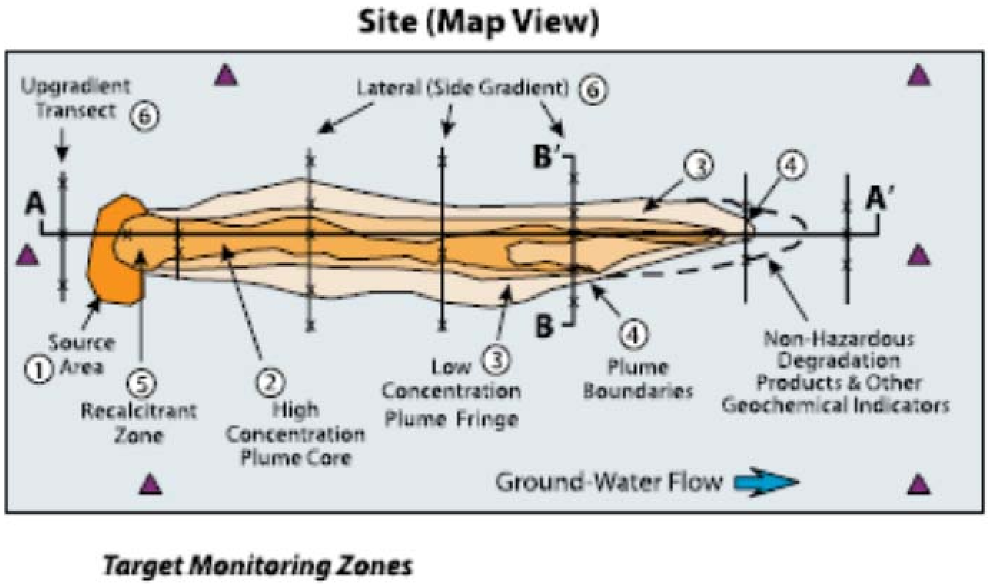


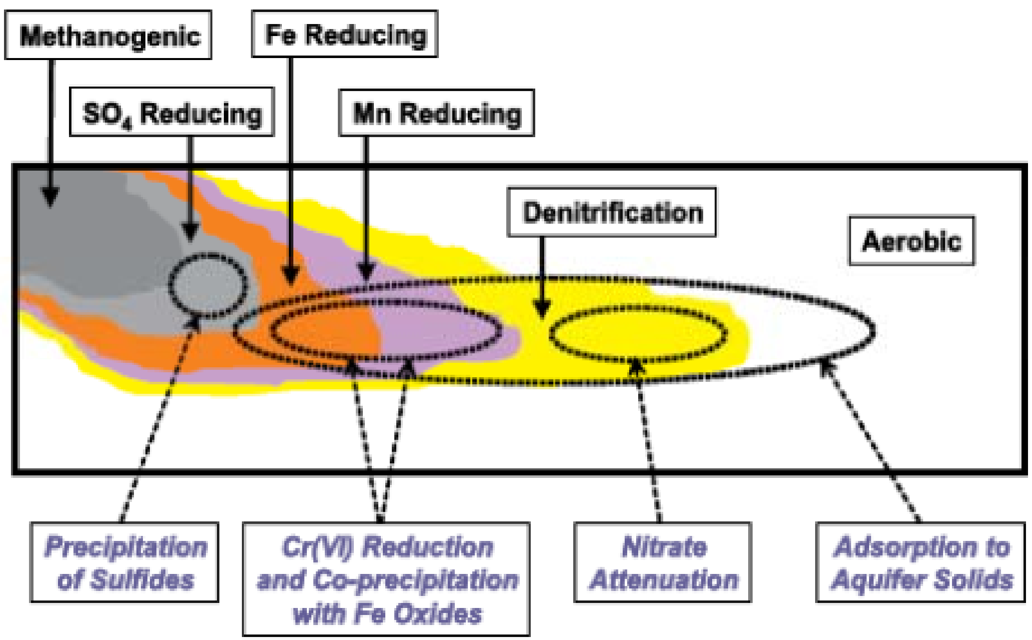
Biogeochemical Characterization-How?



- MNA protocols provide good framework and tools
- Relevant protocols for organics, radionuclides, and non-radionuclide inorganic
- Three lines of evidence for chlorinated solvents

USGS





from *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volumes 1 and 2*

Considerations

- History and stage of plume evolution
- DNAPL or LNAPL presence
- Sample key parts of plume, including "transition zones"
- Multilevel sampling- high resolution
- Spatial and temporal variability
- Interaction with and formation of solids

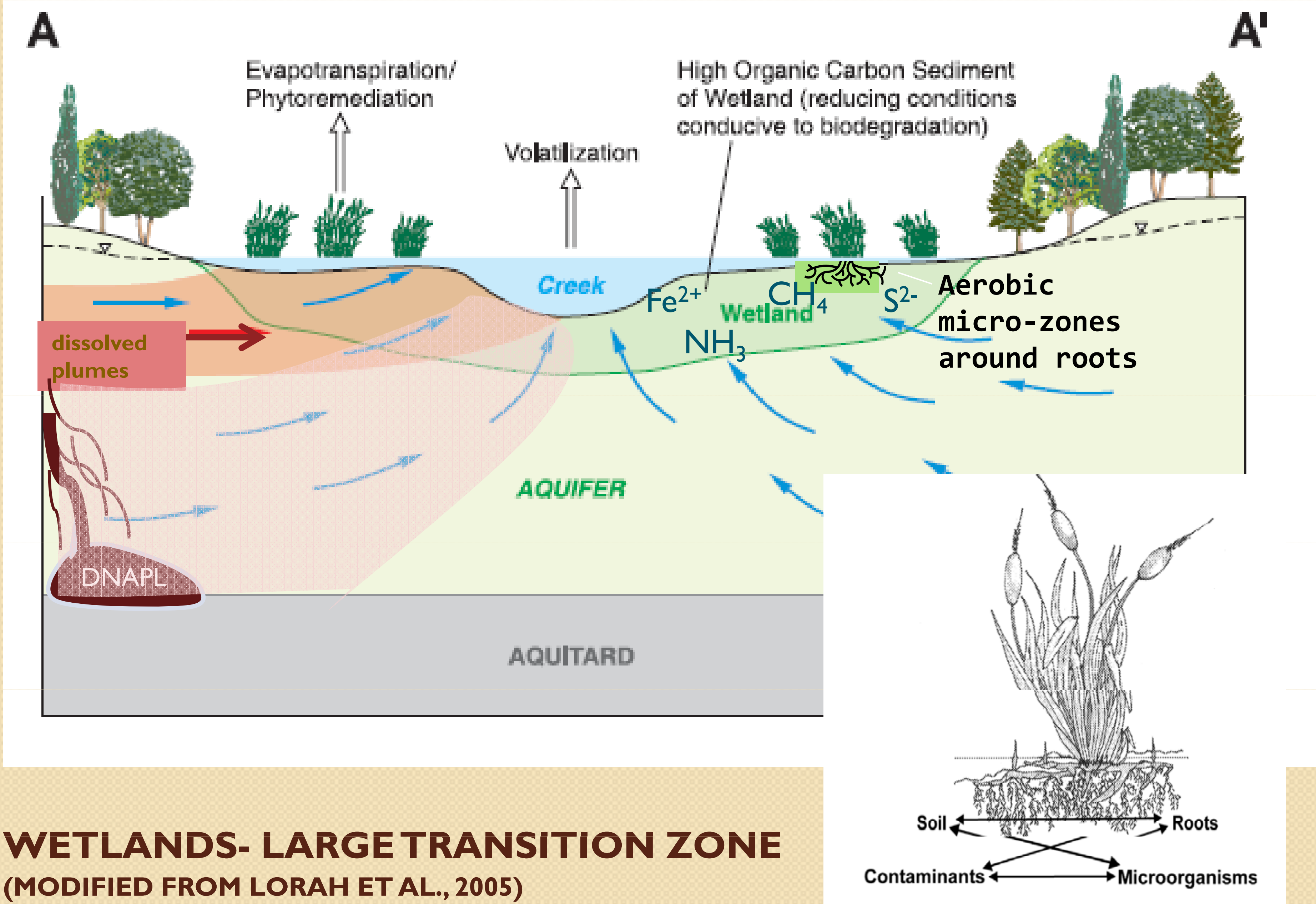


Fig. 1. Possible interactions in the root zone of wetlands for wastewater treatment.

WETLANDS- LARGE TRANSITION ZONE

(MODIFIED FROM LORAH ET AL., 2005)

Canal Creek Area, Aberdeen Proving Ground

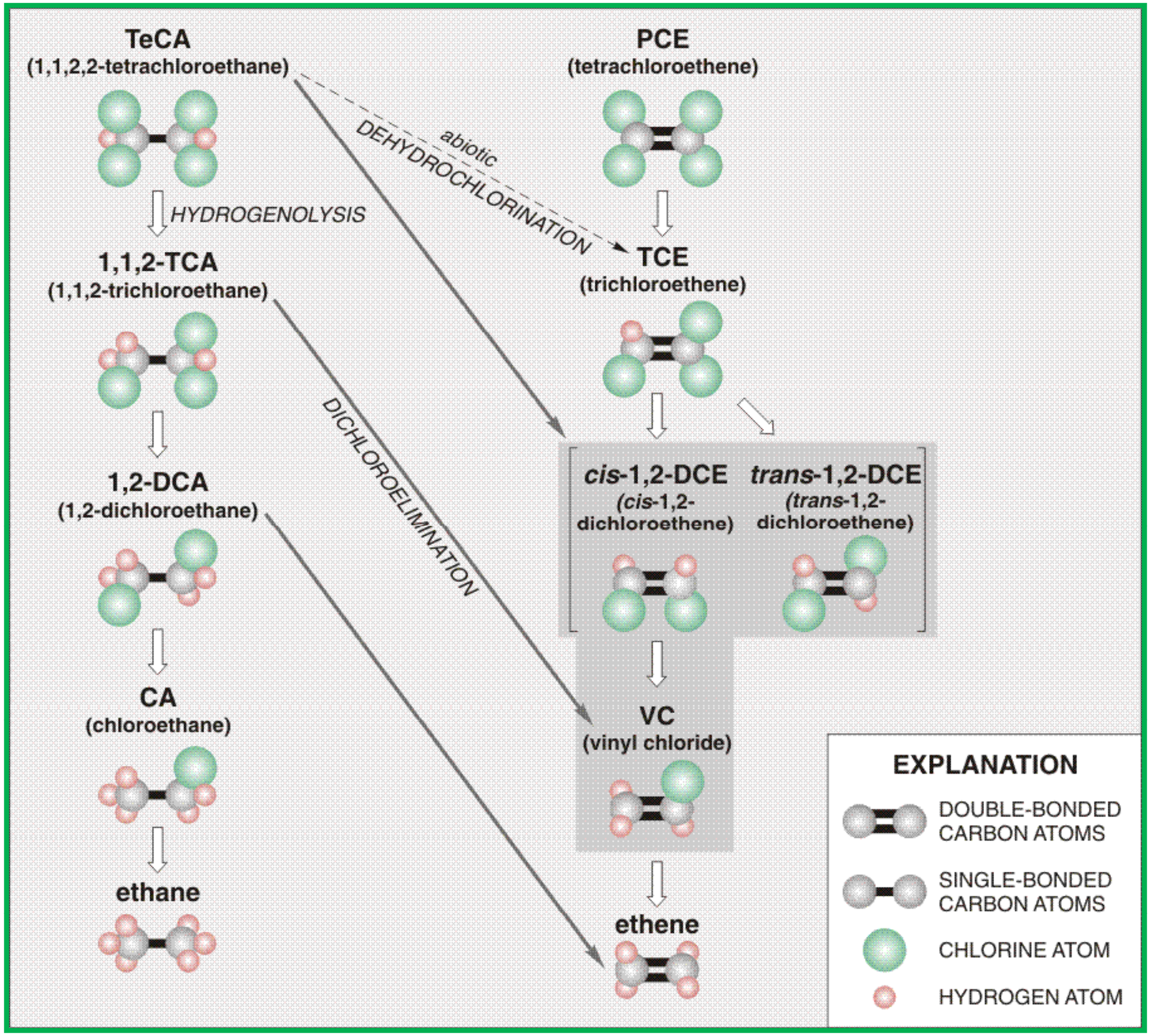
Chlorinated VOCs- Anaerobic degradation

Parent Contaminants

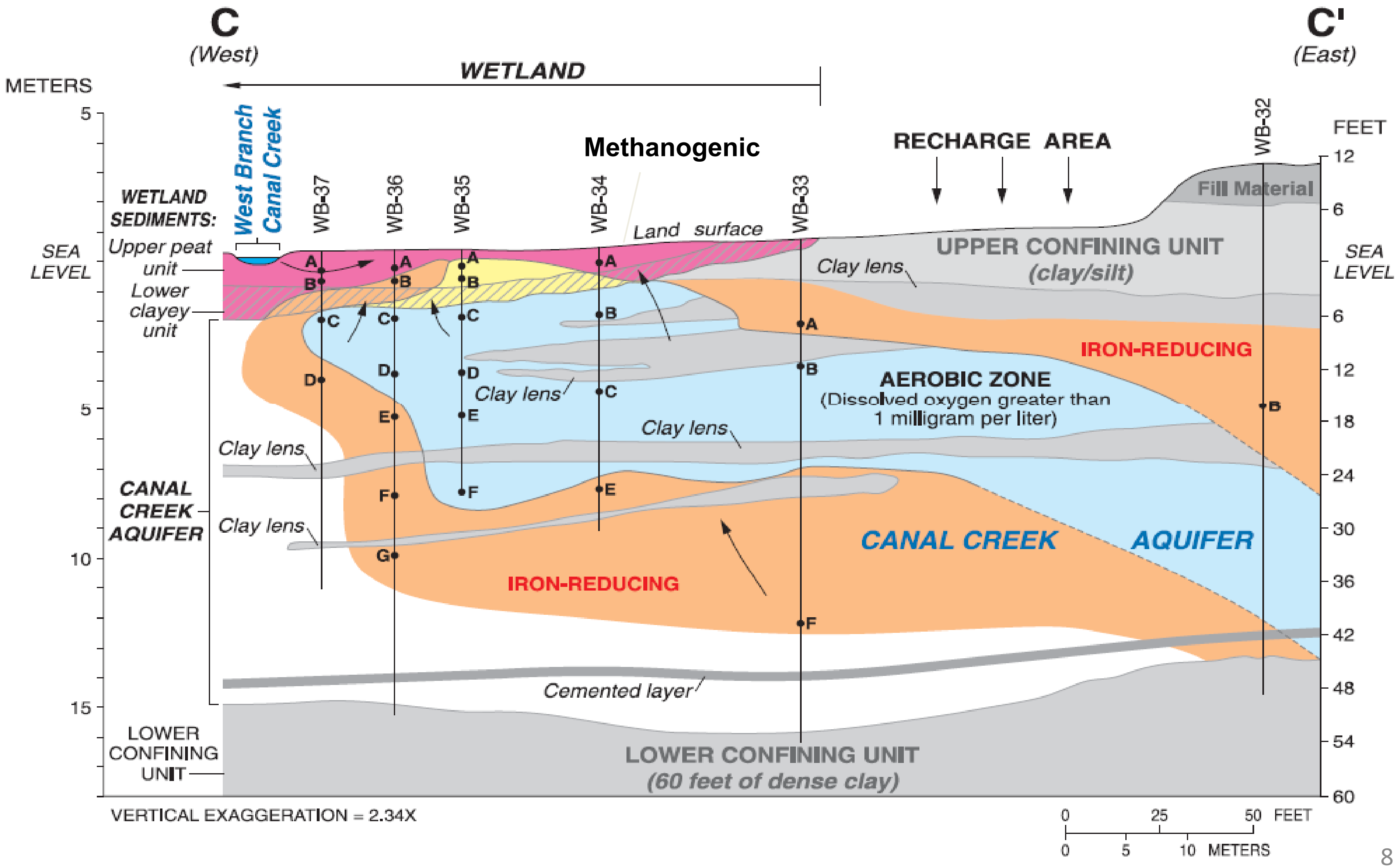
Chlorinated ethanes:
HCA= hexachloroethane
PtCA= pentachloroethane
1122TeCA= 1,1,2,2-tetrachloroethane

Chlorinated ethenes:
PCE= tetrachloroethene
TCE= trichloroethene

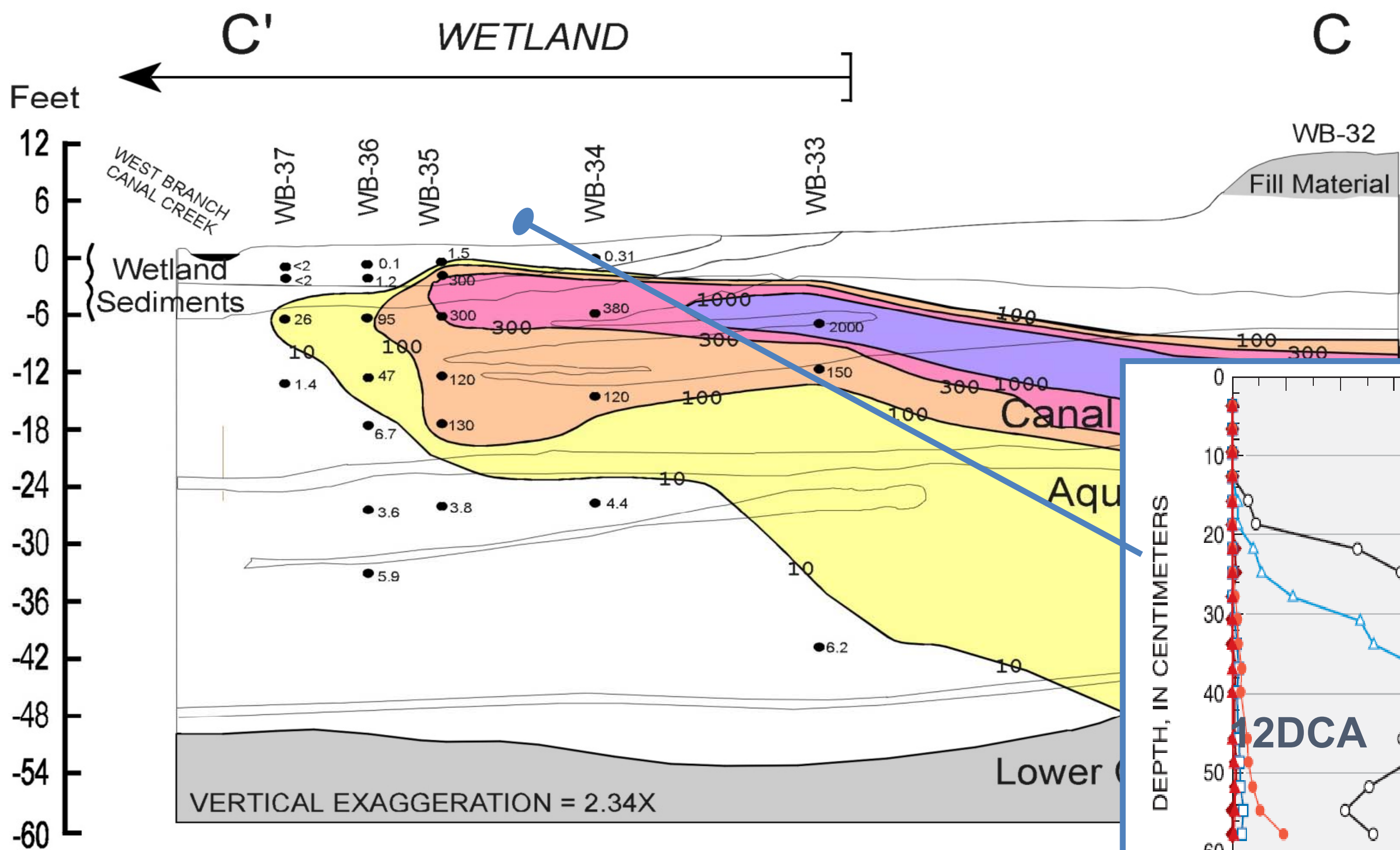
Chlorinated methanes:
CT= carbon tetrachloride
CF= chloroform



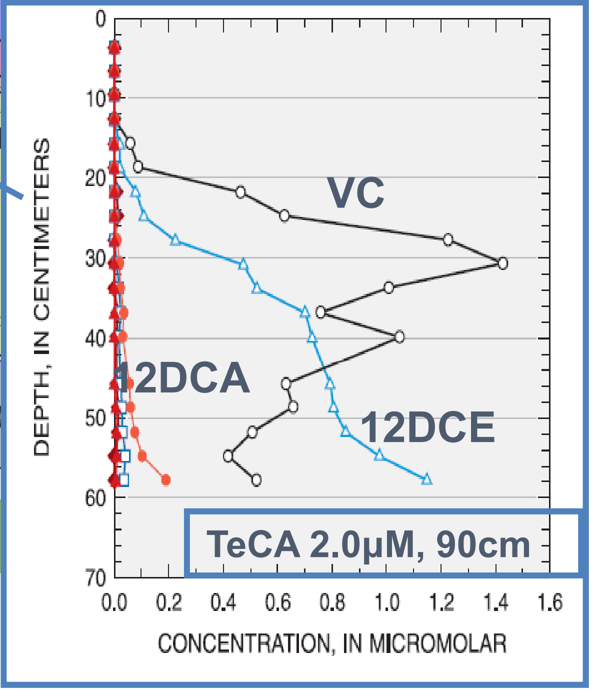
West Branch Canal Creek, Natural Attenuation Study Area: Redox

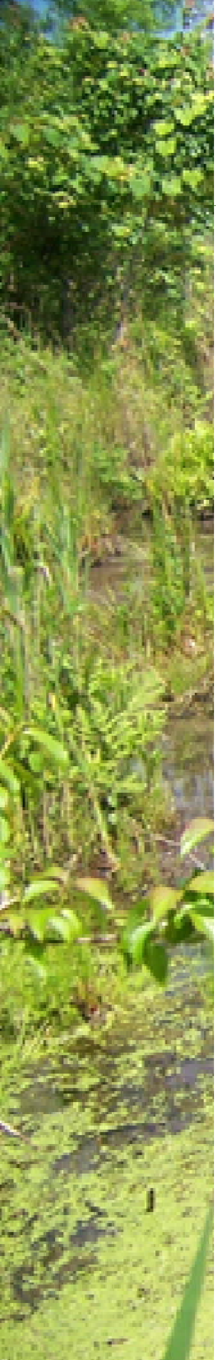


West Branch Canal Creek, Natural Attenuation Study Area: VOCs

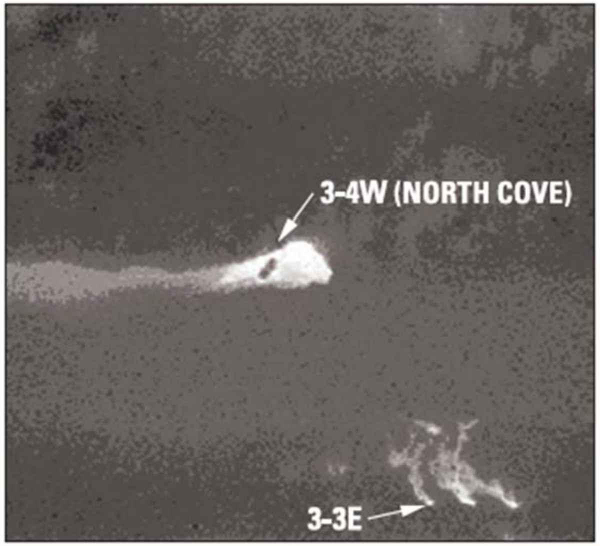


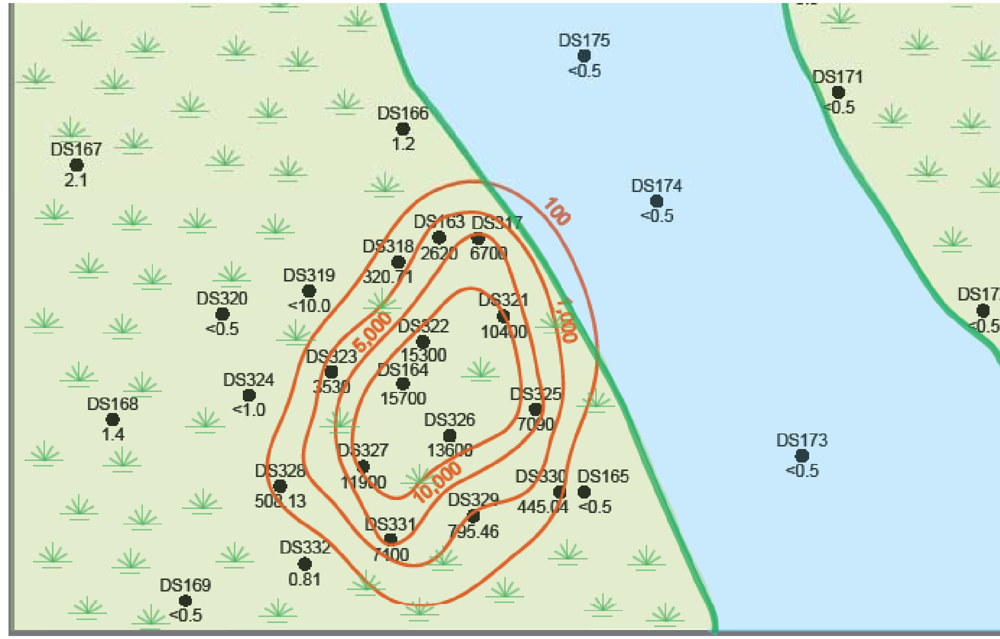
1,1,2,2-Tetrachloroethane (µg/L)

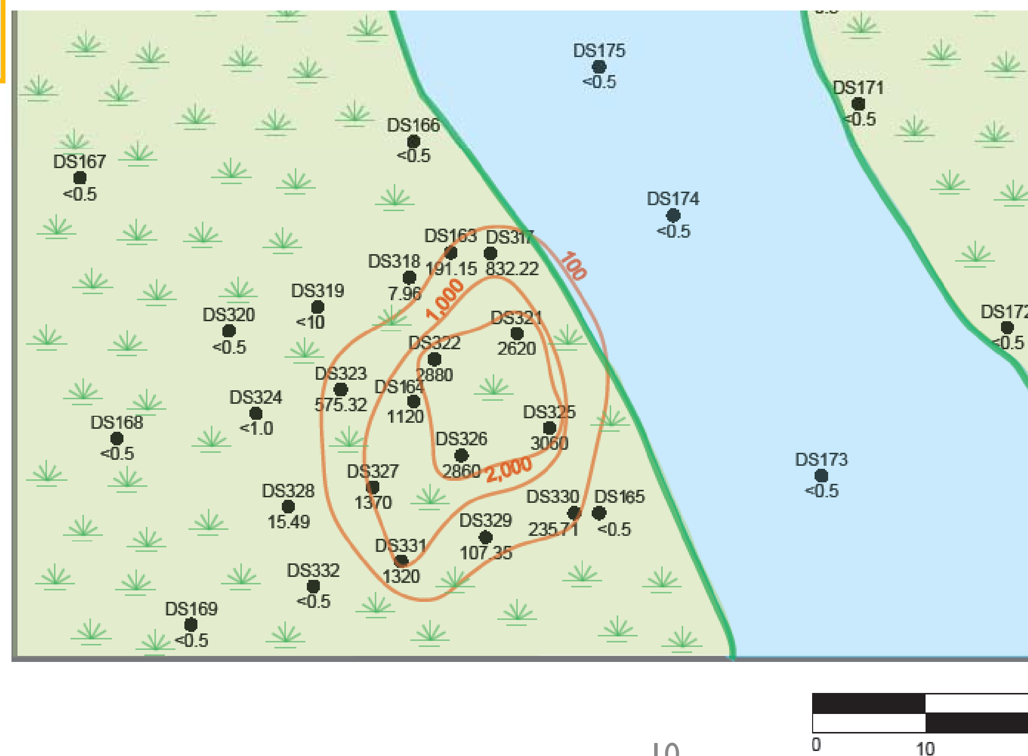




Seep Areas


3-4W (NORTH COVE)
3-3E

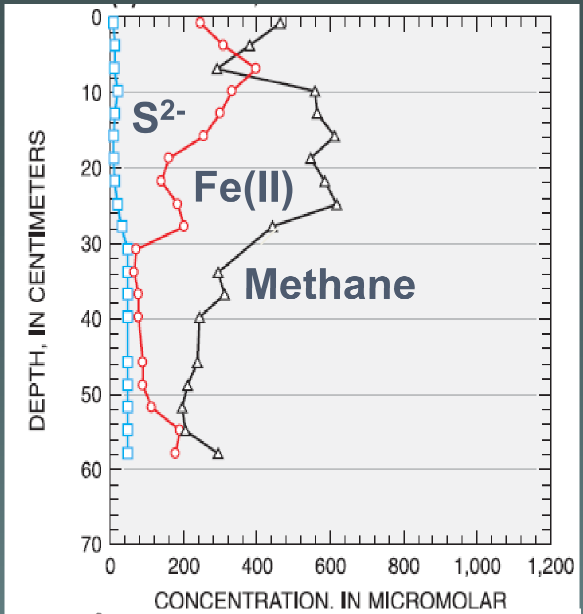

DS175 <0.5
DS171 <0.5
DS166 1.2
DS167 2.1
DS174 <0.5
100
DS163 2620
DS317 6700
DS318 320.71
DS319 <10.0
DS320 <0.5
DS321 10400
5,000
1,000
DS322 15300
DS172 <0.5
DS323 3530
DS164 15700
DS324 <1.0
DS168 1.4
DS325 7090
DS326 13600
DS173 <0.5
DS327 11900
DS328 508.13
10,000
DS330 445.04
DS165 <0.5
DS329 795.46
DS331 7100
DS332 0.81
DS169 <0.5

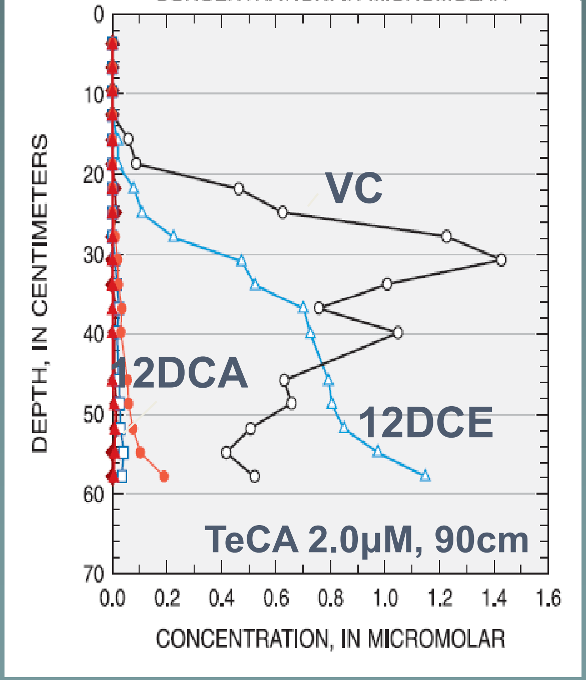

DS175 <0.5
DS171 <0.5
DS166 <0.5
DS167 <0.5
DS174 <0.5
DS163 191.15
DS317 832.22
100
DS318 7.96
1,000
DS319 <10
DS320 <0.5
DS321 2620
DS322 2880
DS172 <0.5
DS323 575.32
DS164 1120
DS324 <1.0
DS168 <0.5
DS325 3060
DS326 2860
2,000
DS173 <0.5
DS327 1370
DS328 15.49
DS330 235.71
DS165 <0.5
DS329 107.35
DS331 1320
DS332 <0.5
DS169 <0.5
0 10 20

West Branch Canal Creek

Degradation in non-seep areas where relatively slow flow allows strongly reducing conditions.

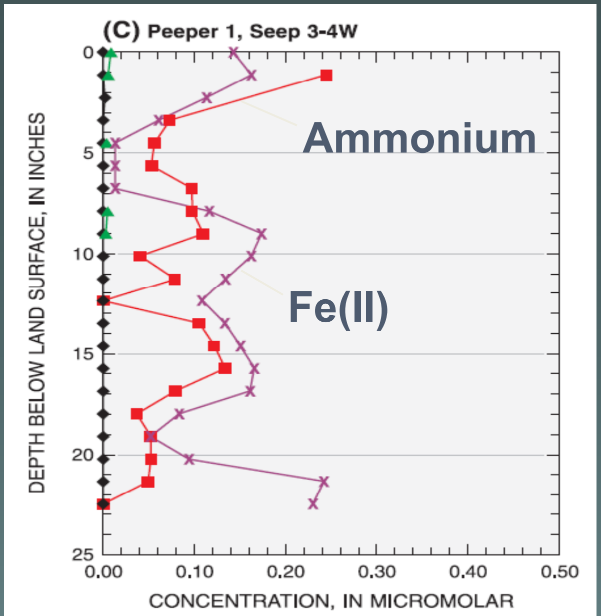
NON-SEEP AREA

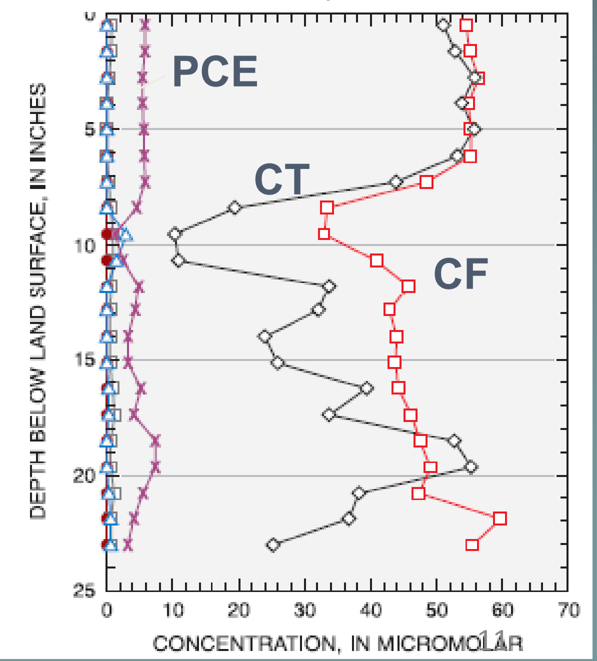




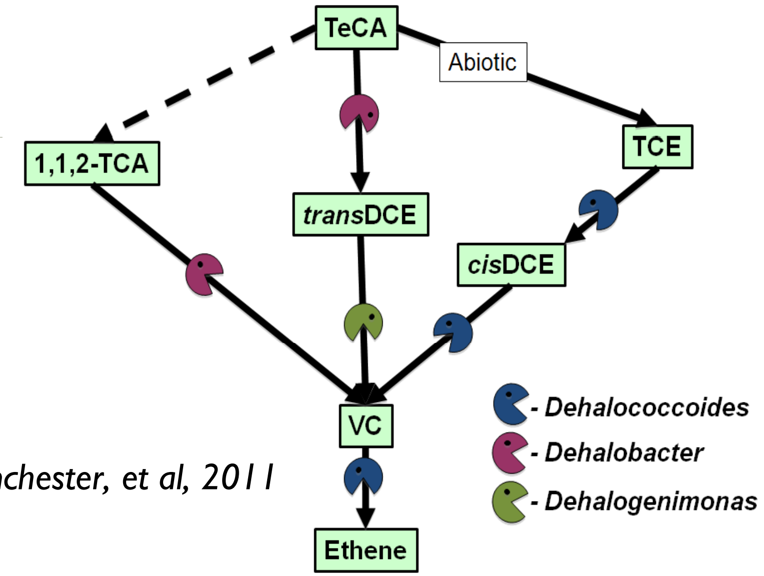
Upward flow

SEEP AREA

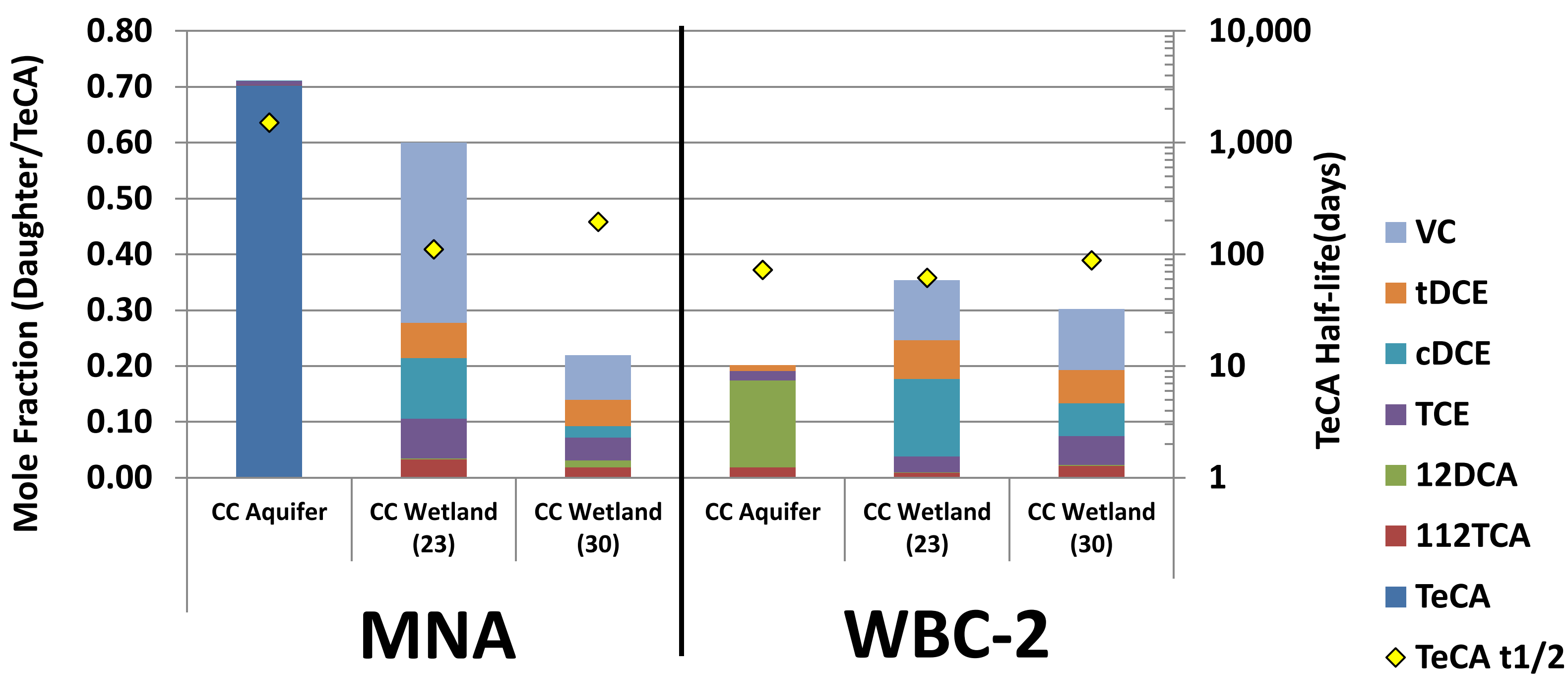




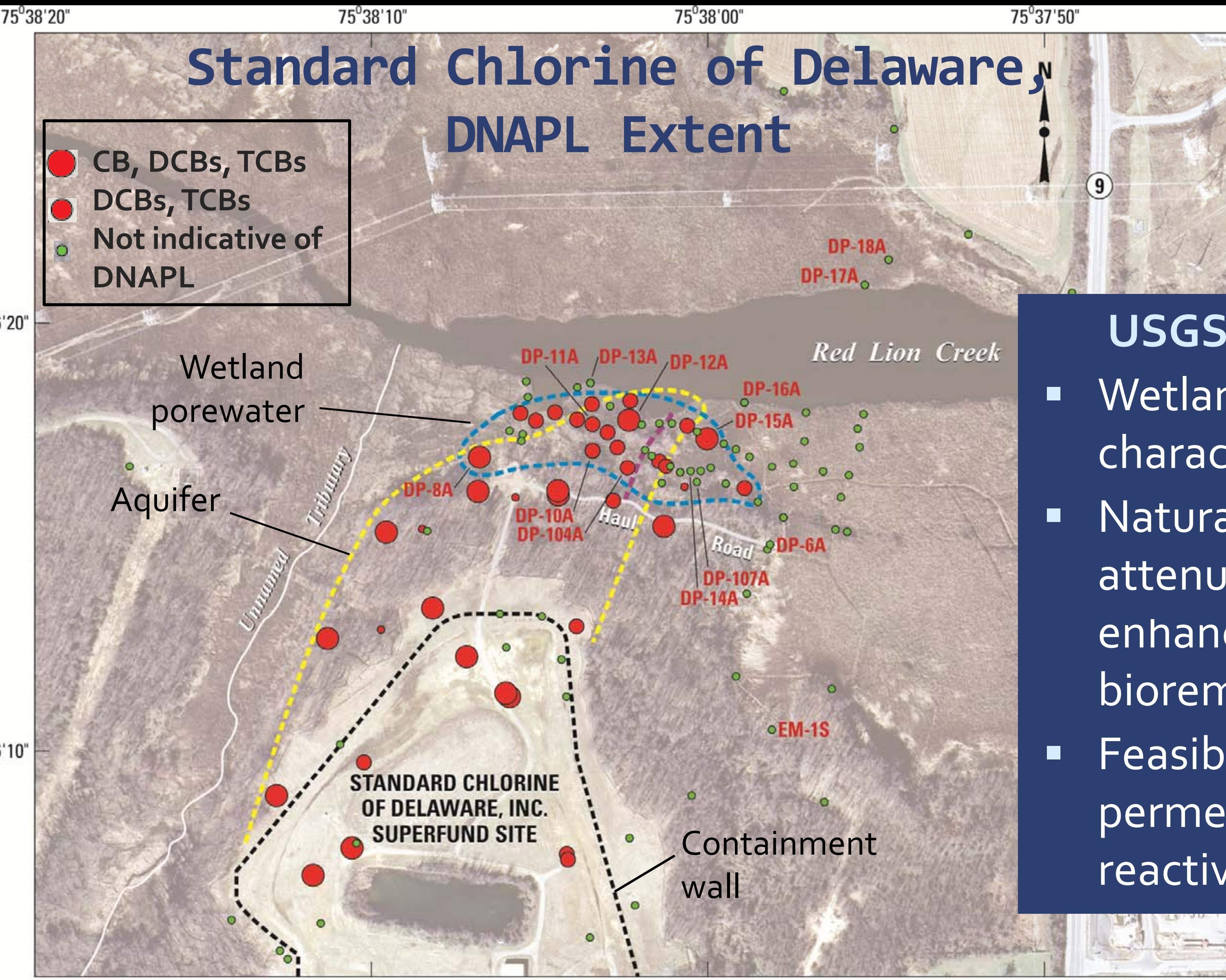
WBC-2 Dechlorinating Consortium, developed to degrade 1,1,2,2-tetrachloroethane (TeCA)



Manchester, et al, 2011



Standard Chlorine of Delaware, DNAPL Extent



Imagery from U.S. Geological Survey, Delaware Valley Regional Planning Commission, and Department of Homeland Security, 2010, NAD 1983 State Plane Delaware Transverse Mercator Projection

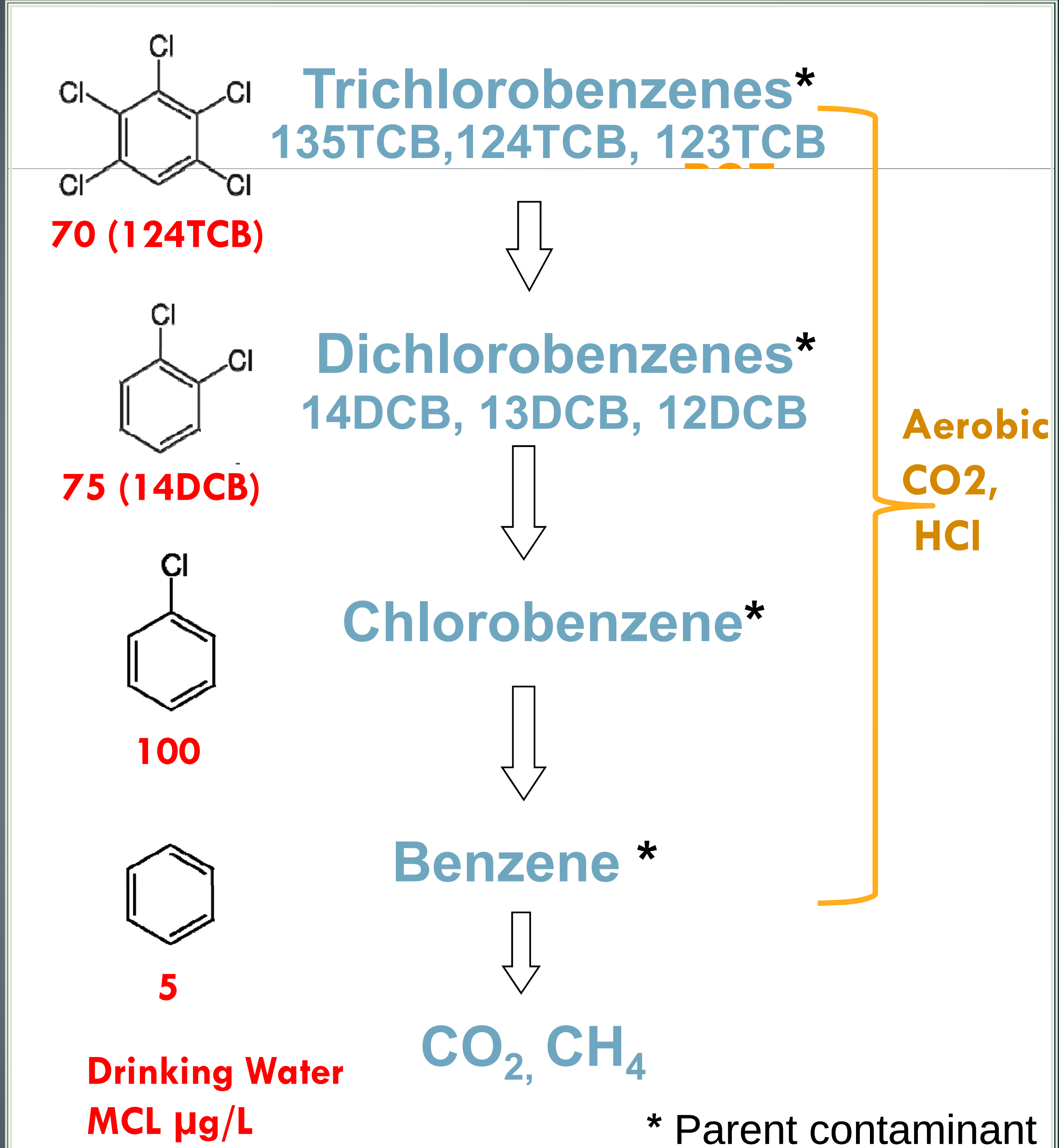
USGS Study

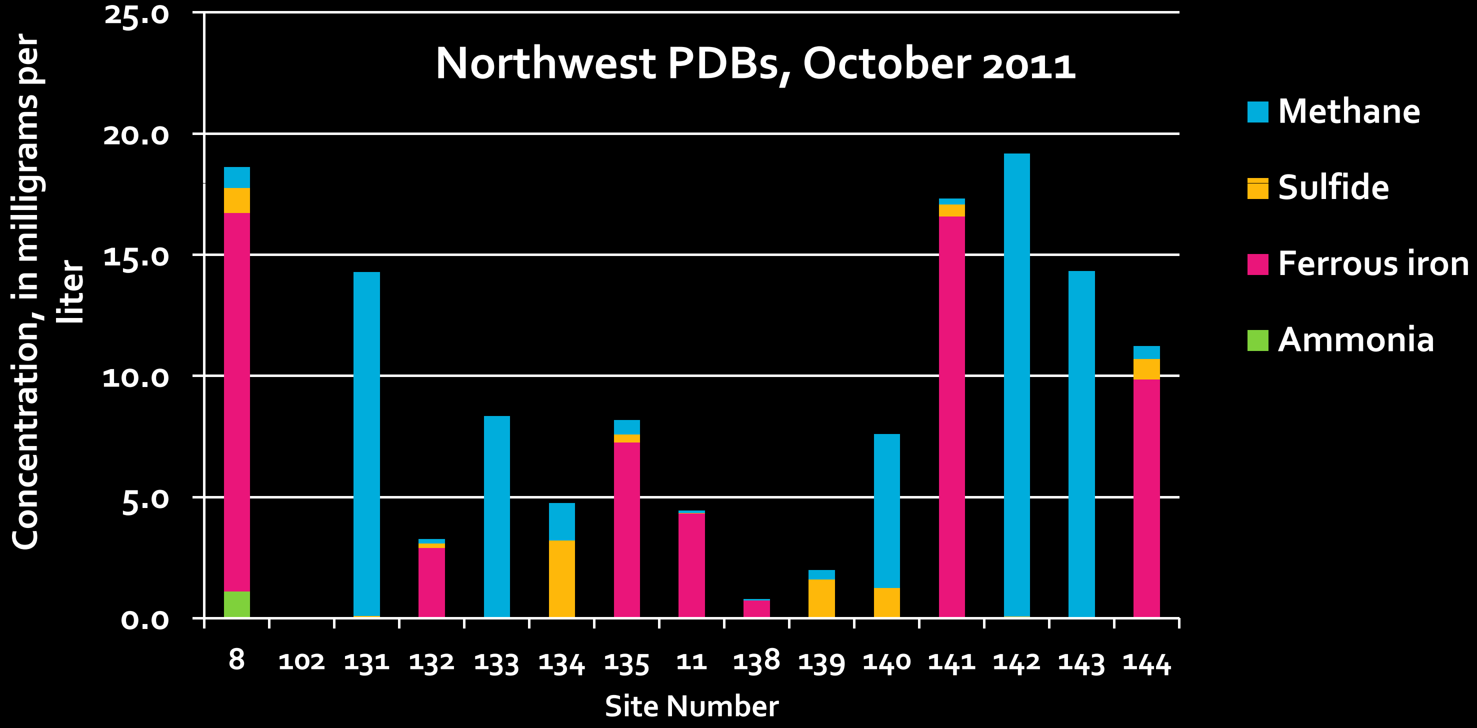
- Wetland characterization
- Natural attenuation; enhanced bioremediation
- Feasibility of permeable reactive barrier

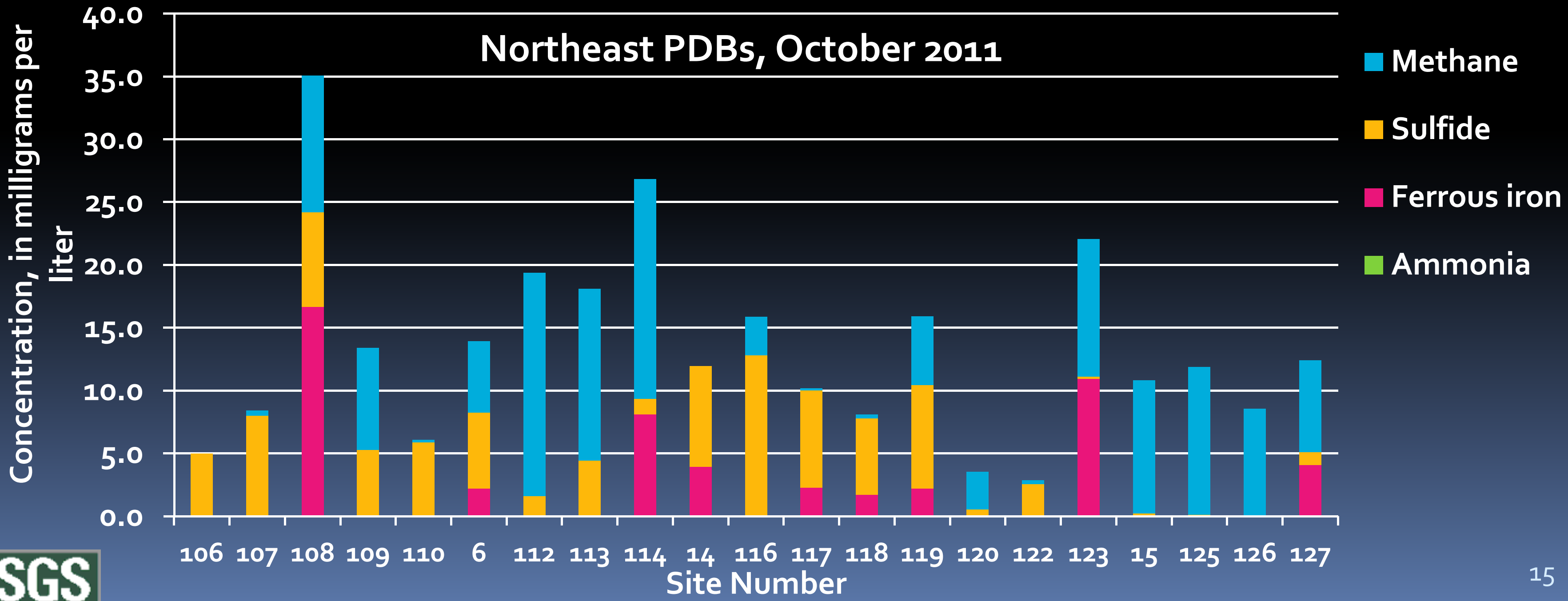
USGS

Chlorobenzenes- Standard Chlorine of Delaware

- Anaerobic (reductive dechlorination)
  - CB serves as terminal electron acceptor
  - Separate e- donor required
  - rate decreases with decreasing number Cl
- Aerobic (oxidation)
  - O_2 required as electron acceptor
  - CBs utilized as C and e donor
  - Short-lived intermediates
  - rate increases with decreasing number Cl

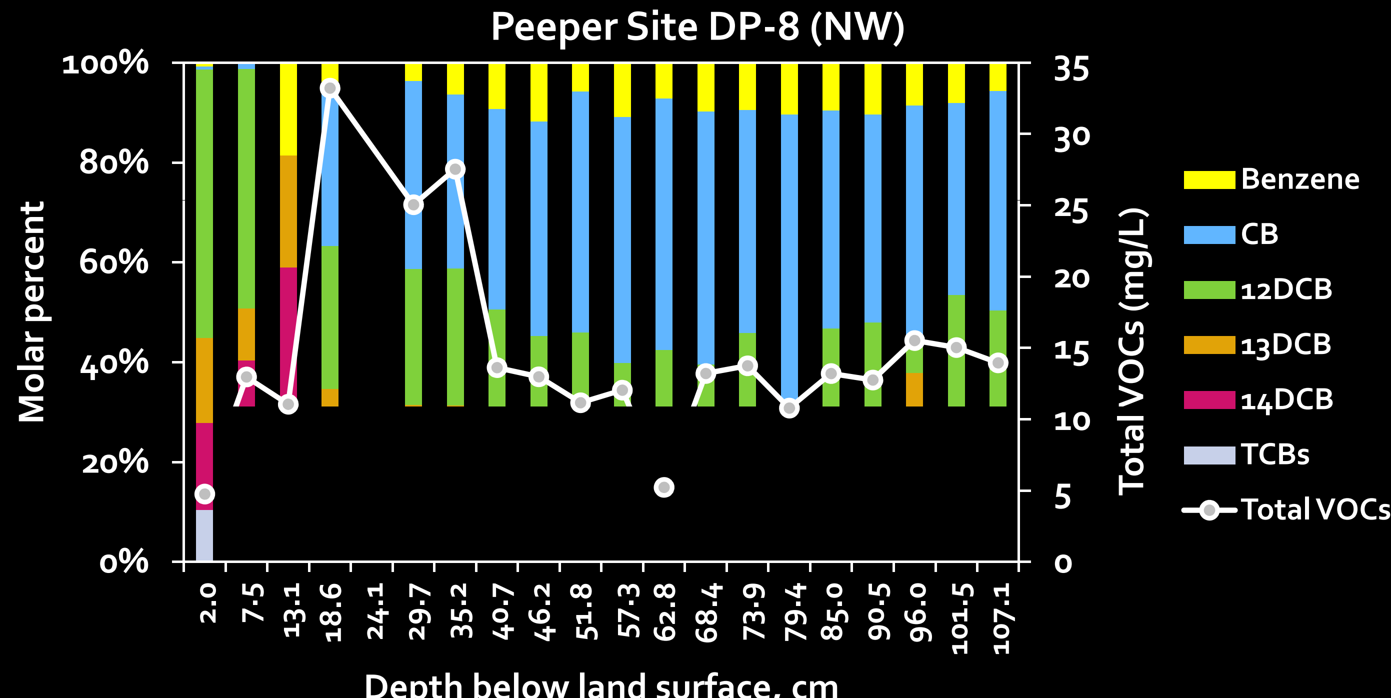



Northwest PDBs, October 2011
Concentration, in milligrams per liter
25.0
20.0
15.0
10.0
5.0
0.0
8
102
131
132
133
134
135
11
138
139
140
141
142
143
144
Site Number
Methane
Sulfide
Ferrous iron
Ammonia

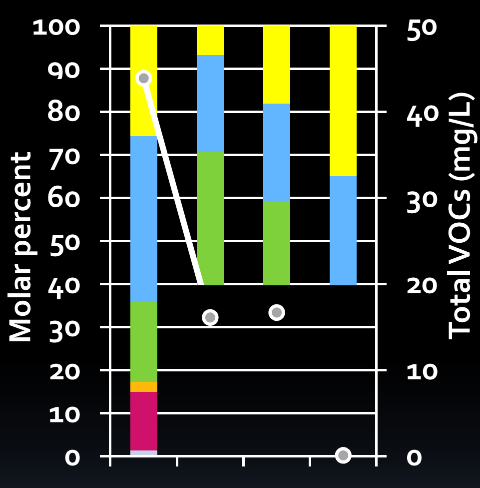

Northeast PDBs, October 2011
Concentration, in milligrams per liter
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
106
107
108
109
110
6
112
113
114
14
116
117
118
119
120
122
123
15
125
126
127
Site Number
Methane
Sulfide
Ferrous iron
Ammonia

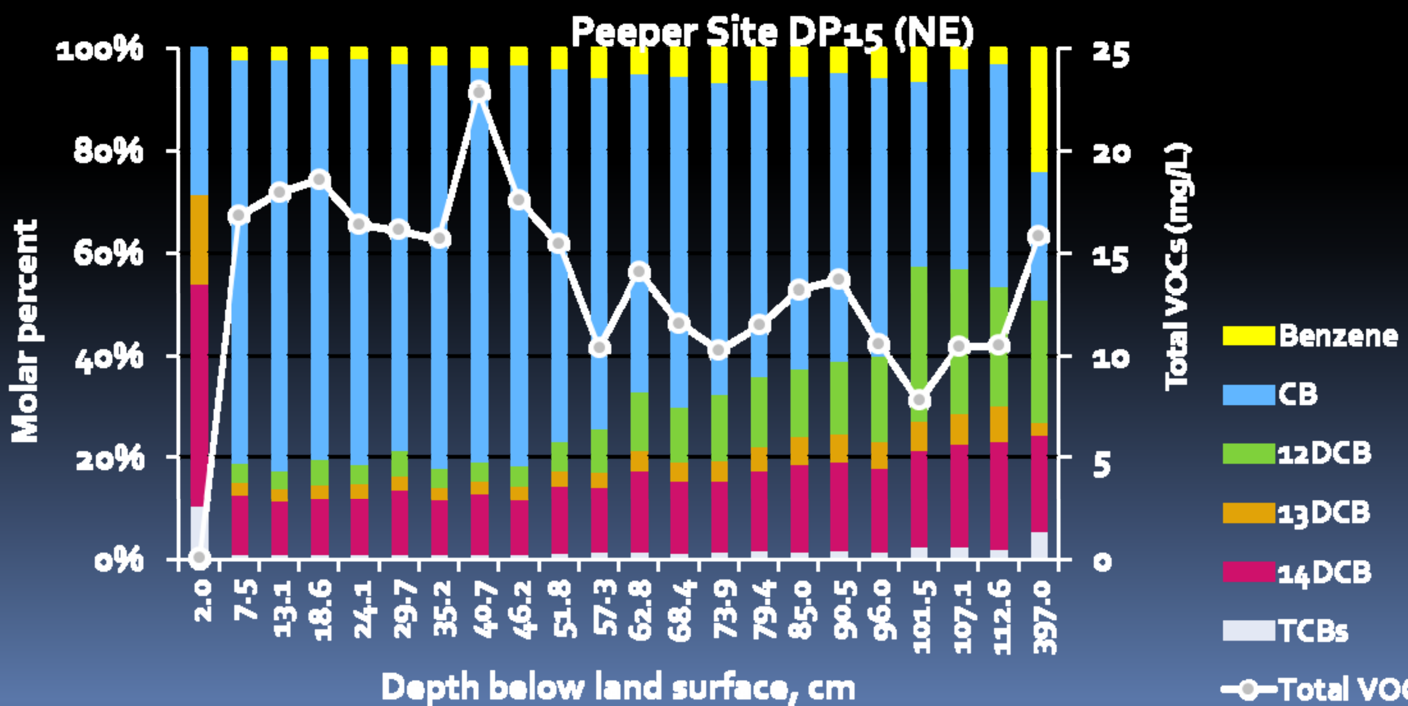
USGS

SCD, VOCs in Peepers



Upland Wells, Oct . 2011





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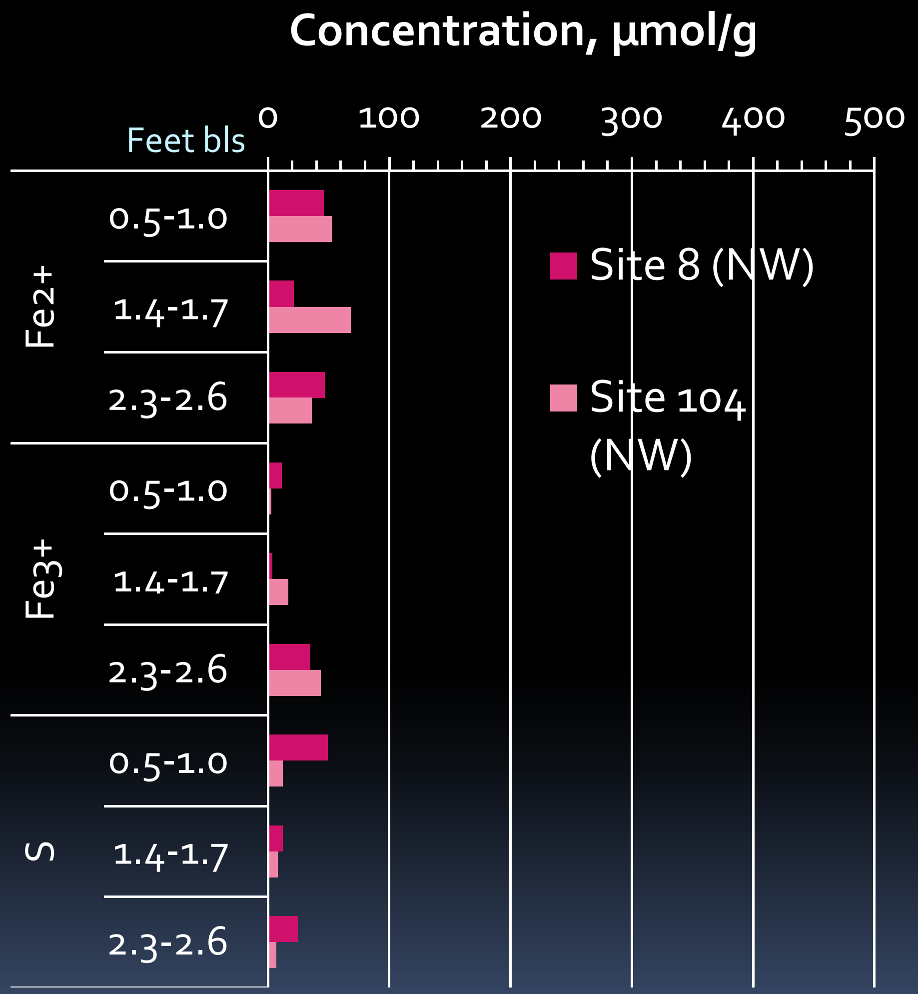
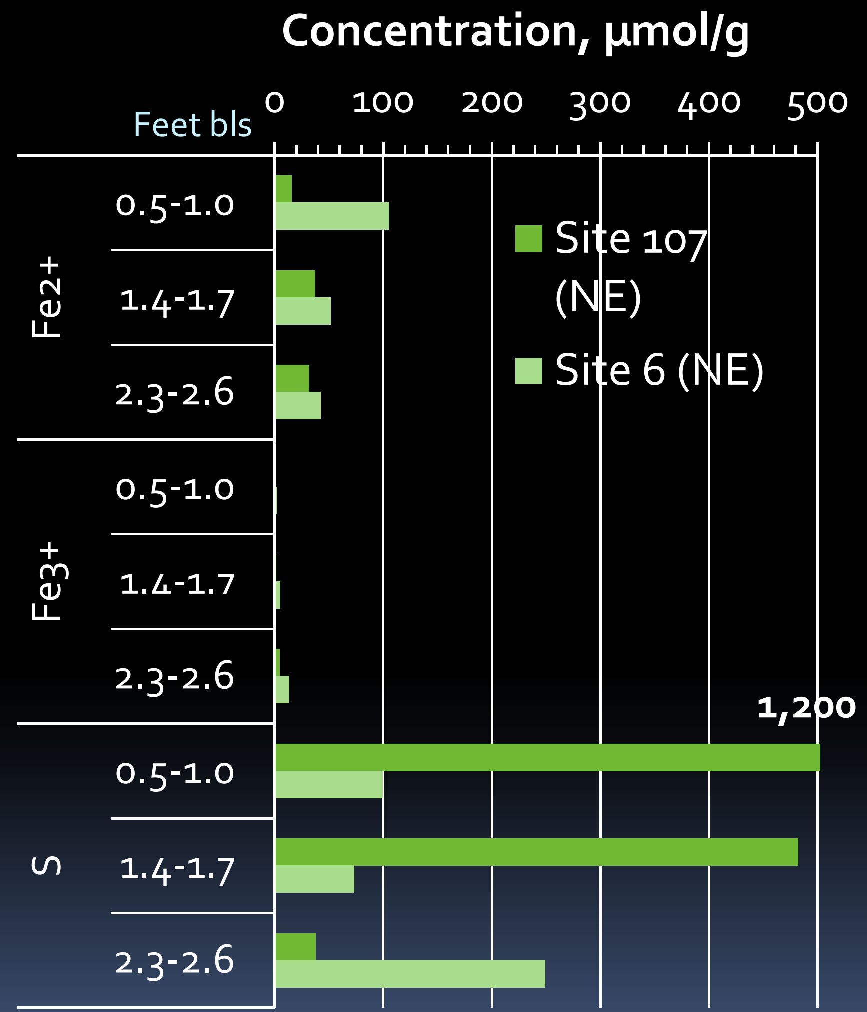
Iron, Sulfide- Sediment Cores

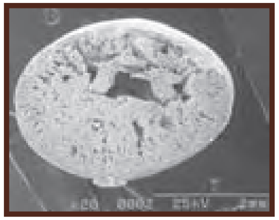




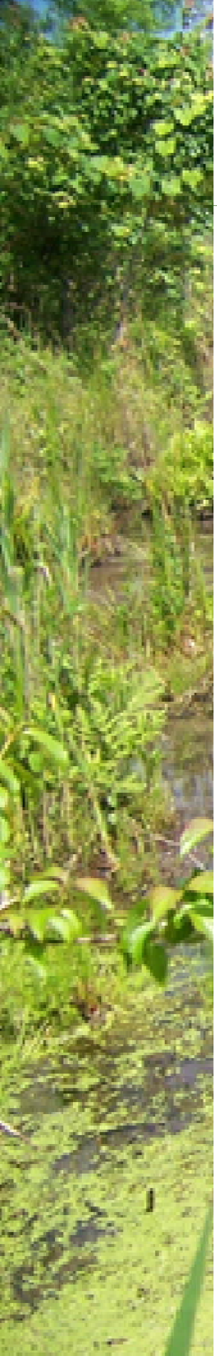
Tools to Evaluate Biodegradation

- Molecular Biological Tools
  - Quantitative PCR- Counts genes, taxonomic or functional, for specific targets; micro-arrays (QuantArray, MI)
  - Terminal Restriction Fragment Length Polymorphisms (TRFLP)- fingerprint of the microbial community
  - Next-generation sequencing (high throughput)- in depth profile of the microbial community; Illumina, 454 sequencing
- Stable Isotopes
  - SIP, Stable Isotope Probing- ^{13}C used as a tracer
  - CSIA, Compound Specific Isotope Analysis- isotopic fractionation in parent and metabolites

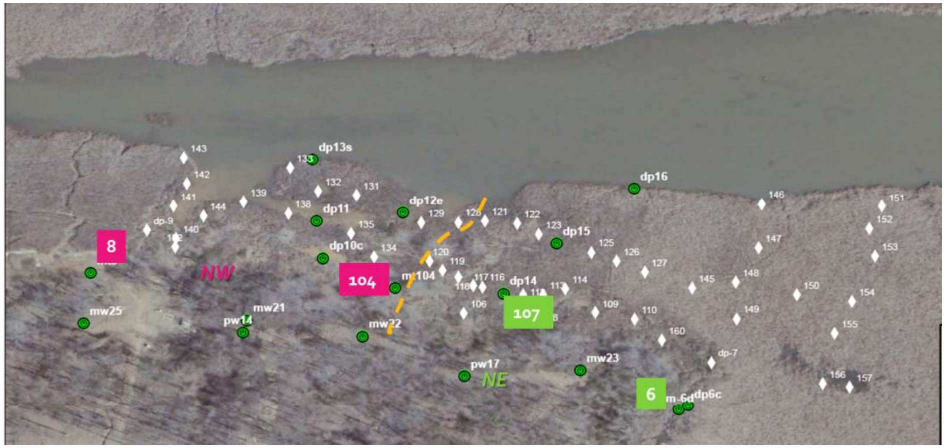
Bio-Traps, Microbial Insights

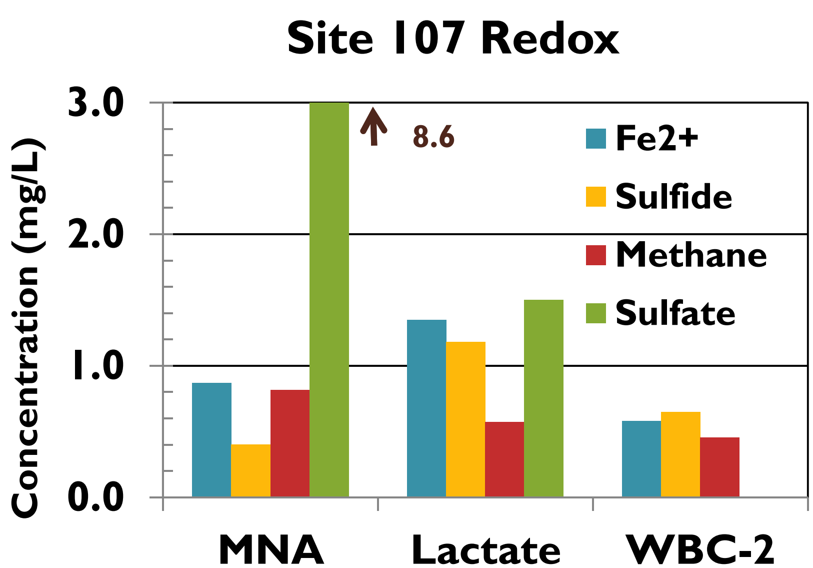


Bio-Sep® beads provide a large surface area for microbial attachment



In situ microcosms with Bio-Traps (Microbial Insights)



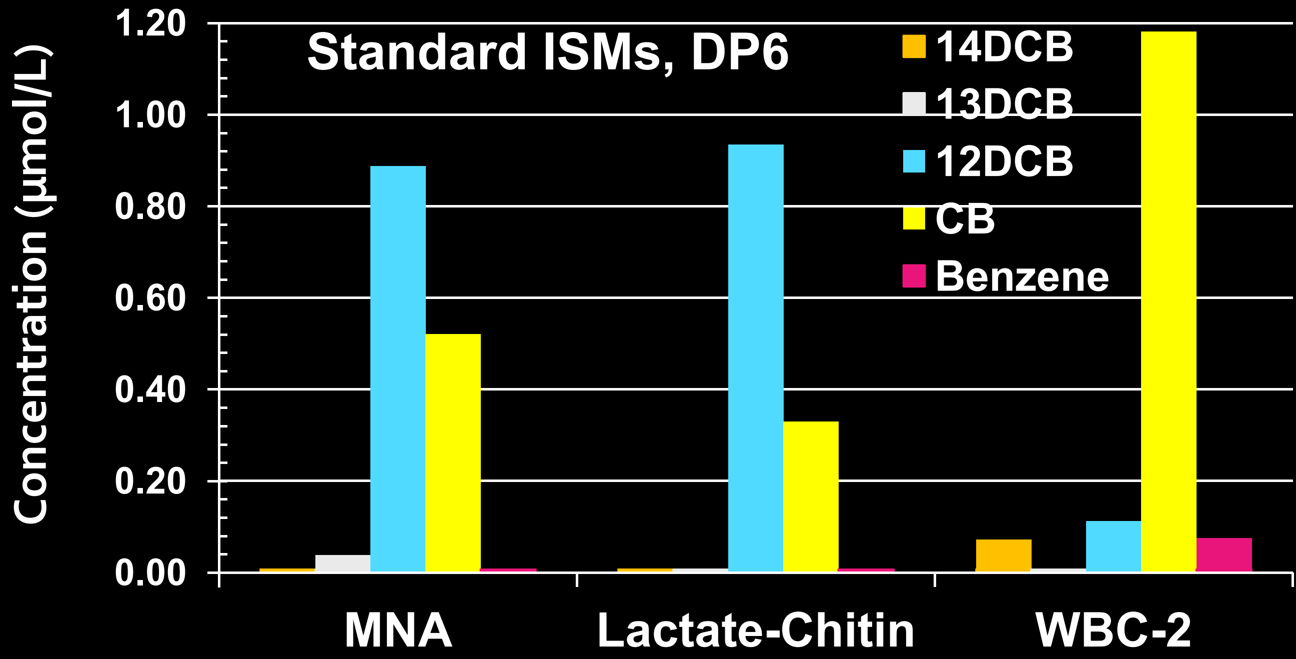


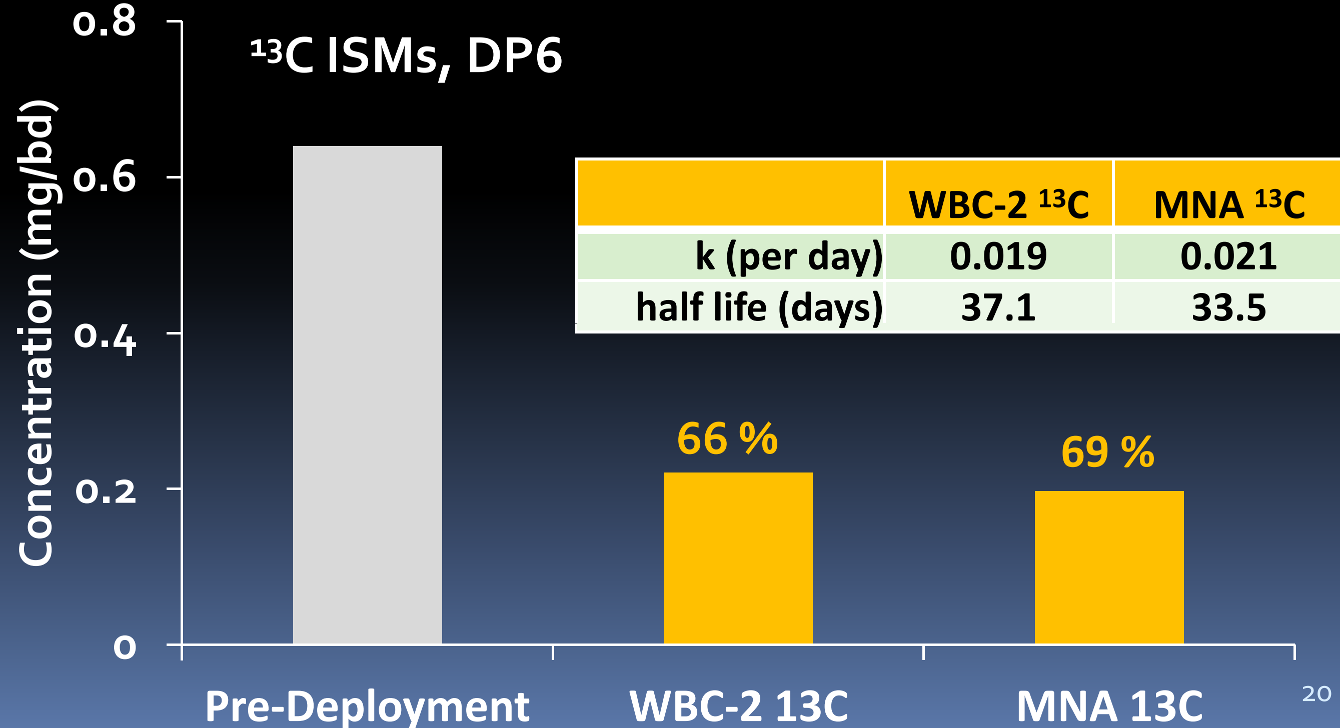
- Two each northwest and northeast sites
- Three standard treatments and three ^{13}C-labeled treatments
  - MNA, monitored natural attenuation (no amendments)
  - Lactate, biostimulated with lactate +chitin
  - WBC-2, bioaugmented
- ^{13}C-labeled chlorobenzene
- QuantArray analysis of species and functional genes for aerobic and anaerobic biodegradation

USGS

ISM Results:

- *Complete degradation of DCBs evident in WBC-2 treatment in standard ISMs*
- *13C-labeled ISMs showed complete degradation of monochloro-benzene in MNA and WBC-2*



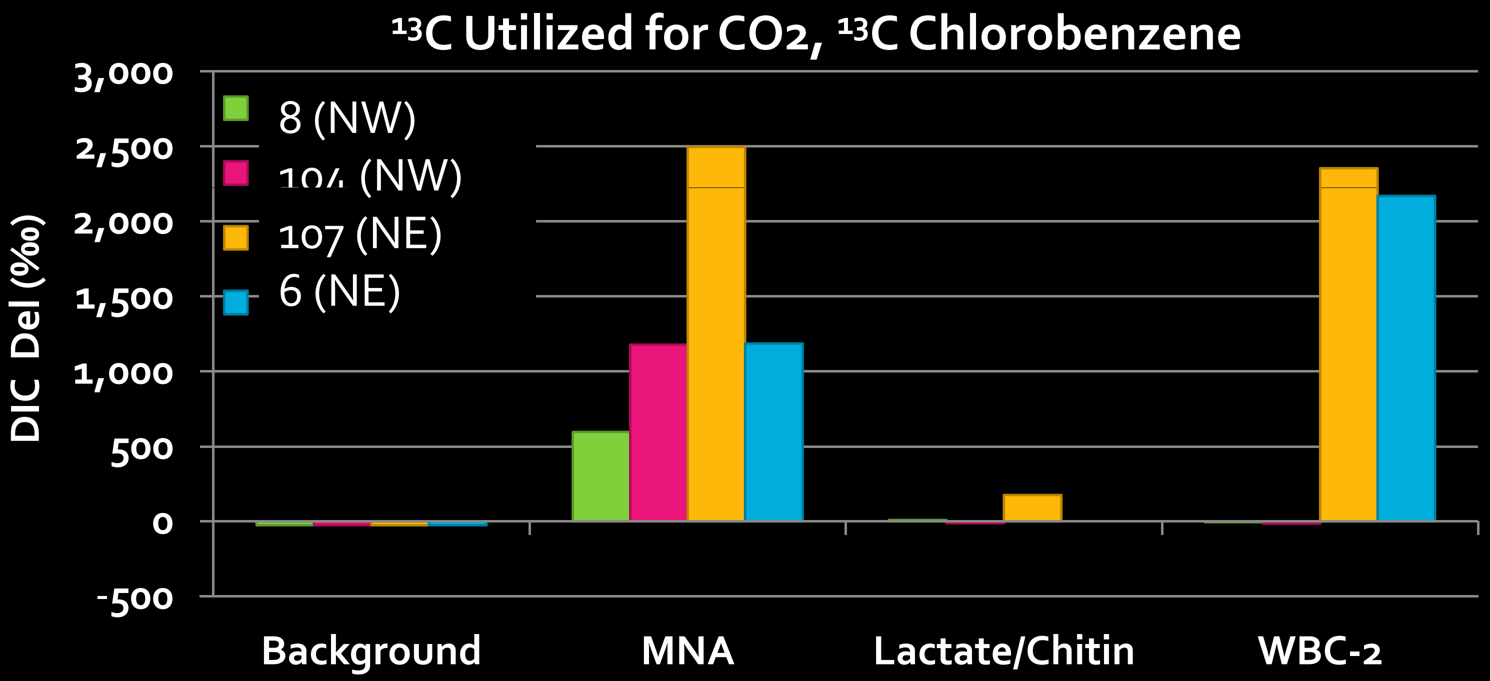


	WBC-2 ^{13}C	MNA ^{13}C
k (per day)	0.019	0.021
half life (days)	37.1	33.5

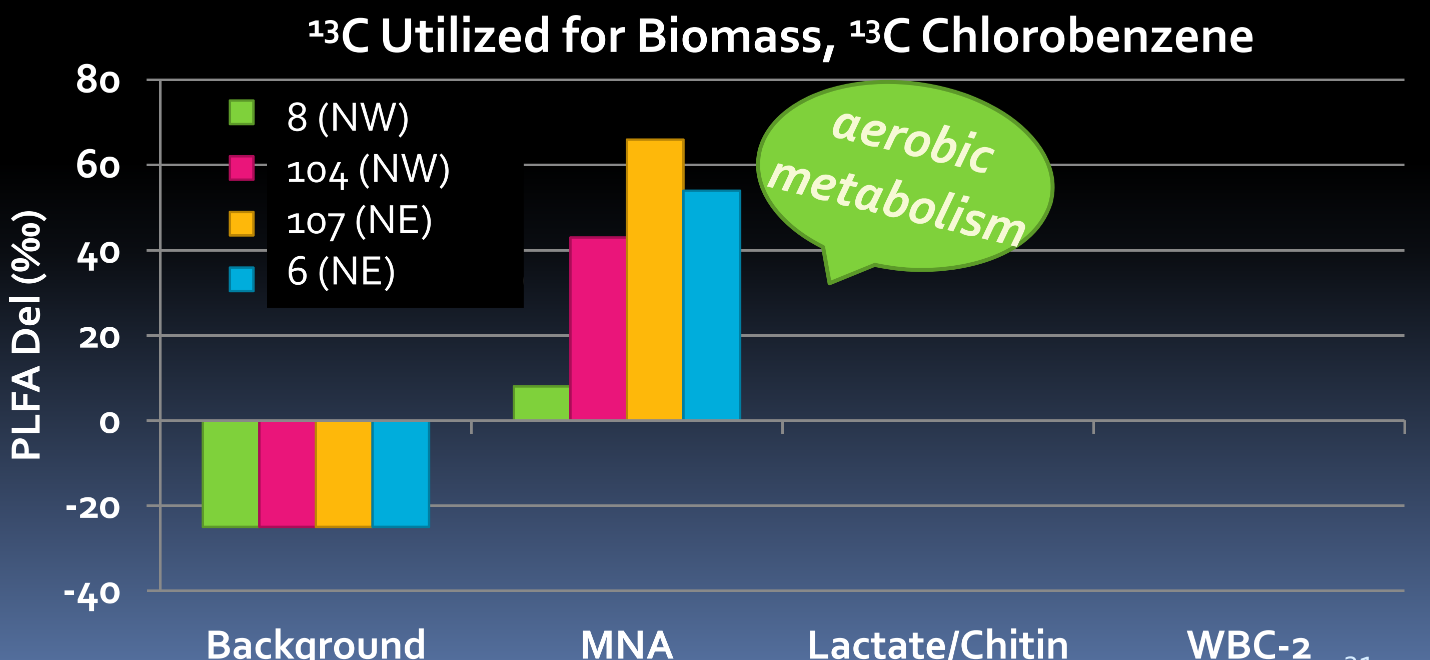
USGS

Bio-Traps: ^{13}C-labeled Chloro-benzene

Incorporation in dissolved inorganic carbon = Mineralization



Incorporation in PLFA = Metabolism (C for growth)



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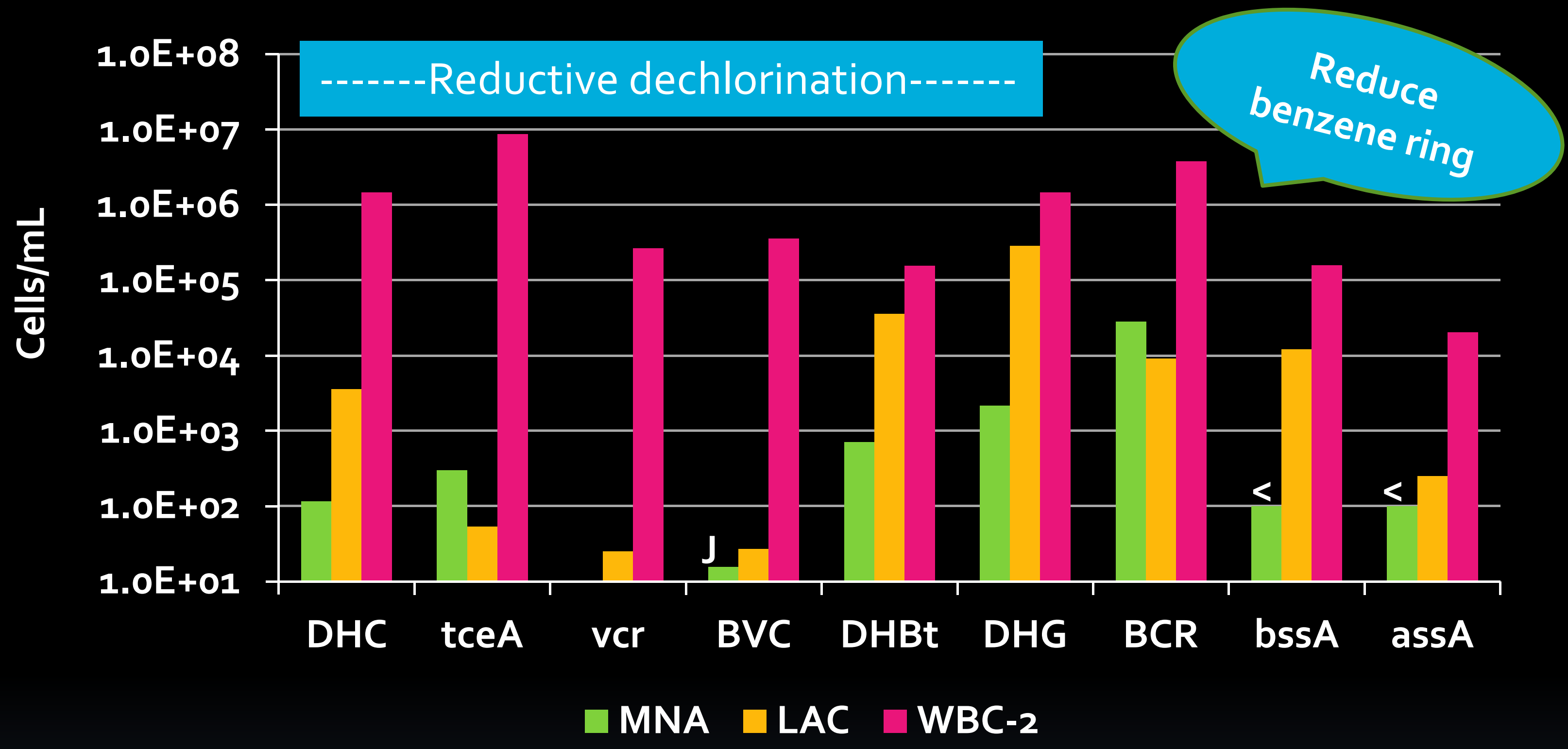
QuantArray Microbial Analysis- Anaerobic



Reductive dechlorination:

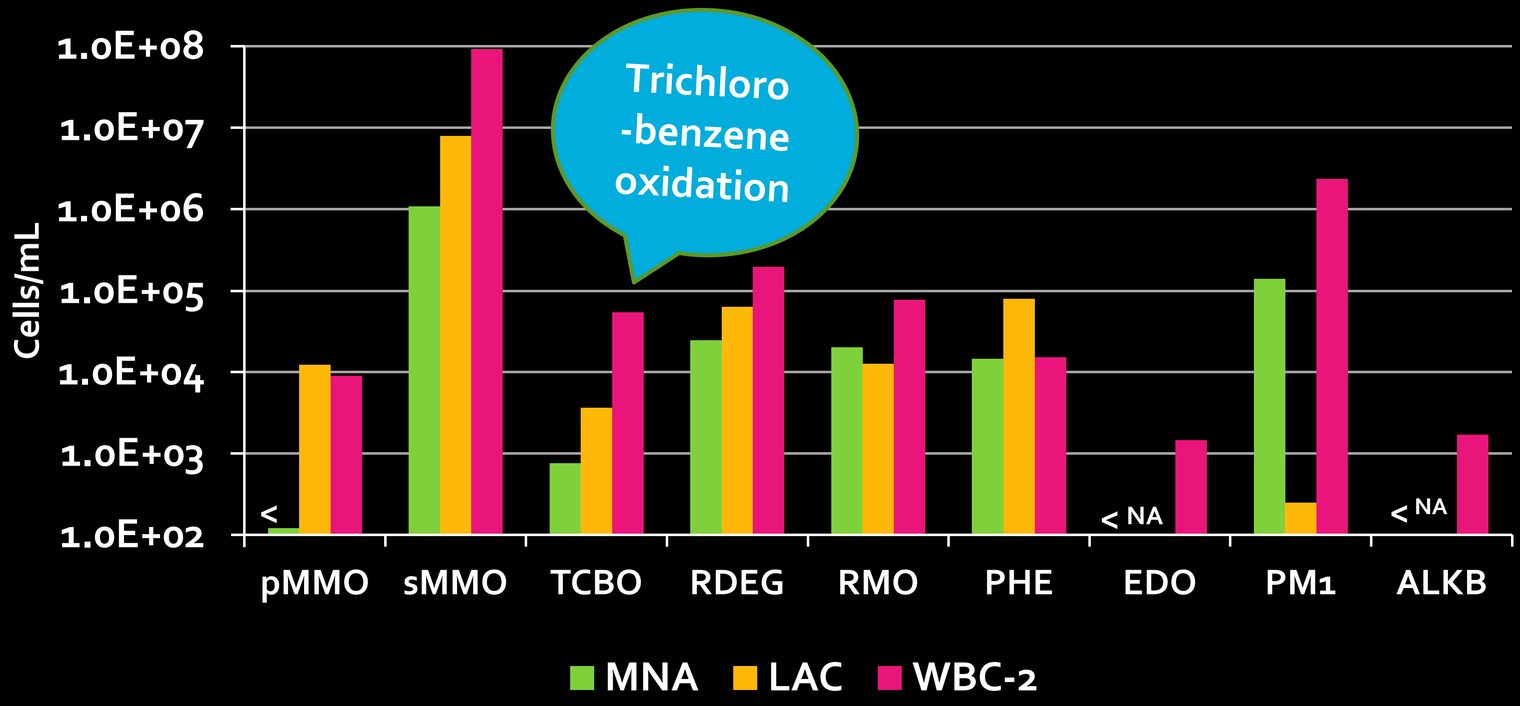
DHC , Dehalococcoides spp.
TCE, tceA reductase
VCR, vinyl chloride reductase
BV1 , vinyl chloride reductase
DHBt, Dehalobacter spp.
DHG, Dehalogenimonas spp.

BTEX, PAHs and alkanes:

BCR, Benzoyl coenzyme A reductase
bssA, benzylsuccinate synthase
assA, alkylsuccinate synthase

USGS

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/isopropyl-benzene dioxygenase
PM1, Methylibium petroliphilum PM1
ALKB, alkane monooxygenase

Changing Paradigm

Previous paradigm for chlorinated VOCs:

- Anaerobic reductive dechlorination only process in apparent low redox zones
- Aerobic oxidation requires measurable oxygen
- Anaerobic oxidation responsible for losses of lower VOCs at anaerobic plume fringes

Isolation of an aerobic vinyl chloride oxidizer from anaerobic groundwater

Fullerton et al. 2014

Perils of Categorical Thinking: "Oxic/Anoxic" Conceptual Model in Environmental Remediation

Bradley 2012

Sustained Aerobic Oxidation of Vinyl Chloride at Low Oxygen Concentrations

Gossett 2010

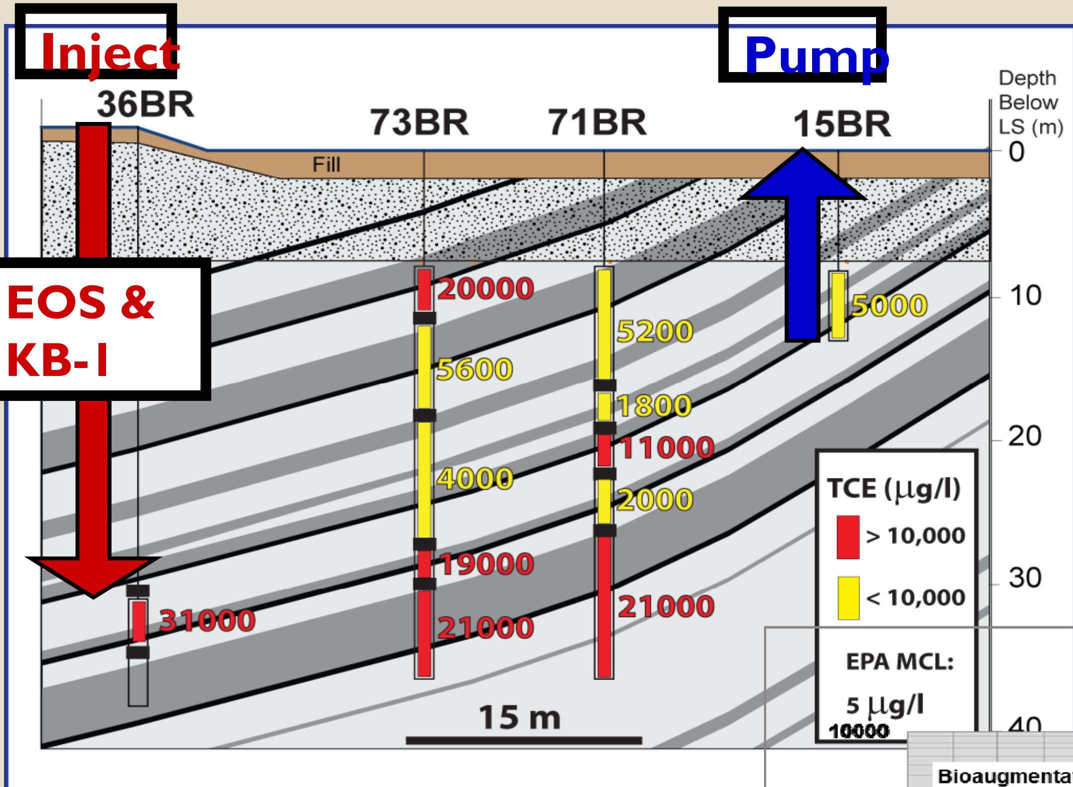
Microbial Mineralization of Dichloroethene and Vinyl Chloride under Hypoxic Conditions

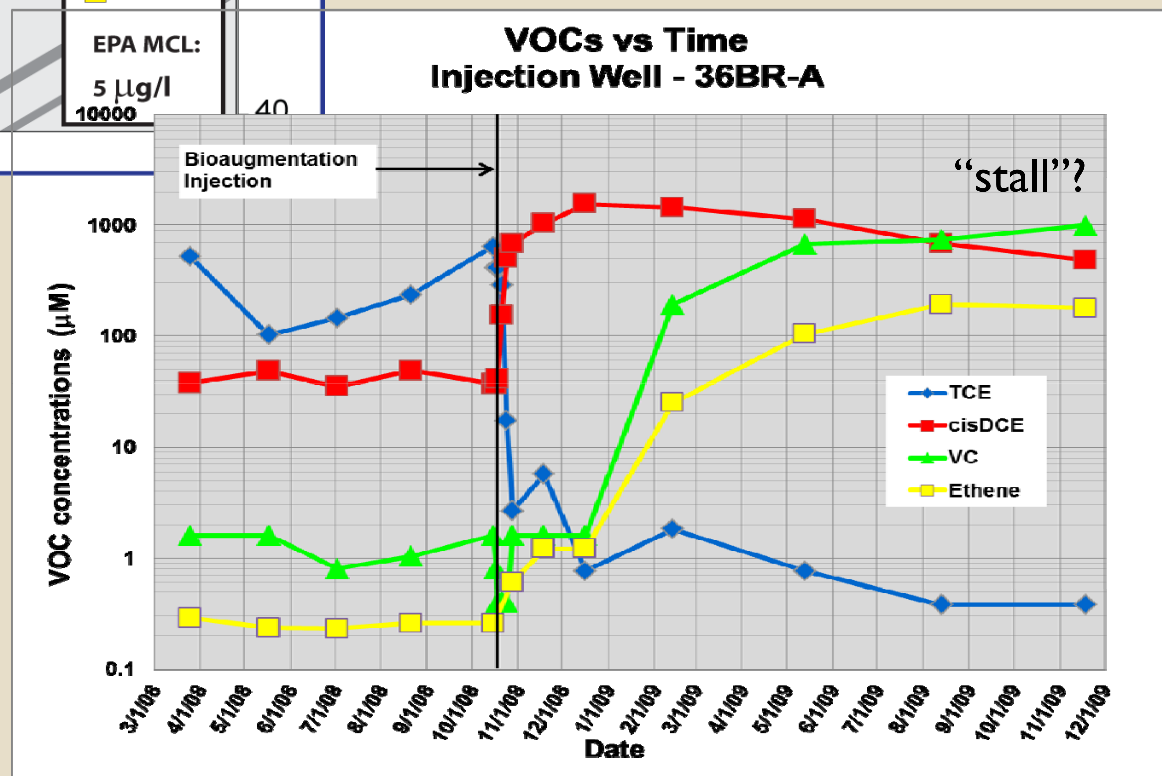
Bradley and Chapelle 2011

Concurrent and Complete Anaerobic Reduction and Microaerophilic Degradation of Mono-, Di-, and Trichlorobenzenes

Burns et al. 2013

Bioaugmentation: Fractured sedimentary rock aquifer, former Naval Air Warfare Center (NAWC)

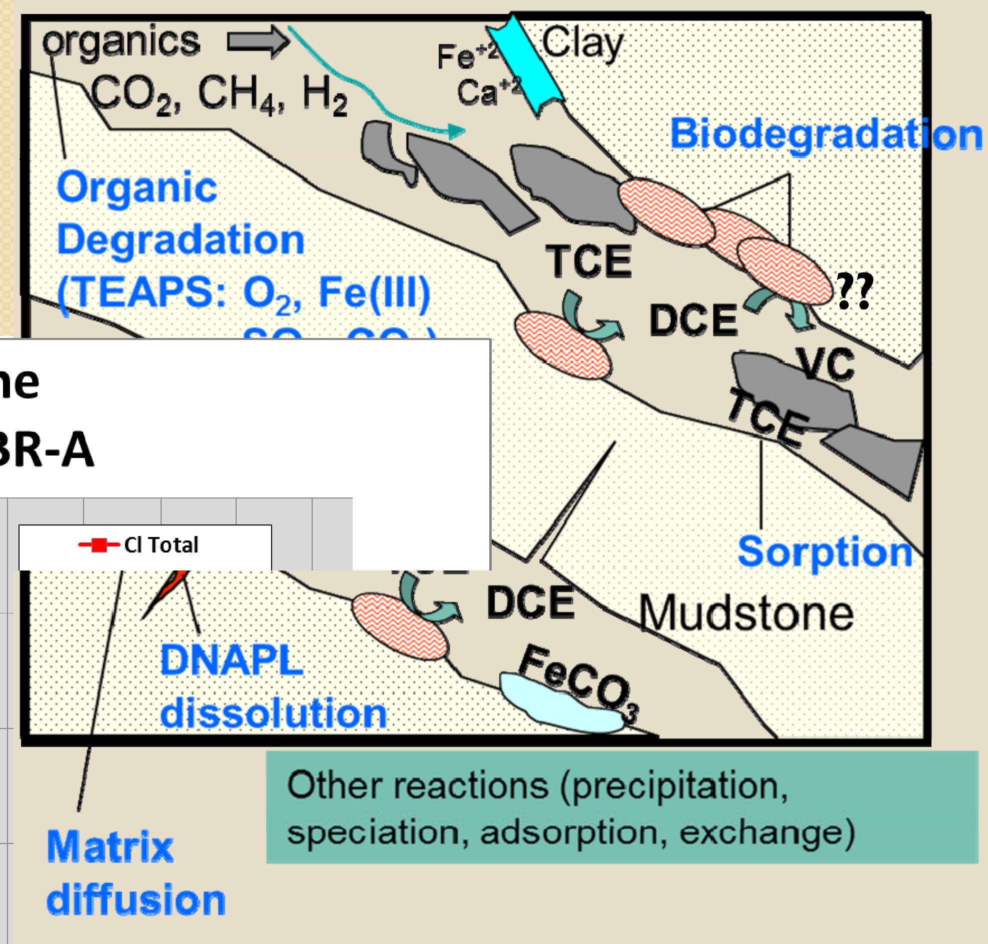


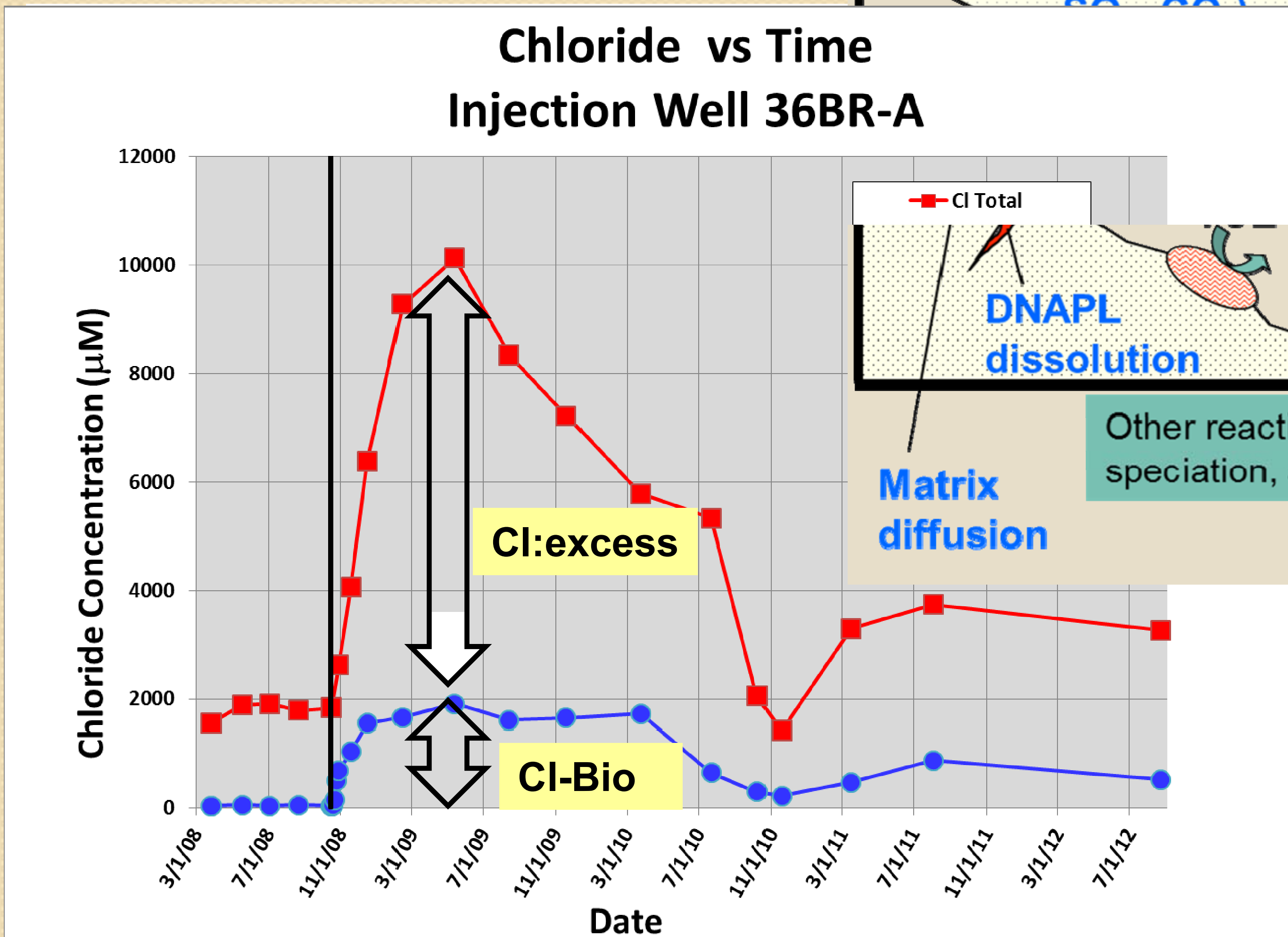


Toxic Substances Hydrology Program
New Jersey Water Science Center
National Research Program

Strategic Environmental Research and Development Program

Matrix diffusion/ DNAPL dissolution

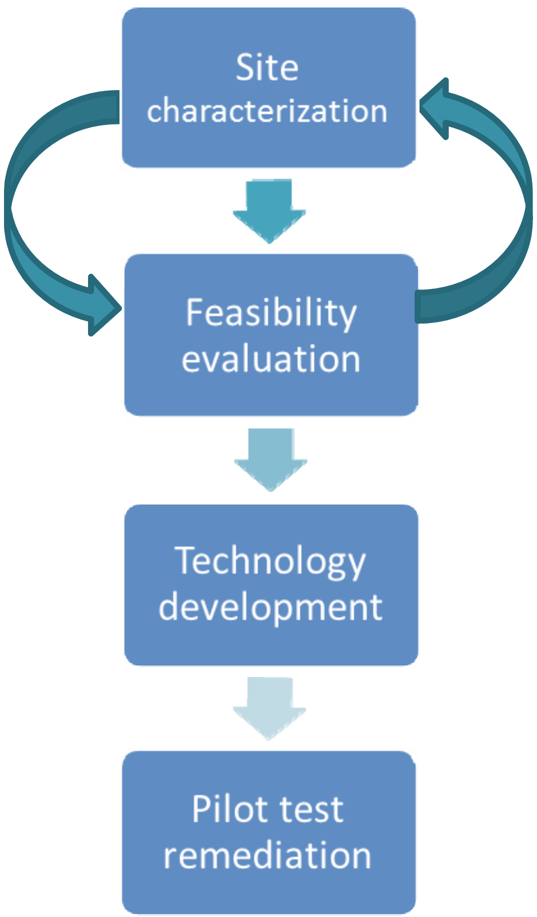


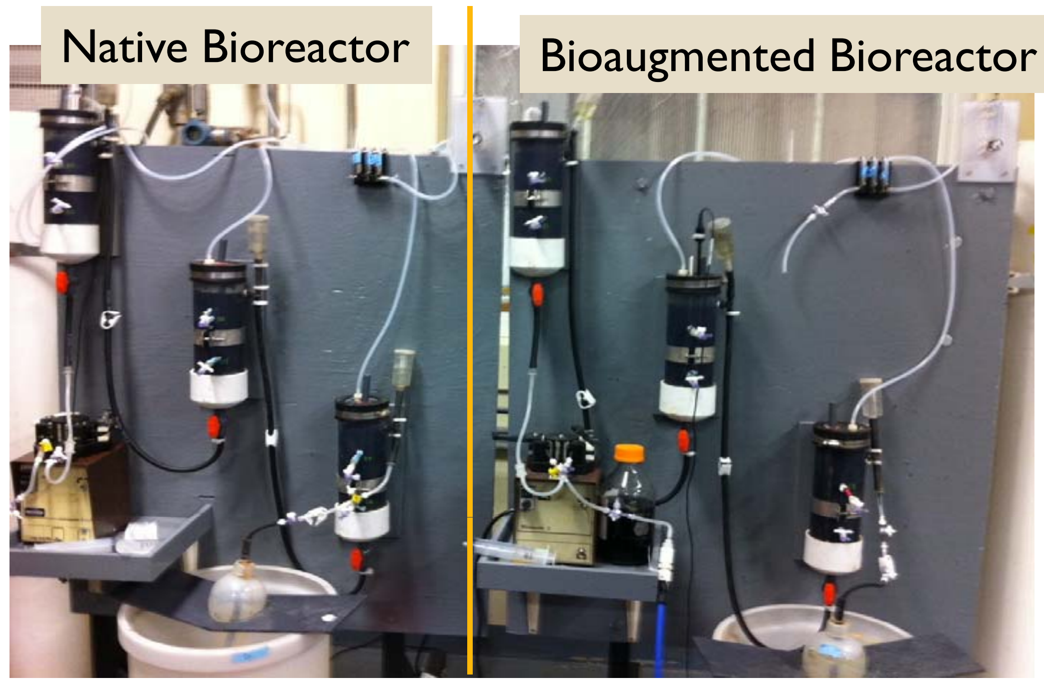


(Modified from Tom Imbrigiotta)

Currently investigating changes in native and bioaugmented microbial communities- toxicity/inhibition effects cause growth of "partial dechlorinators"?

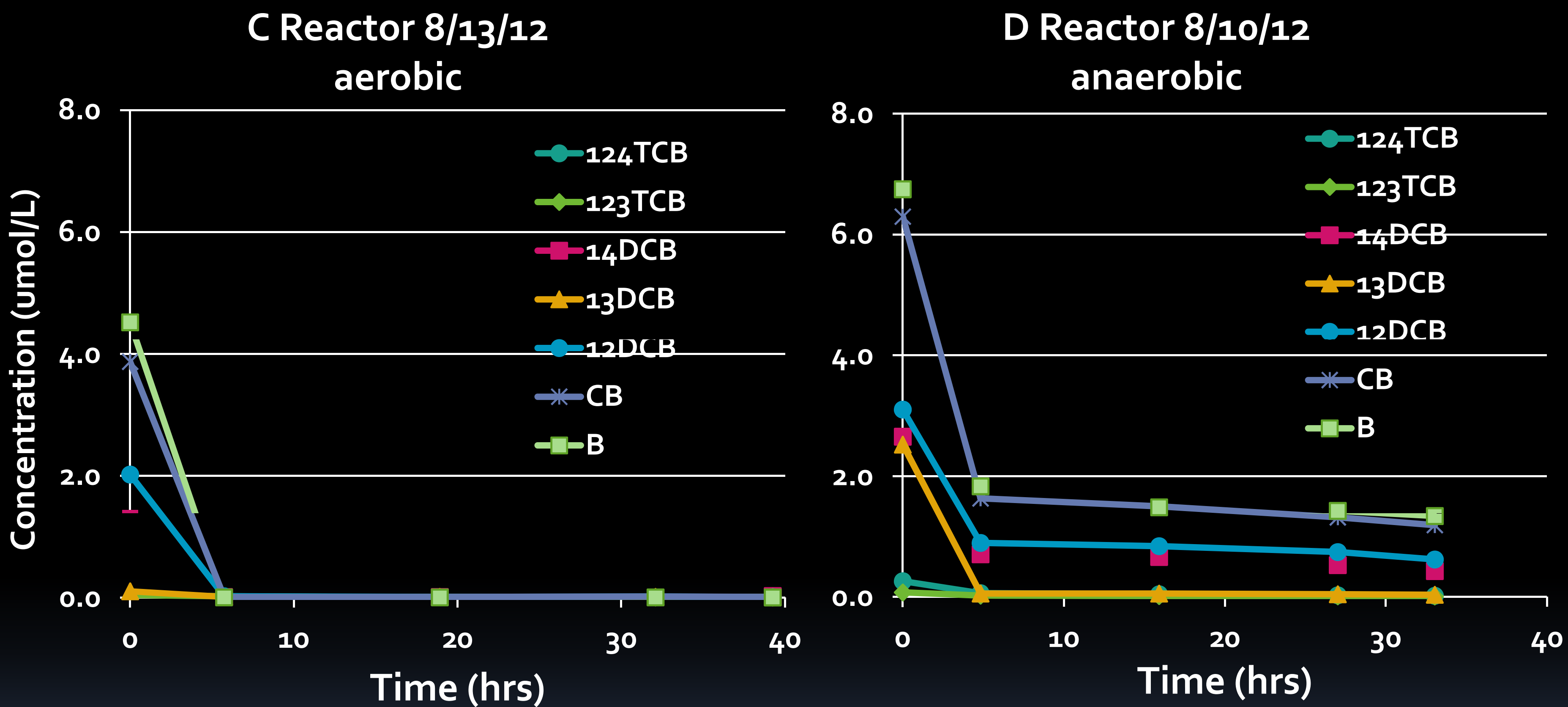
Use of laboratory testing to characterize microbial communities and biodegradation processes



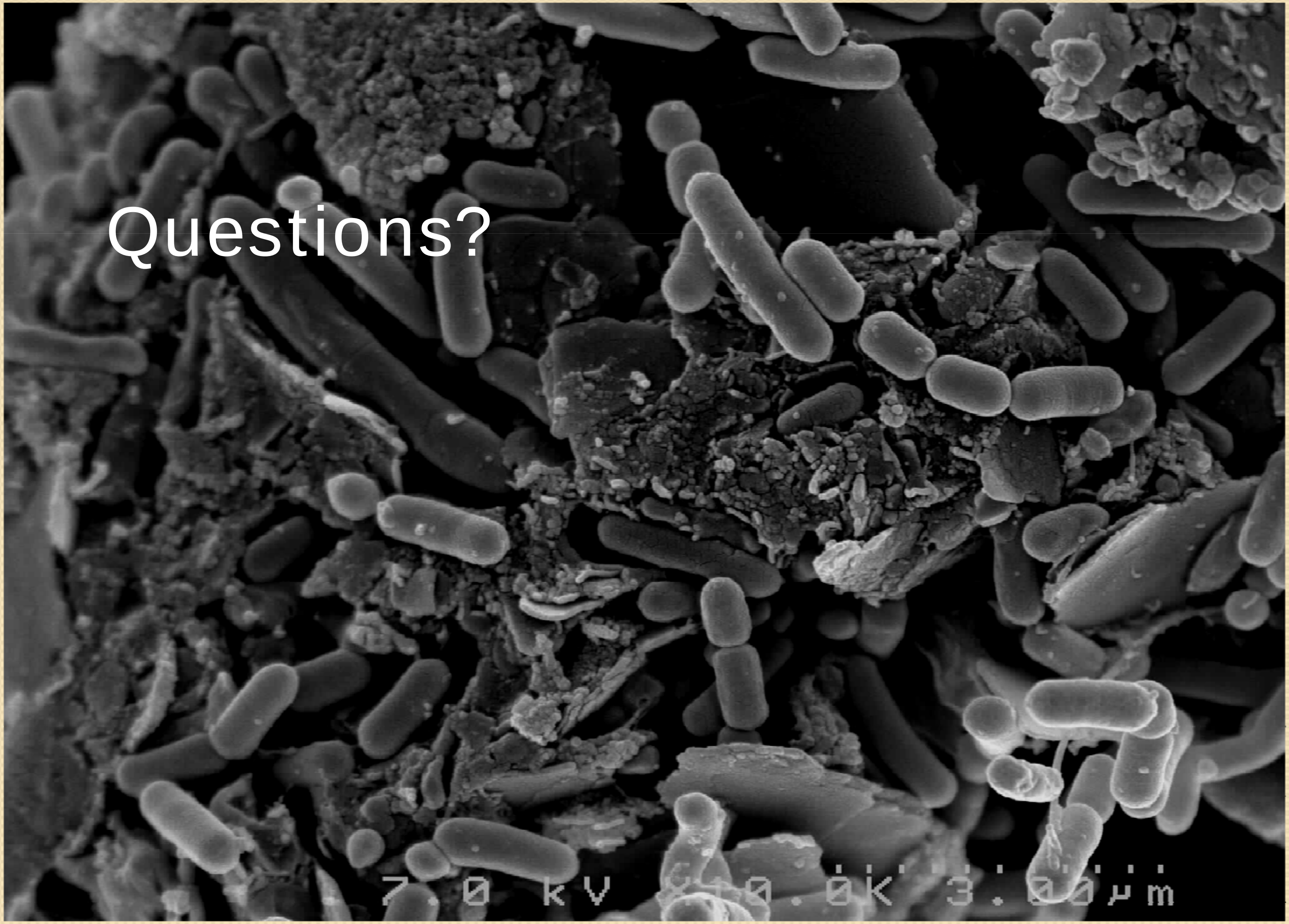


Polyethylene and polyurethane support matrix for building biofilm of native or bioaugmented microorganisms

SCD Bioreactors- Aerobic vs. Anaerobic



- *occurrence of aerobic and anaerobic degradation by native bacteria*
- *aerobic degradation faster than anaerobic biodegradation*
- *WBC-2 able to degrade chlorinated benzenes and benzene anaerobically*
- *accumulation of daughter products not evident*


Questions?
7.0 kV X10.0K 3.00µm

Acknowledgements

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Fate and Bioremediation Team

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US Army, Aberdeen Proving Ground Installation Restoration Program

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