Evaluation of Bioremediation of Chlorinated Benzenes and Benzene by a Native Wetland Microbial Community and a Bioaugmented Anaerobic Culture

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and

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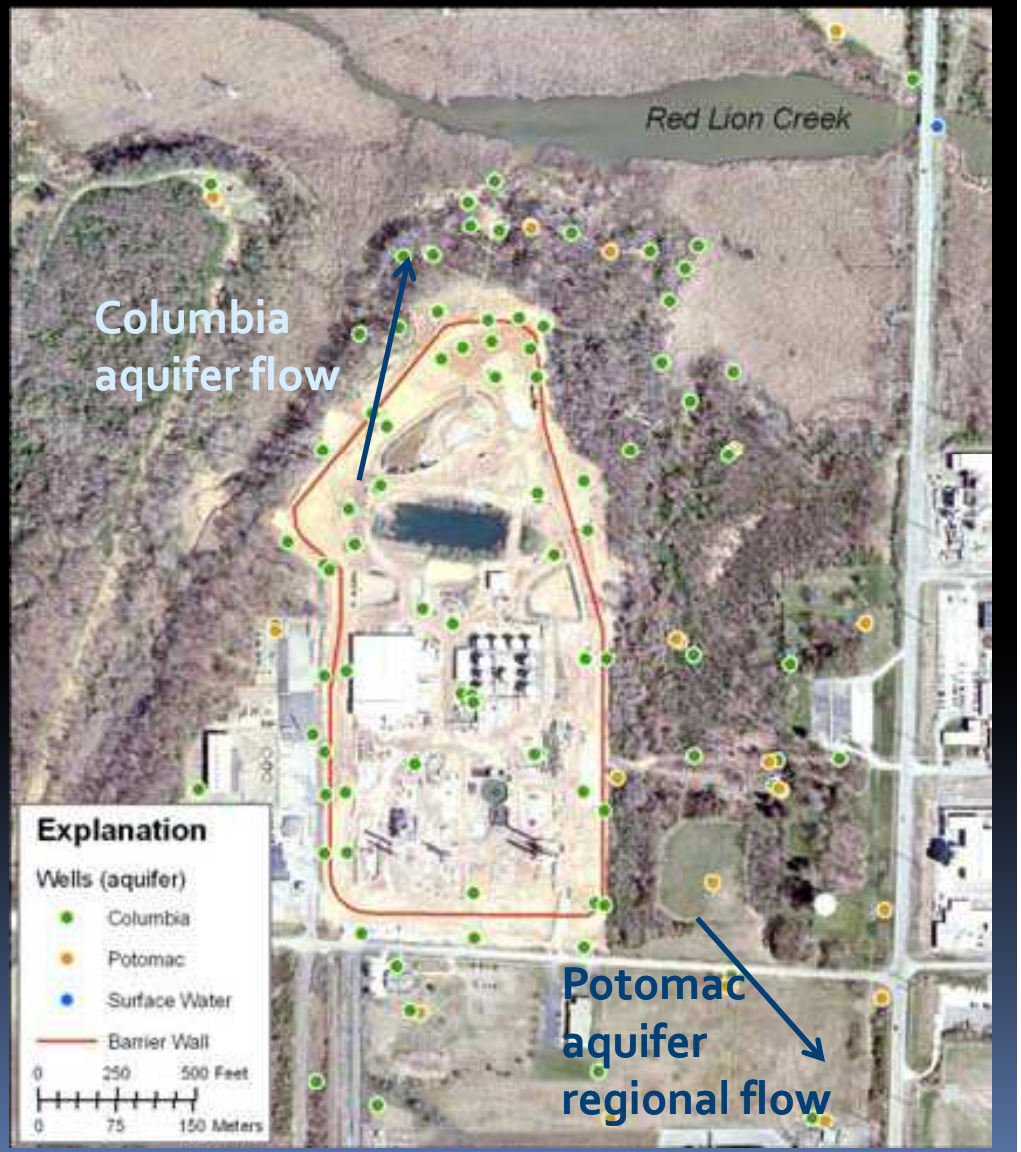
in Cooperation with USEPA, Region III

USGS

Standard Chlorine of Delaware, Inc., Superfund Site

- Chemical plant built in 1965 to manufacture chlorinated benzenes
- Operated 1966-2002
- Leaky catchment basin (repaired 1976)
- Two major spills: 1981 (railroad tanker, 5,000 gal CB); 1986 (storage tanks-579,000 gal 14DCB and TCBs)
- Superfund site in 1987

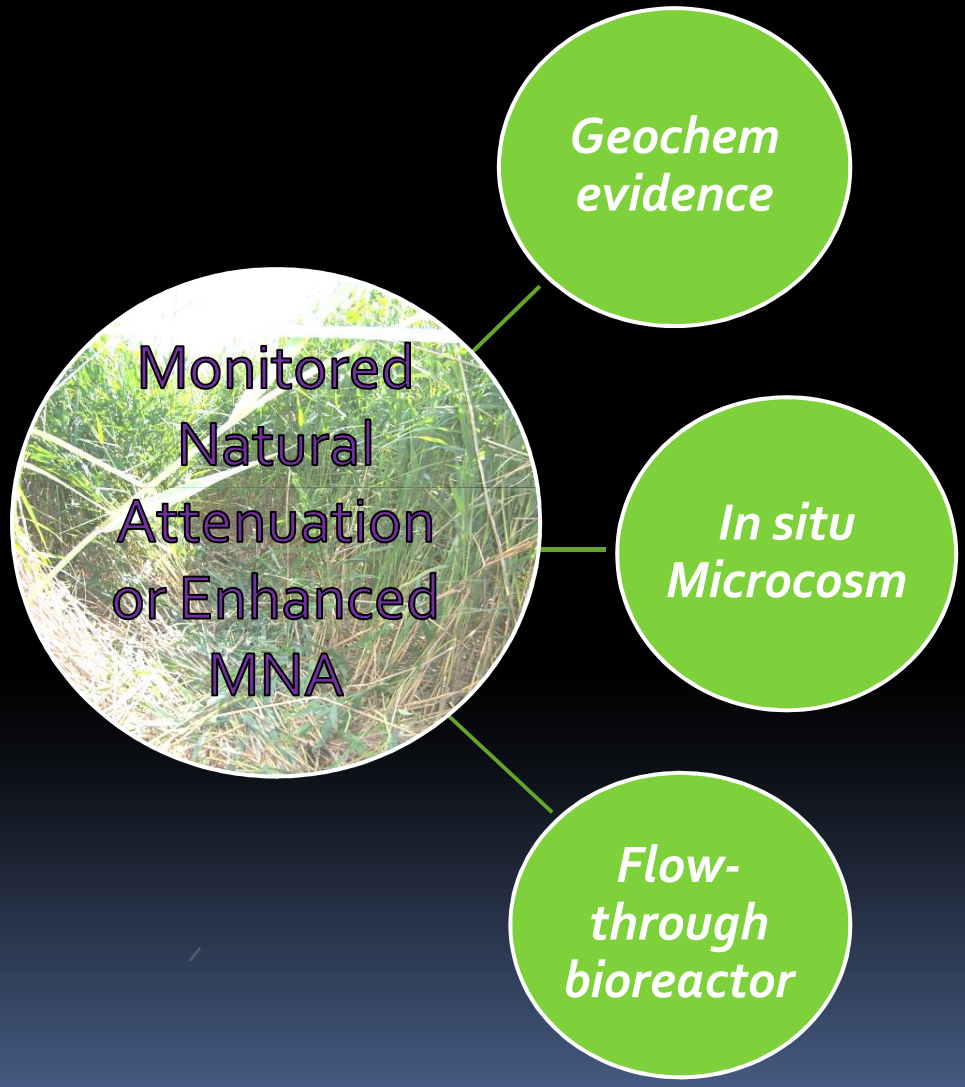


Wetland Remedial Alternatives

- 1995 ROD stated treatment for soils and wetland sediments either by bioremediation or low temperature thermal desorption (LTTD)
  - Initial bioremediation treatability test with soil and sediment was not promising
  - LTTD was cost-prohibitive (>$50 million)
- In situ chemical oxidation (ISCO) pilot test in wetland was not promising and had long-term adverse affect on vegetation (HGL, 2009)
- These problems and advances in bioremediation led to a second look at bioremediation

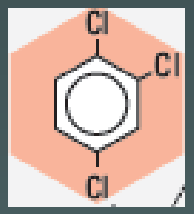
Objectives and Outline

- Wetland characterization
  - hydrogeology
  - groundwater contaminant distribution
- Natural attenuation in wetland (MNA)
- Potential for enhanced bioremediation
  - biostimulation
  - bioaugmentation-WBC-2 culture



Biodegradation Pathways

- Anaerobic reductive dechlorination
  - rate decreases with decreasing number of chlorines
  - monochlorobenzene recalcitrant
- Oxidation reaction pathways
  - typically aerobic
  - rate decreases with increasing number of chlorines

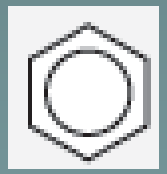


Trichlorobenzenes * 124TCB,123TCB

Dichlorobenzenes * 12DCB, 13DCB, 14DCB

Chlorobenzene *

??

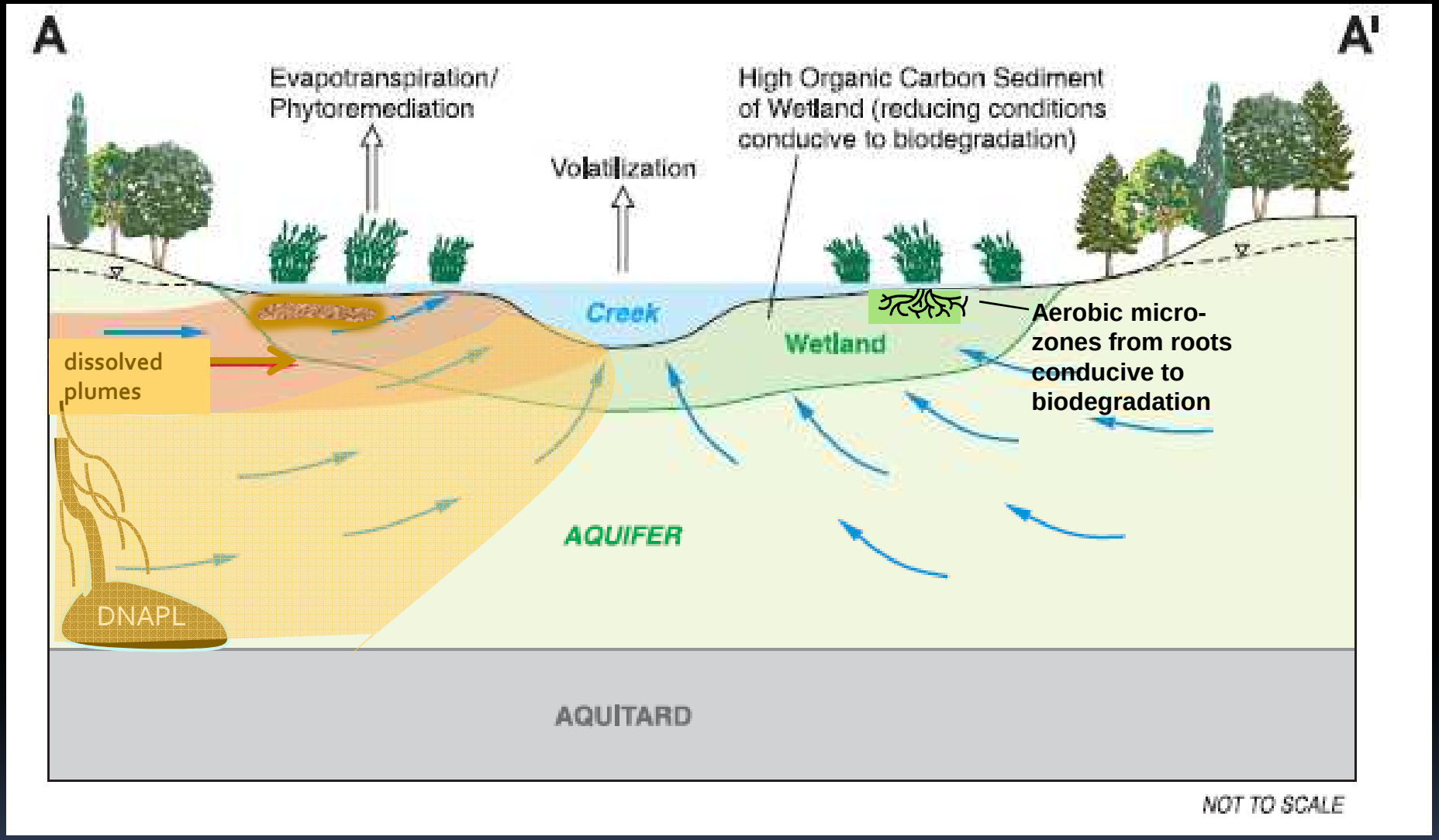


Benzene *

CO_2, CH_4

Aerobic to CO_2

* Parent contaminant at site



Conceptual model for chlorinated solvent contamination in wetland

(modified from Lorah et al., 2005)

Geochemical Evidence (Field Sampling)

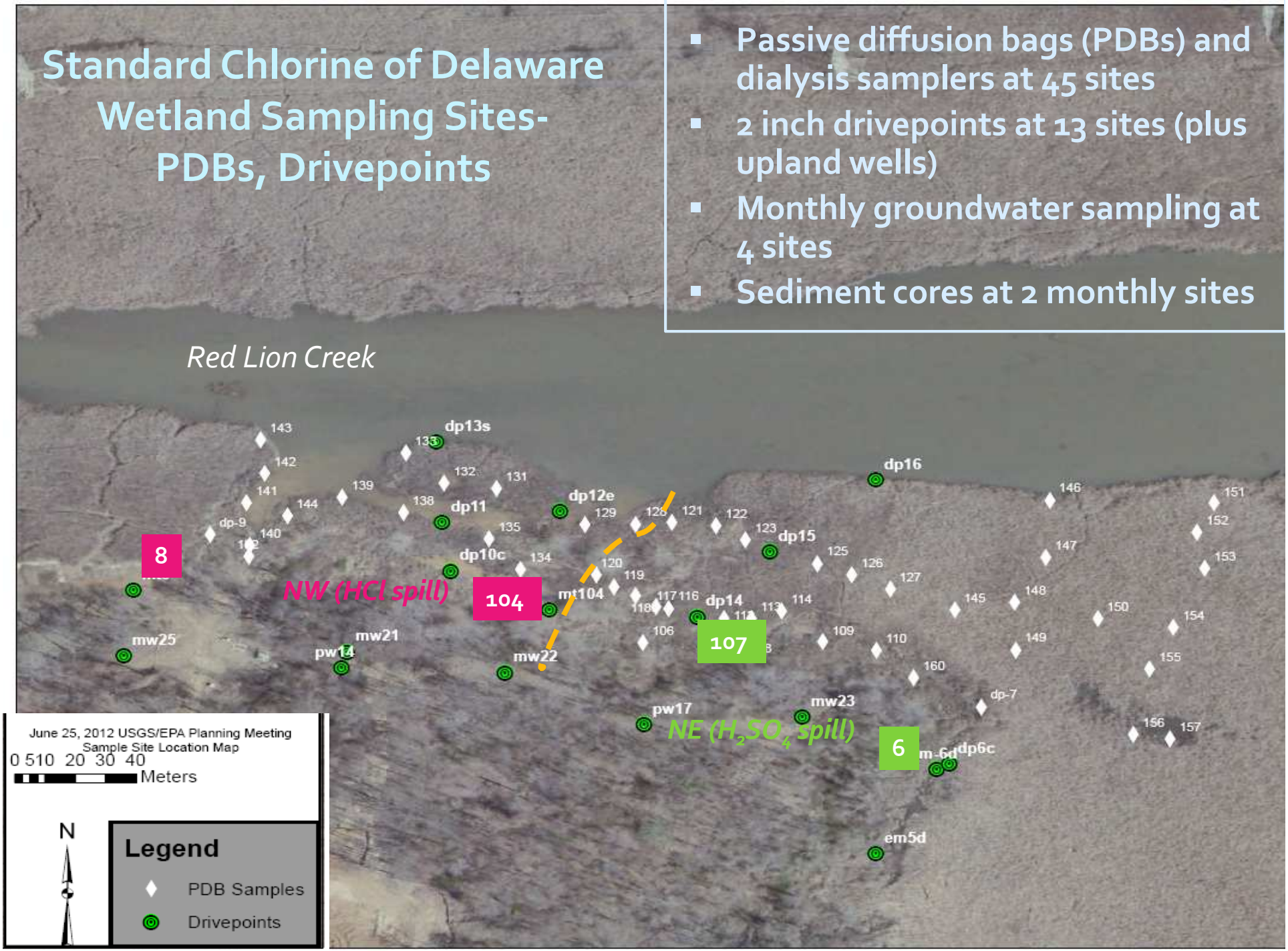
Geochem evidence

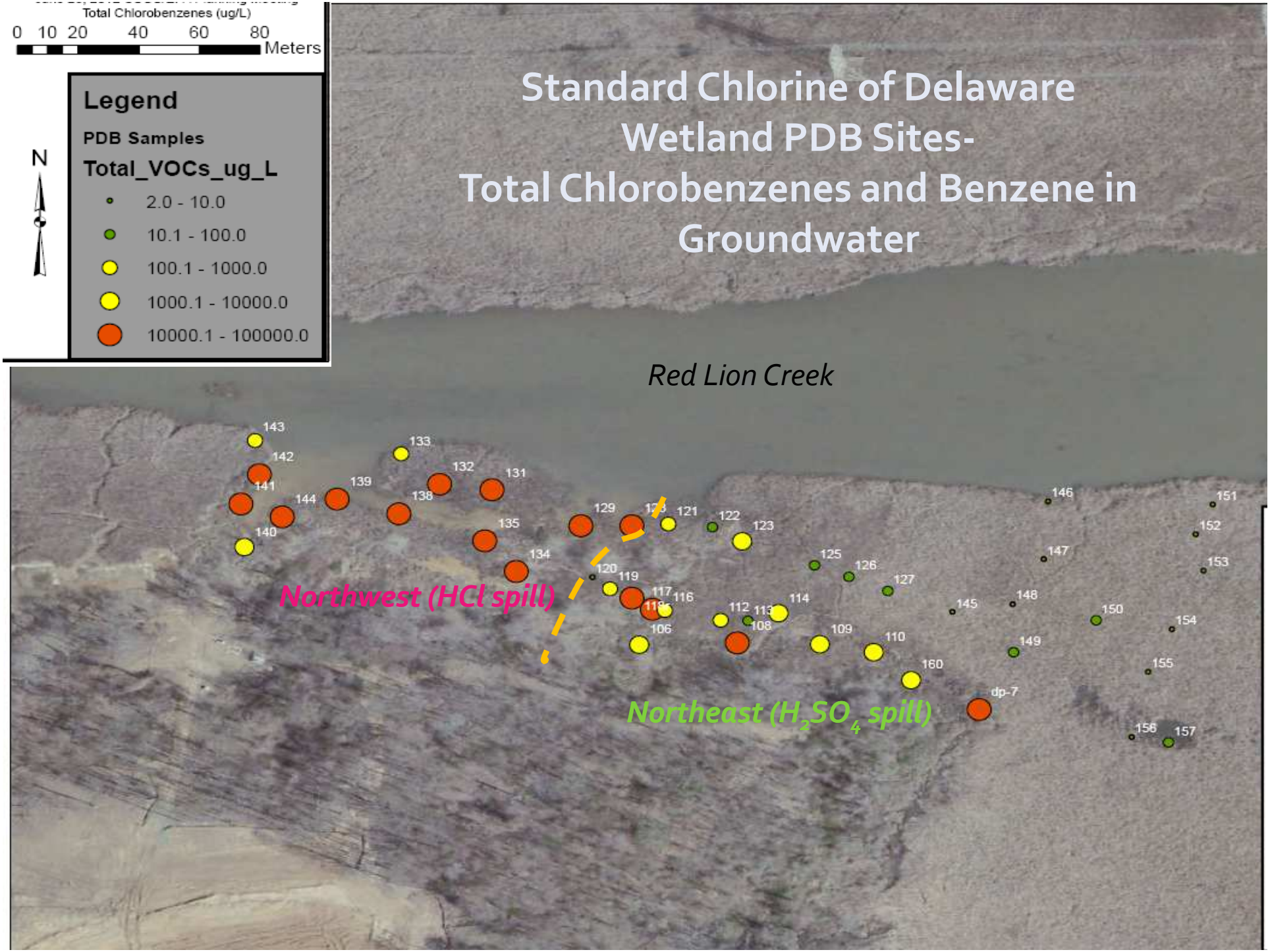
Field Sampling

- **Passive diffusion bags (PDBs) and dialysis samplers at about 45 sites**
- **2 inch drivepoints at 13 sites (plus upland wells)**
- **4-ft long porous membrane samplers (peepers) at 6 sites**
- **Sediment cores at 4 sites**

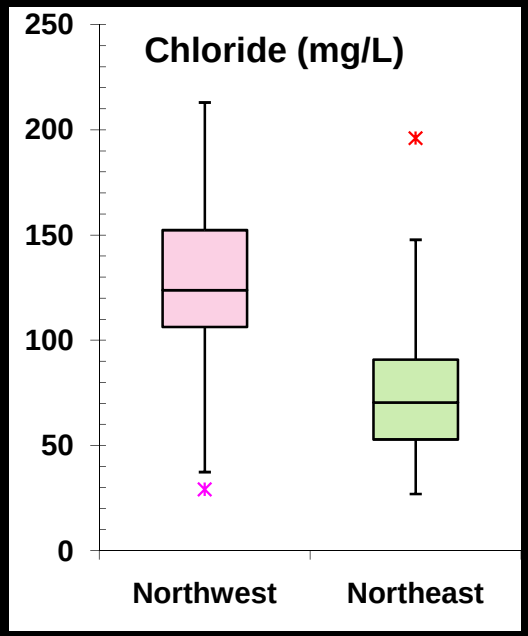
Standard Chlorine of Delaware Wetland Sampling Sites- PDBs, Drivepoints

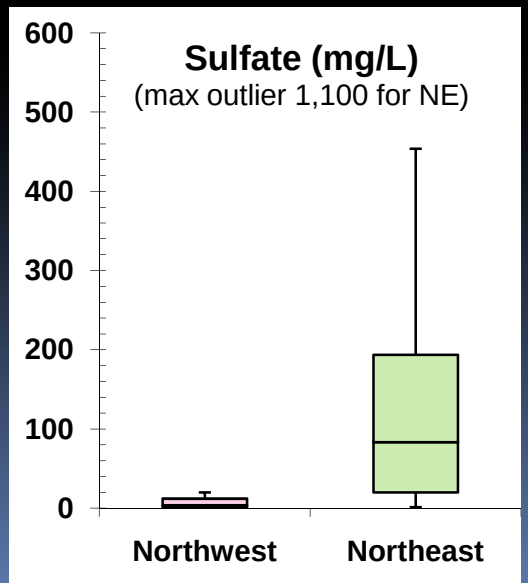
- Passive diffusion bags (PDBs) and dialysis samplers at 45 sites
- 2 inch drivepoints at 13 sites (plus upland wells)
- Monthly groundwater sampling at 4 sites
- Sediment cores at 2 monthly sites

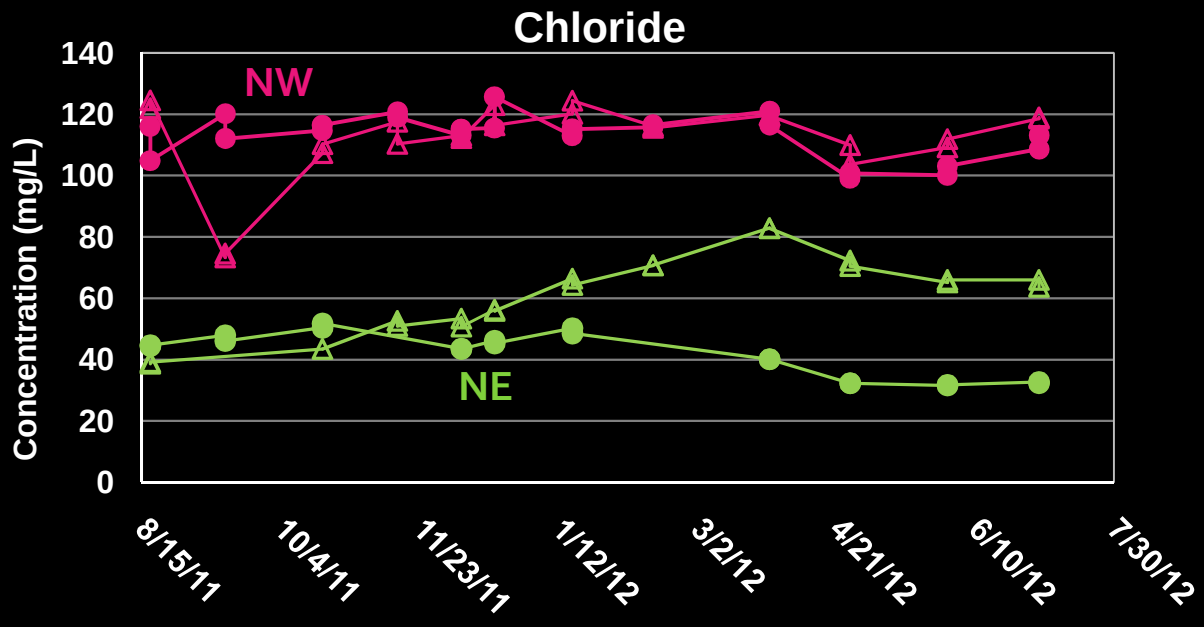


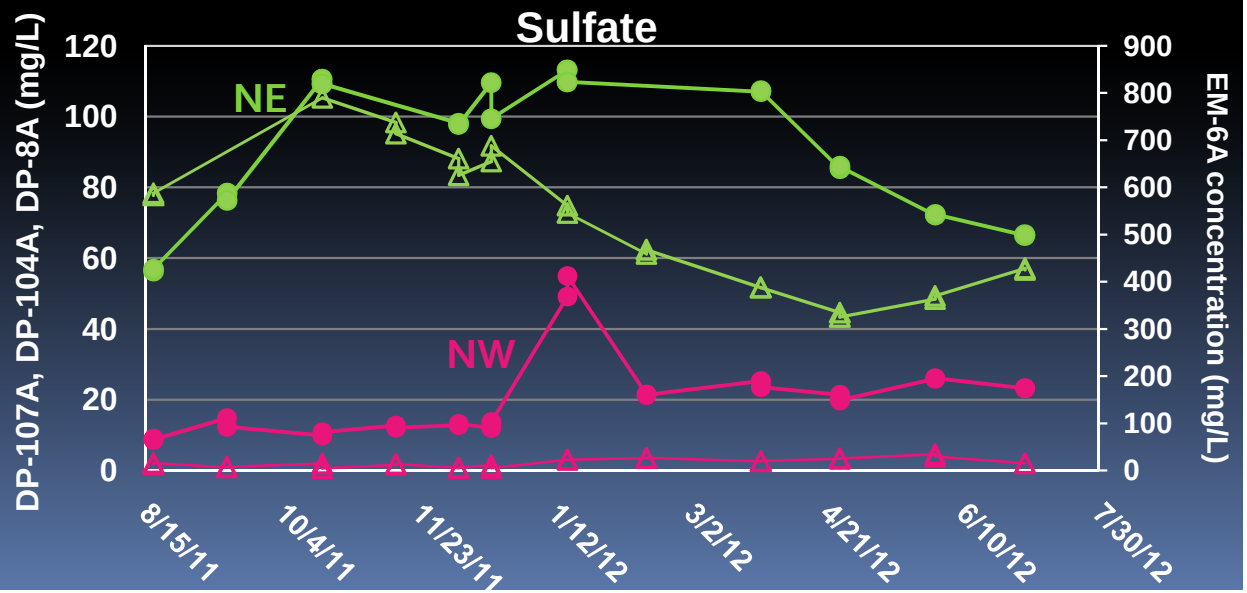

Total Chlorobenzenes (ug/L)
0 10 20 40 60 80
Meters
Legend
PDB Samples
Total_VOCs_ug_L
2.0 - 10.0
10.1 - 100.0
100.1 - 1000.0
1000.1 - 10000.0
10000.1 - 100000.0
N
Standard Chlorine of Delaware
Wetland PDB Sites-
Total Chlorobenzenes and Benzene in
Groundwater
Red Lion Creek
Northwest (HCl spill)
Northeast (H_2SO_4 spill)
143
142
141
144
140
139
138
133
132
131
135
134
129
121
122
123
125
126
127
120
119
117
116
112
113
114
108
106
109
110
160
dp-7
145
148
149
146
147
150
154
155
151
152
153
156
157

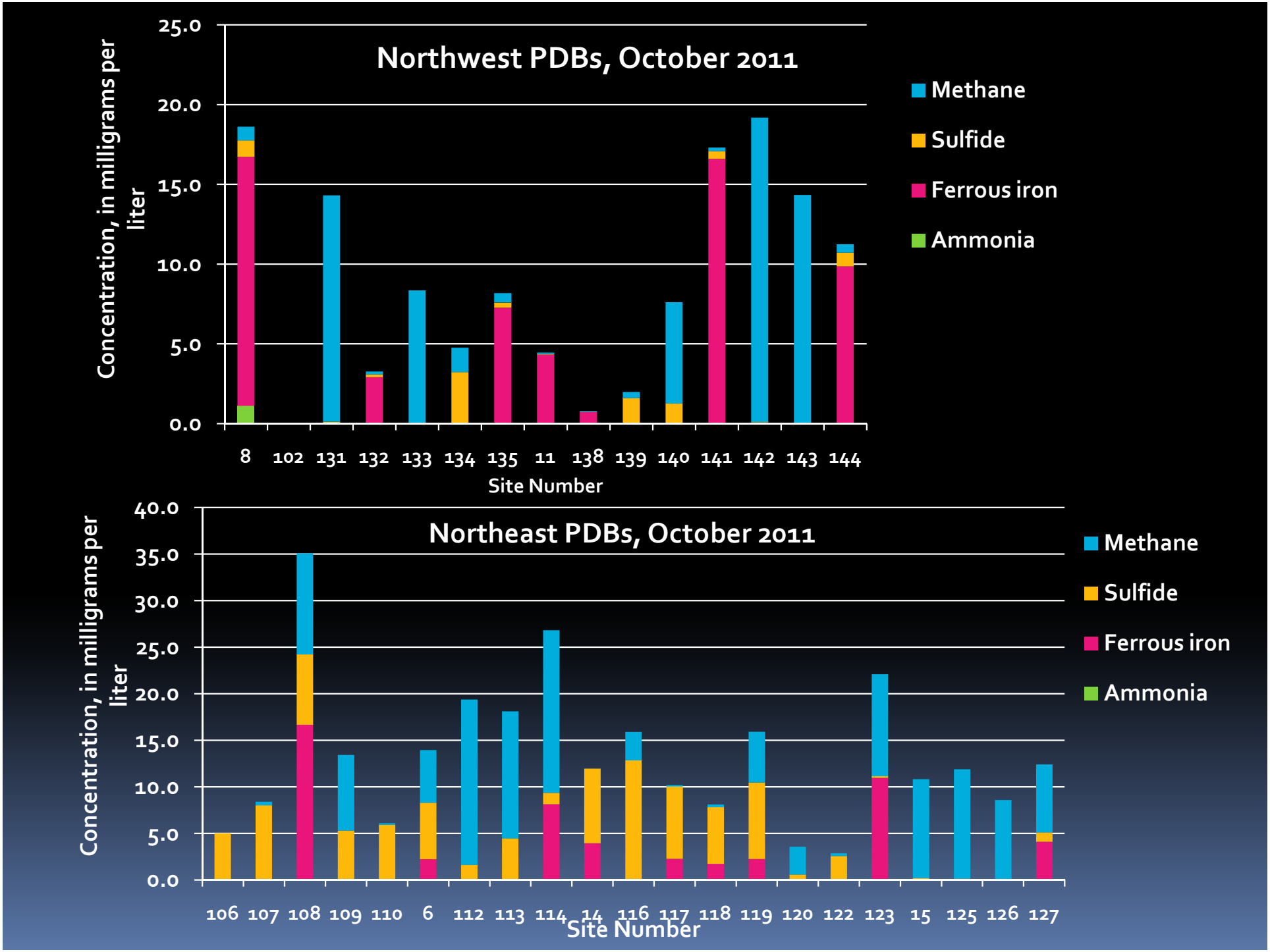
Chloride, Sulfate- Spatial and Temporal





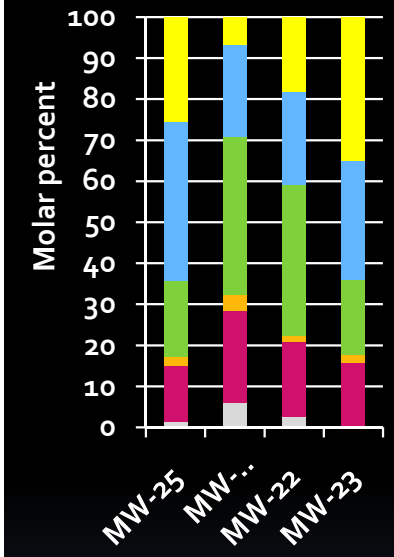


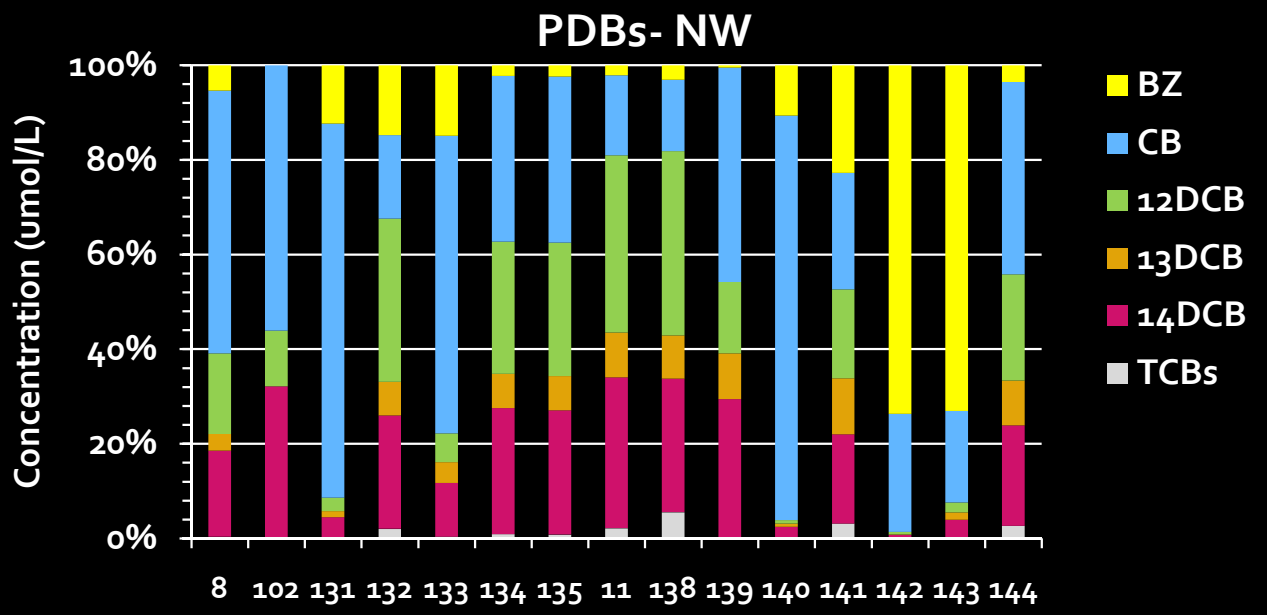


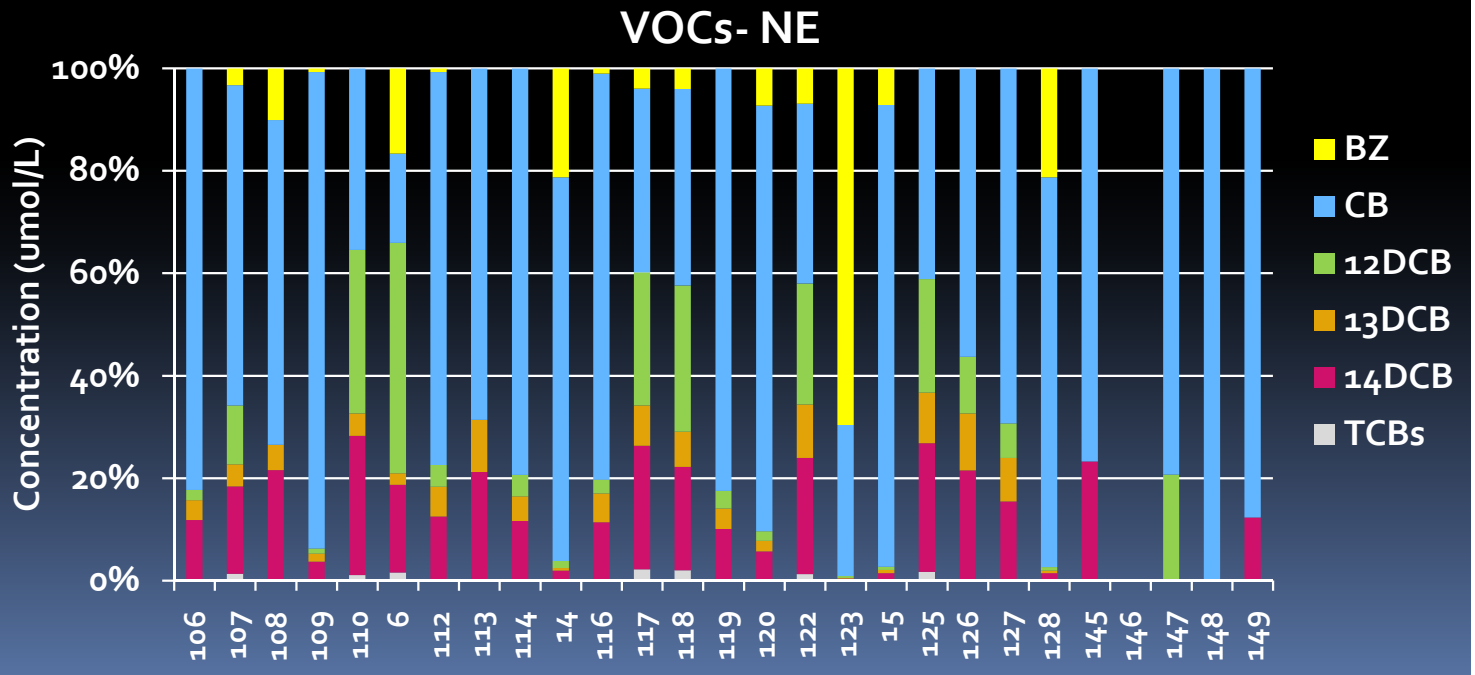

Northwest PDBs, October 2011
Concentration, in milligrams per liter
25.0
20.0
15.0
10.0
5.0
0.0
8
102
131
132
133
134
135
11
138
139
140
141
142
143
144
Site Number
Methane
Sulfide
Ferrous iron
Ammonia
Northeast PDBs, October 2011
Concentration, in milligrams per liter
40.0
35.0
30.0
25.0
20.0
15.0
10.0
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

VOCs- PDBs, October 2011

Upland Wells, Oct . 2011





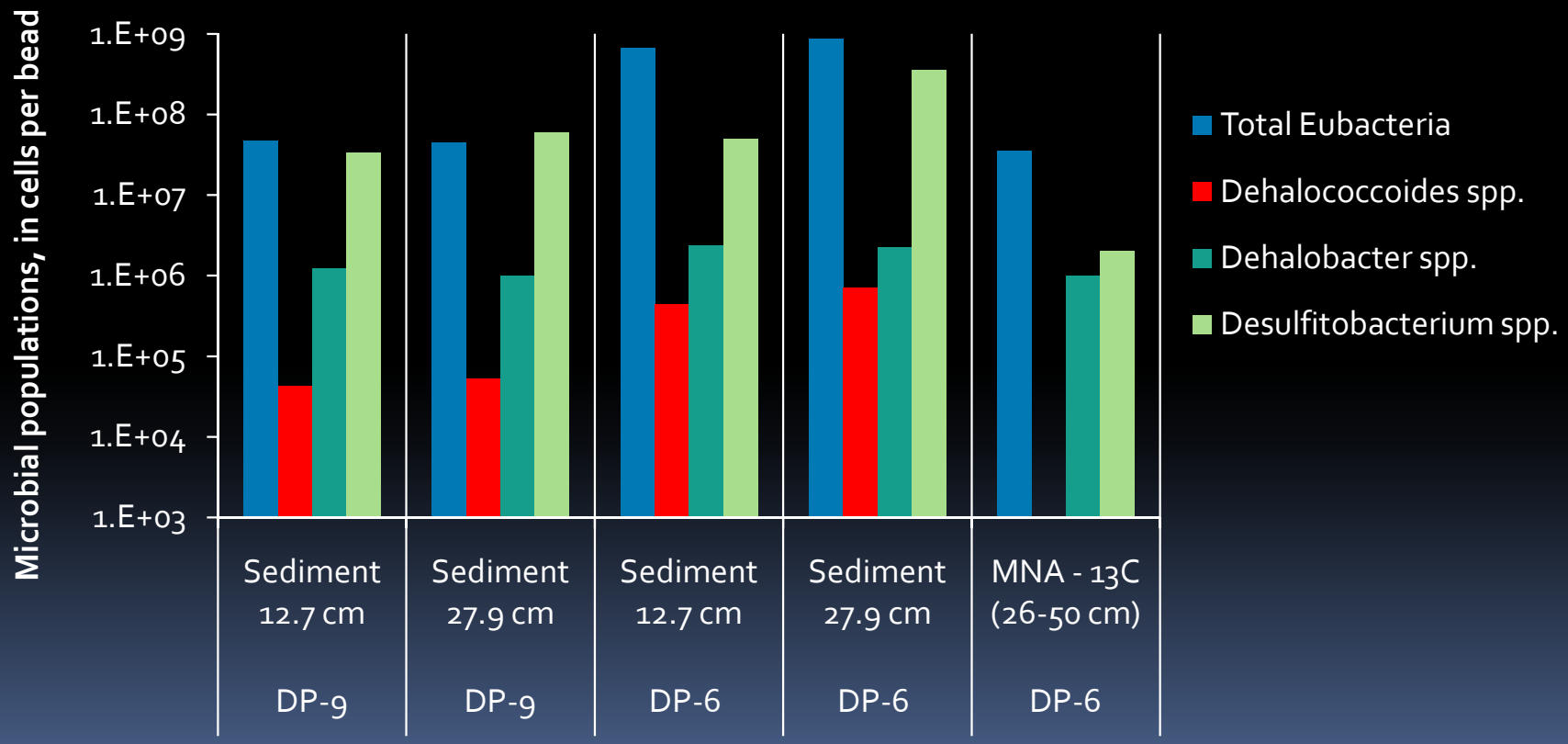


- Contaminant distribution
- Natural biodegradation potential (MNA)

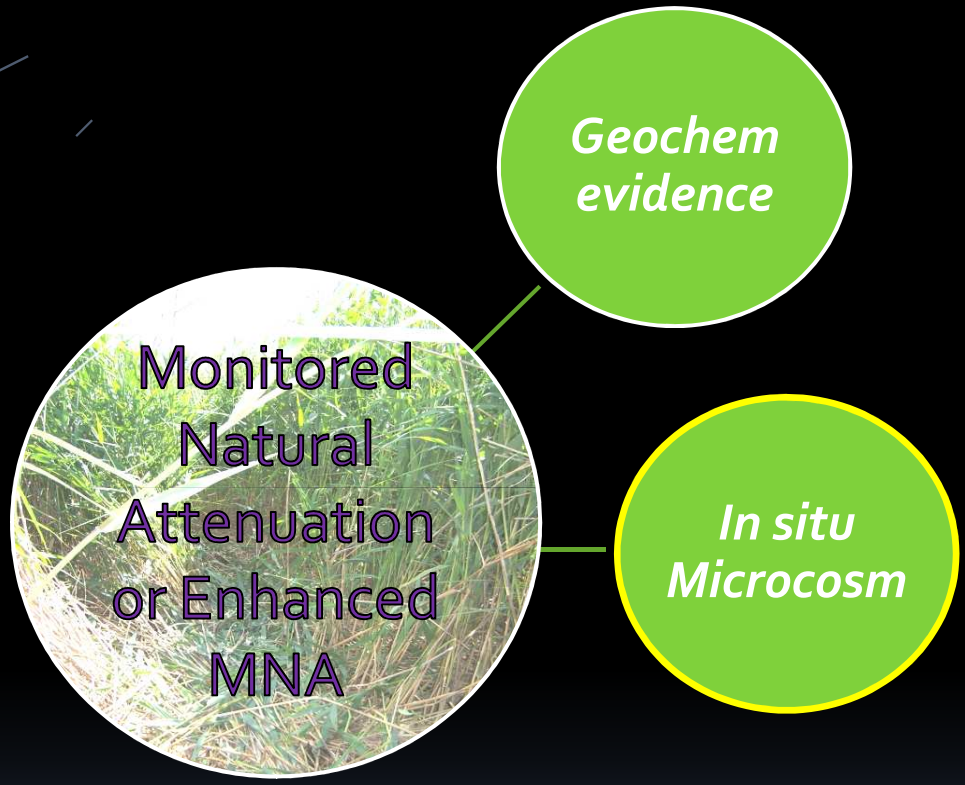
Peepers at 6 sites

120 cm length
22 ports

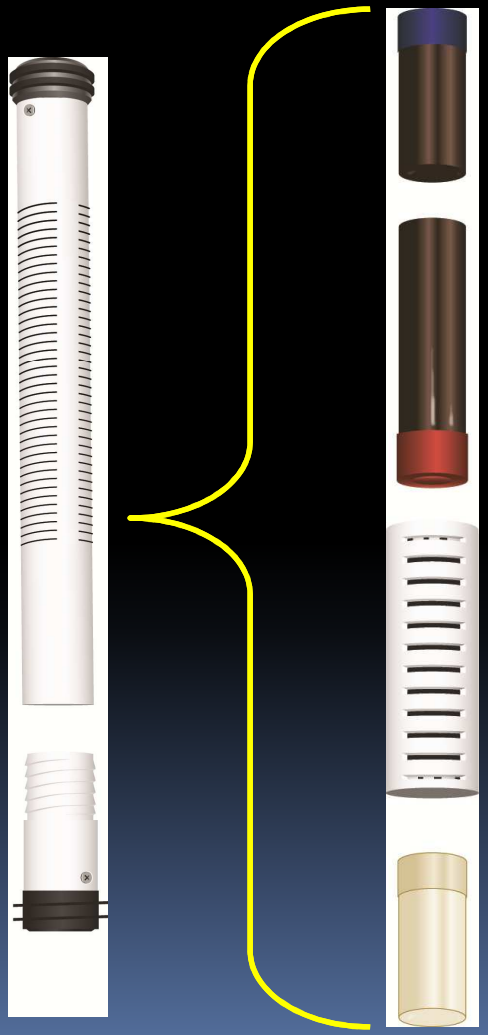
Microbial Populations from qPCR: Sediment and ISM



In Situ Microcosms

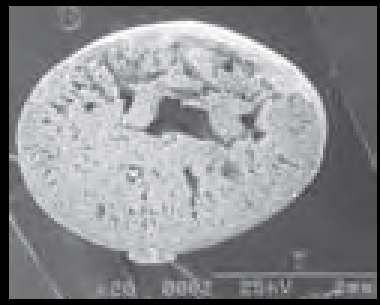


In Situ Microcosms Bio-Traps



GEO
geochemistry:
anions, VFAs

COC
VOCs, redox

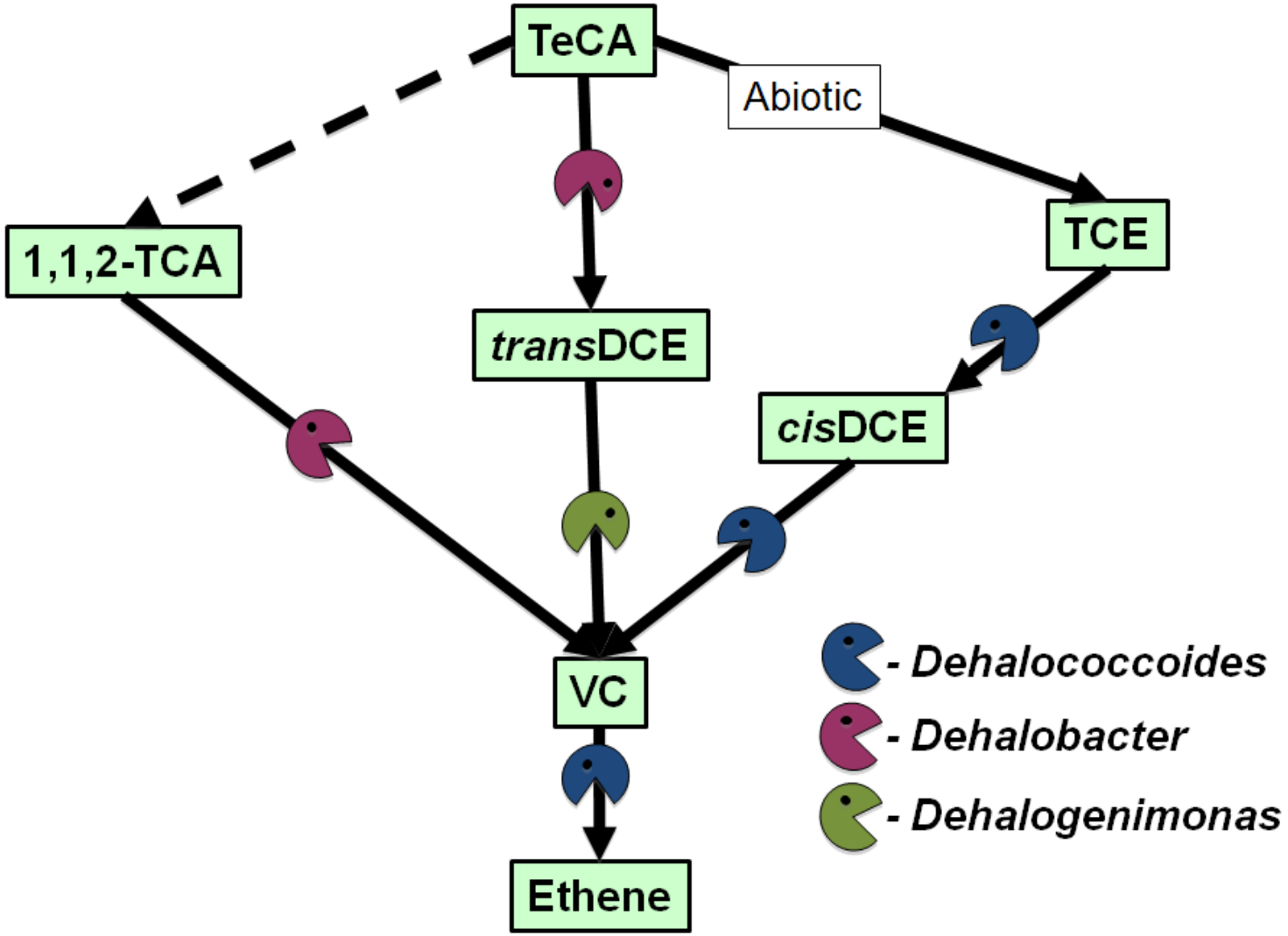


Bio-Sep® beads provide a large surface area for microbial attachment

MICRO- with Bio-Sep
- Sample microbes
- Load with culture
- Load with contaminant ; ^{13}C-VOC

Amendments
i.e. donor, nutrients

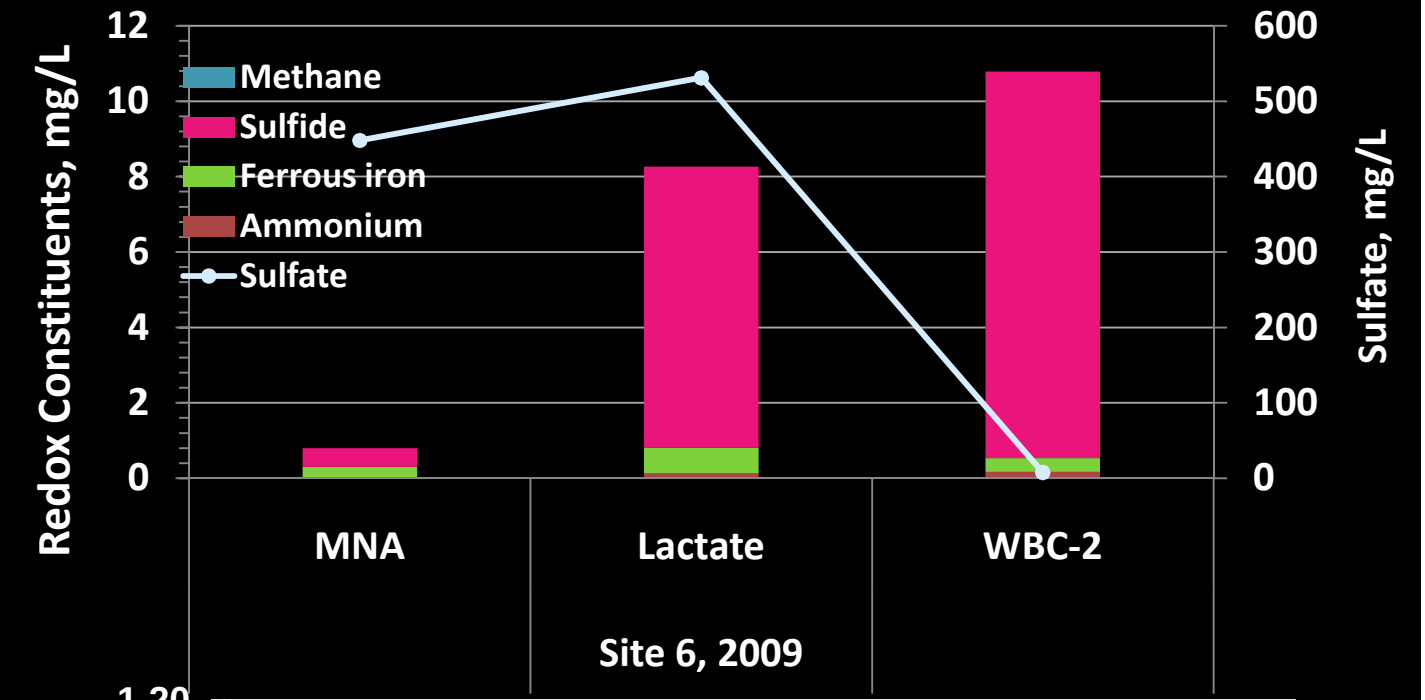
WBC-2 Degradation pathways and dechlorinators

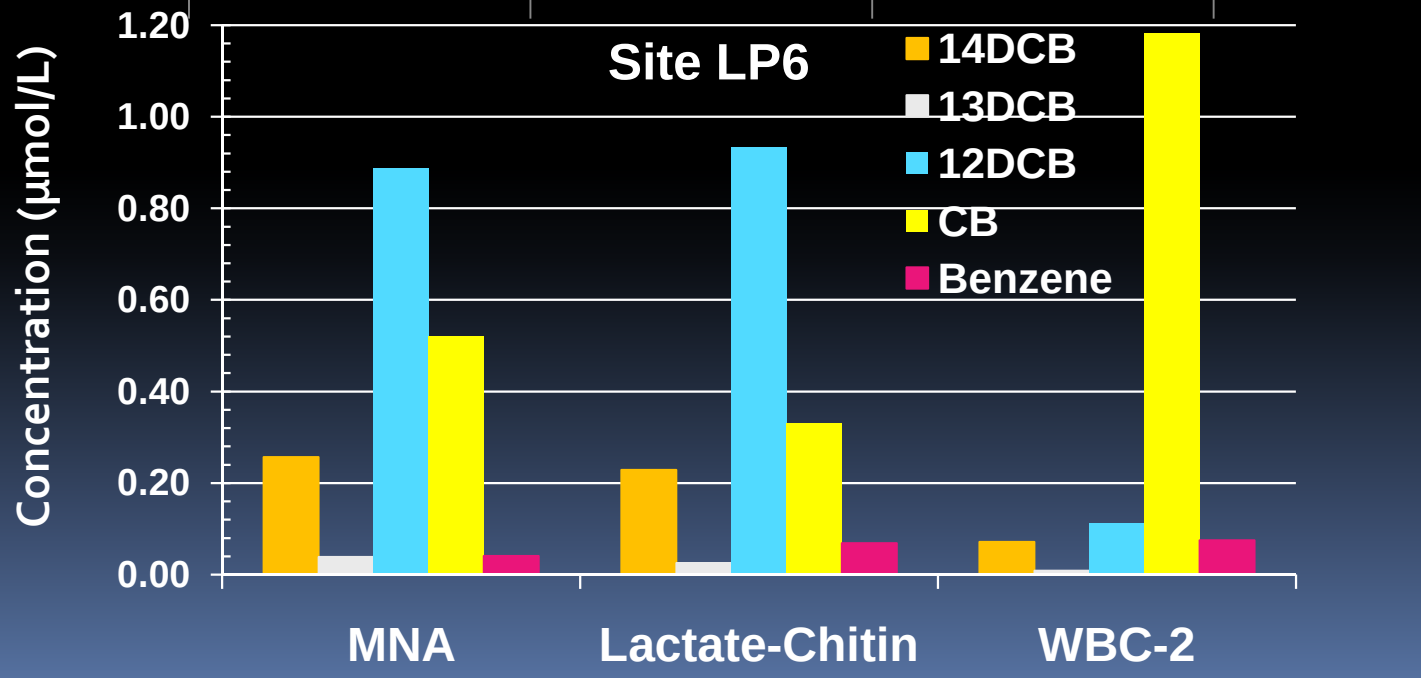


Manchester et al., 2011

ISM Results: Redox and VOCs, LP6

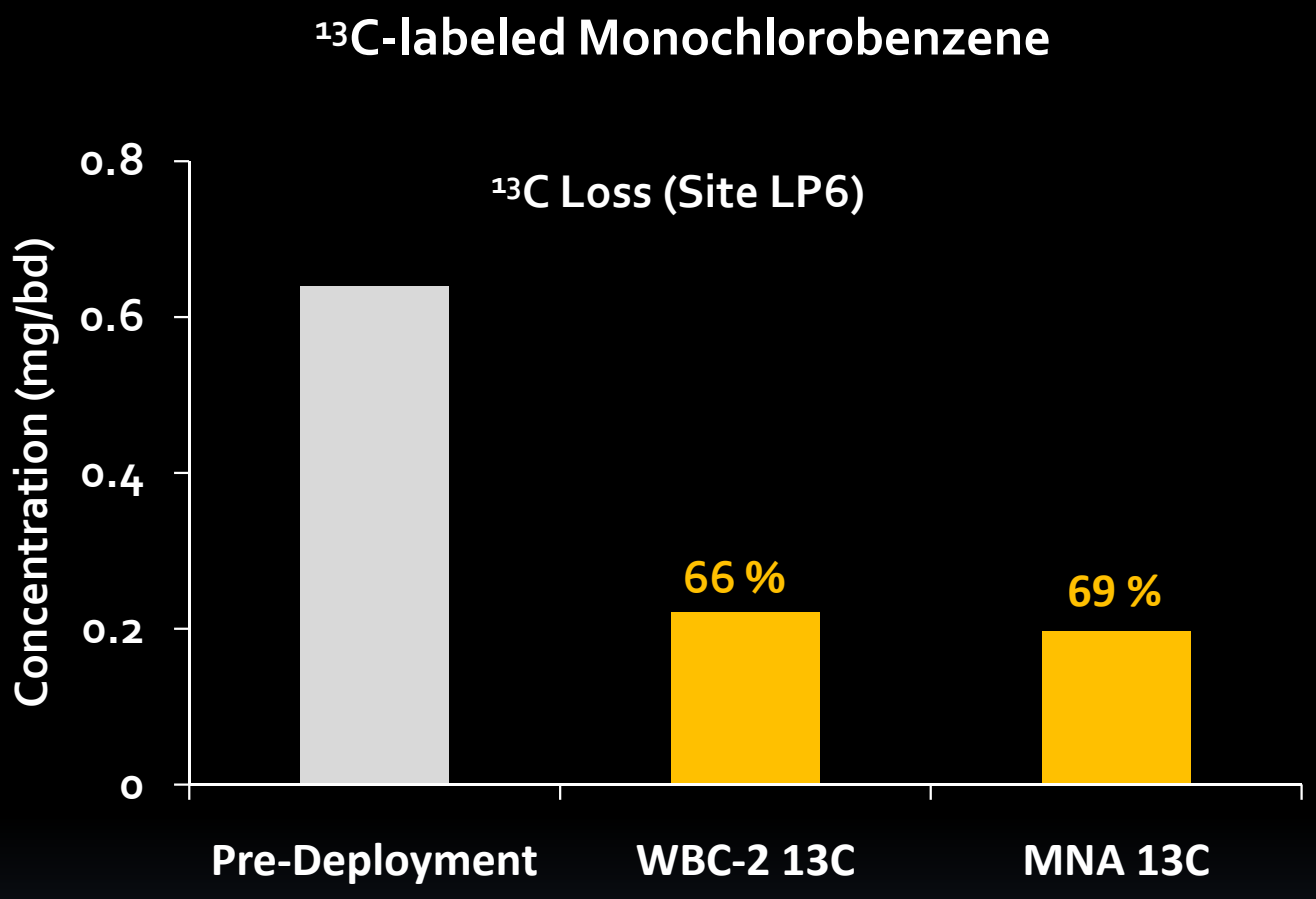
Complete sulfate reduction and degradation of DCBs evident in WBC-2 treatment





ISM Results: ^{13}C

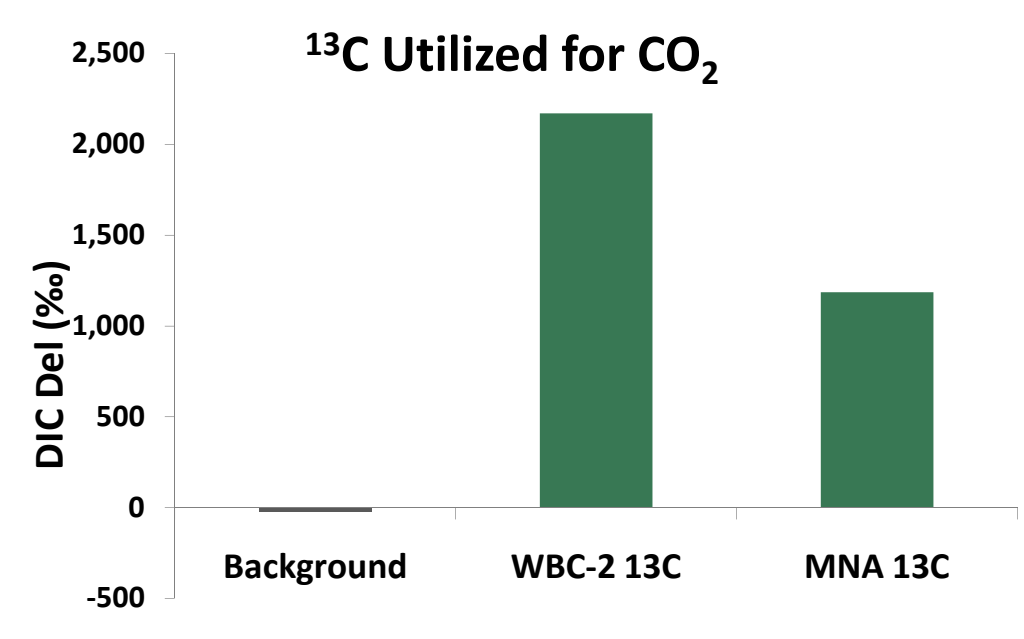
Removal of ^{13}C-labeled chlorobenzene in MNA and WBC-2 bioaugmented treatments- *Definitive evidence of microbial removal*

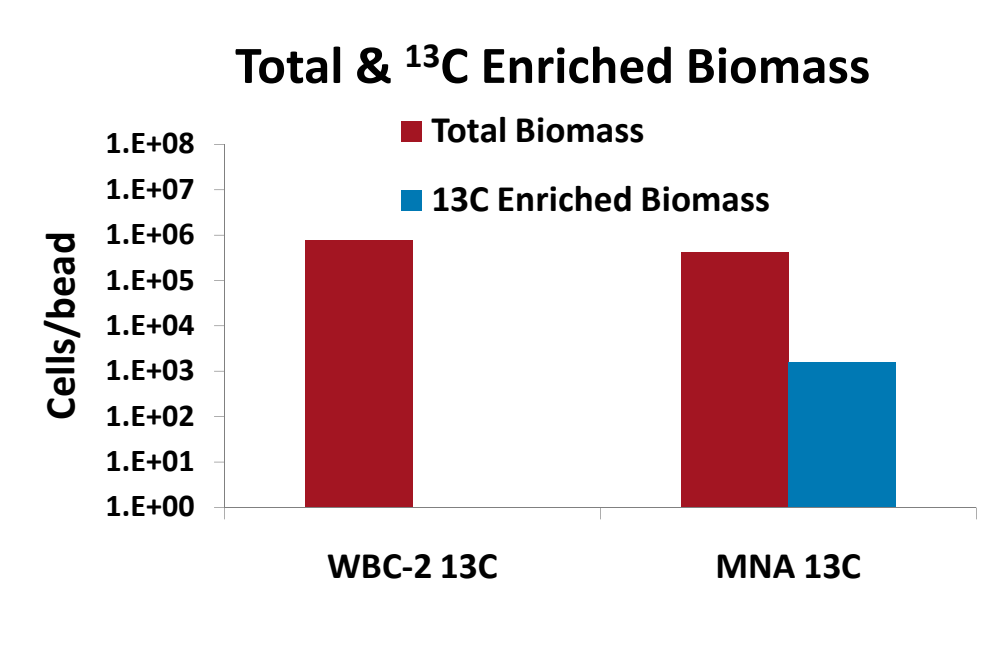


	WBC-2 ^{13}C	MNA ^{13}C
k (per day)	0.019	0.021
half life (days)	37.1	33.5

ISM 2009 Results: ^{13}C Site LP6

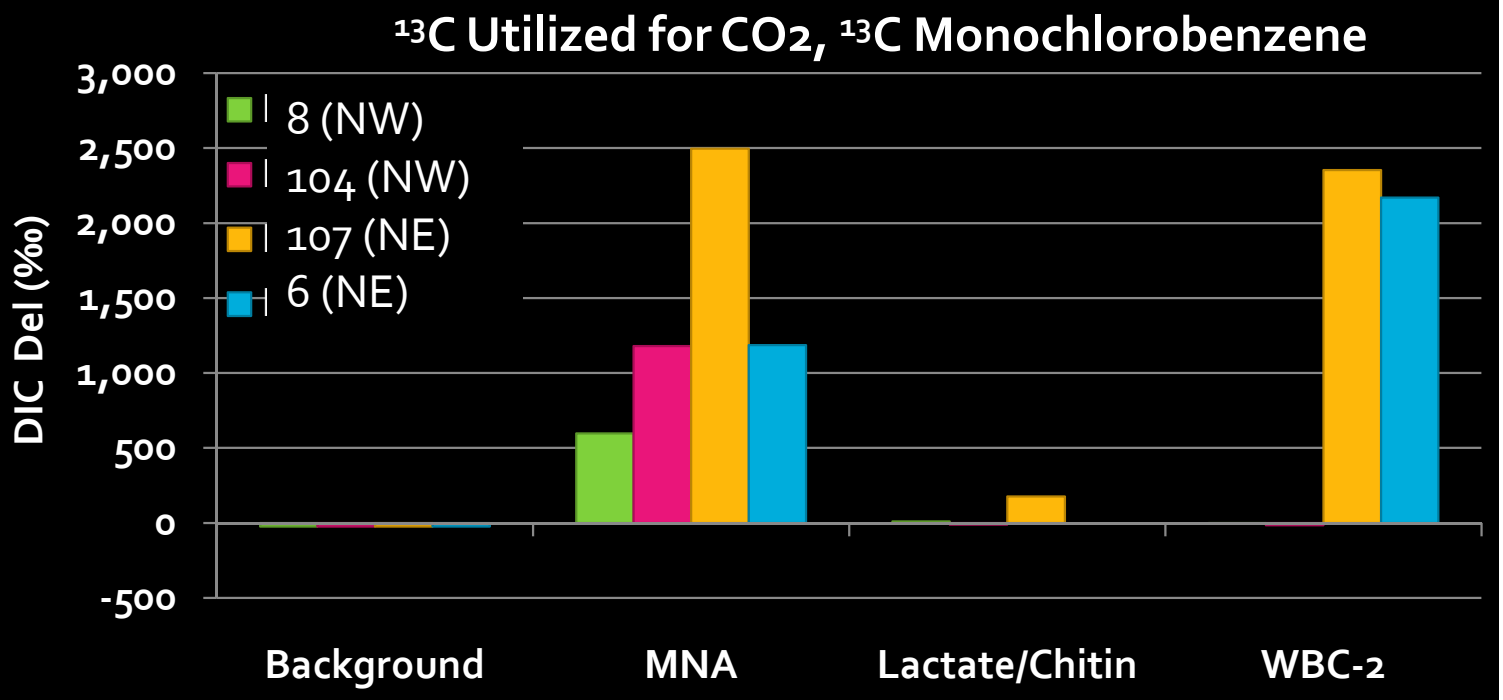
Chlorobenzene degradation by different pathways

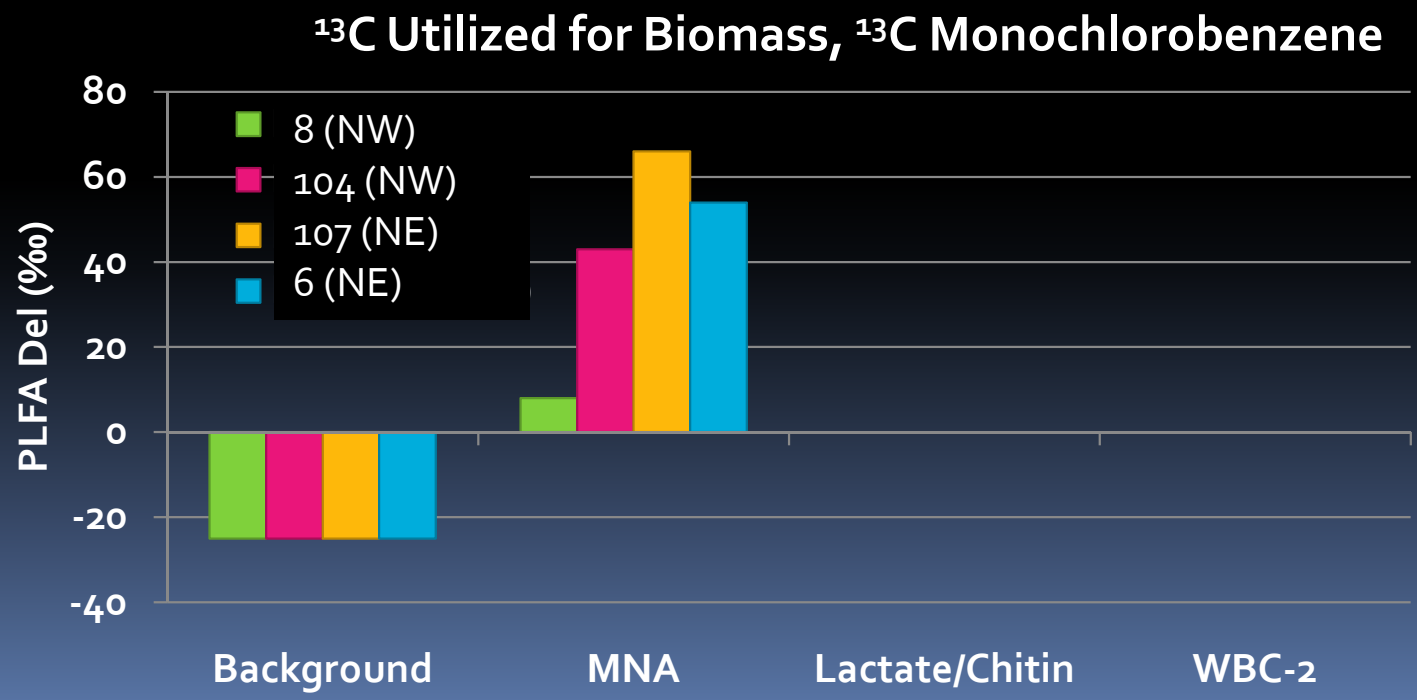




- Oct.-Dec. 2010 ^{13}C ISMs: Chloro-benzene

Chlorobenzene degradation under a range of apparent redox conditions across wetland





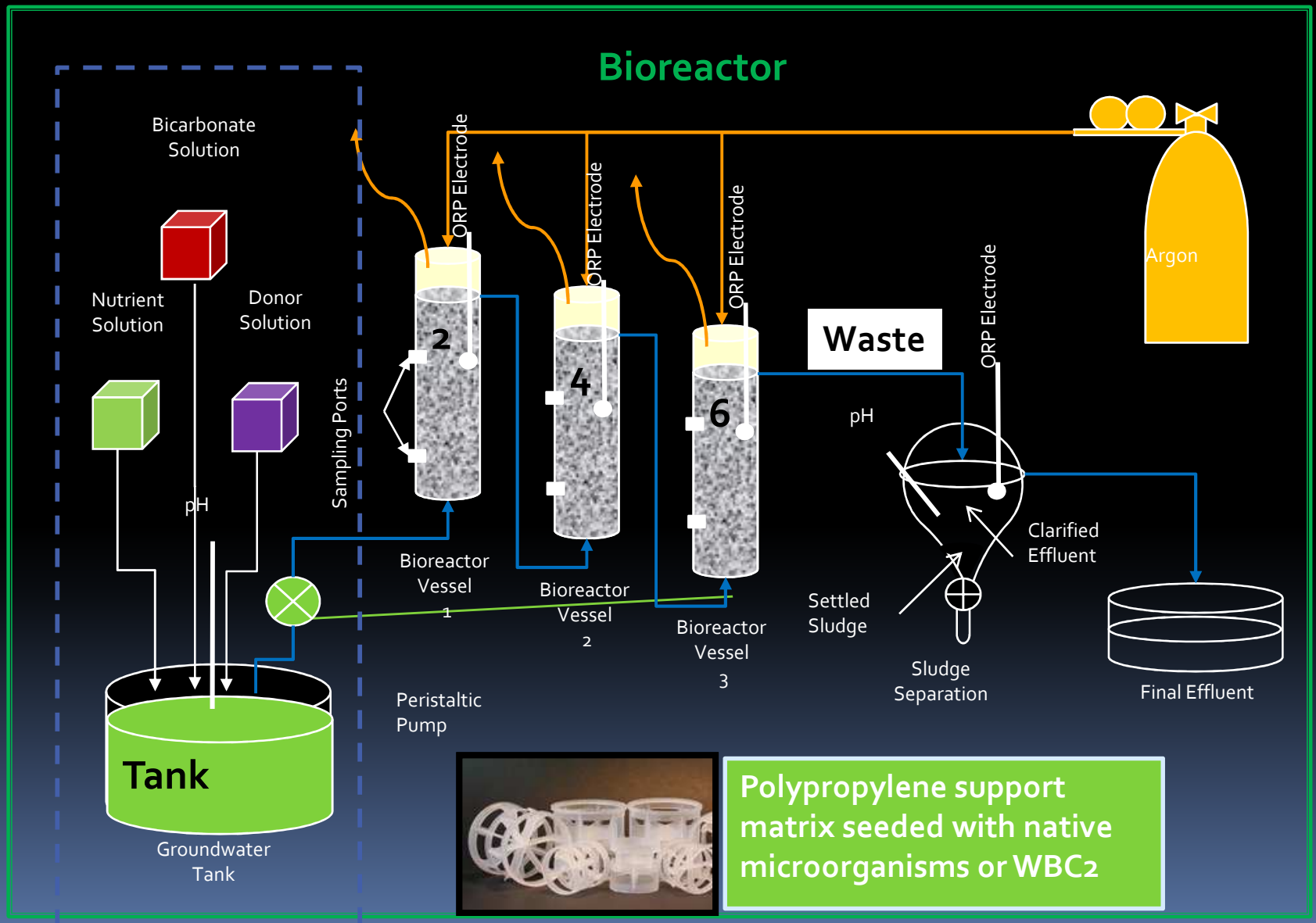
Flow-through bioreactors

Geochem evidence

In situ Microcosm

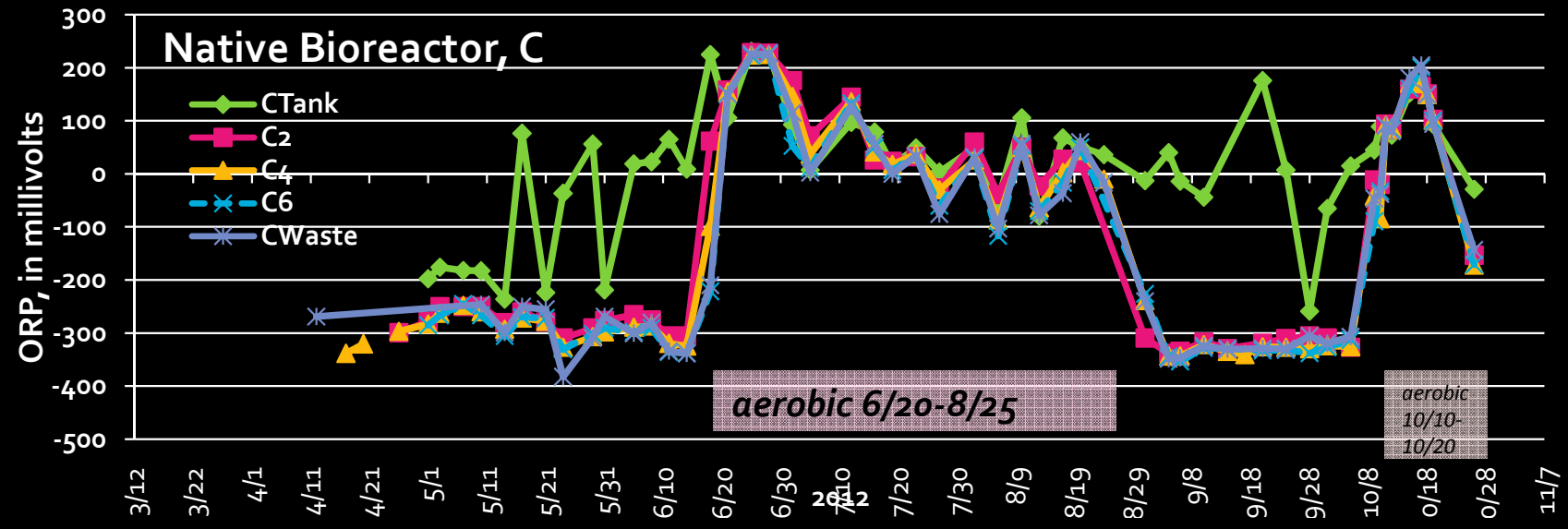
Flow-through bioreactor

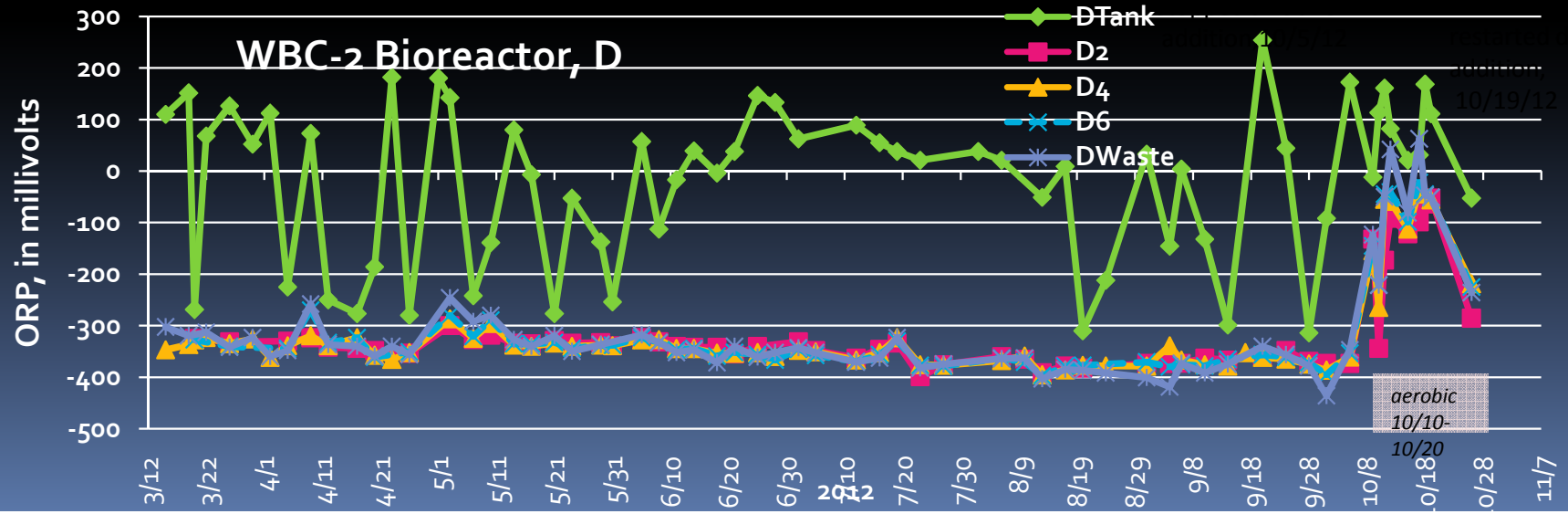
Anaerobic Fixed-Film Bioreactors



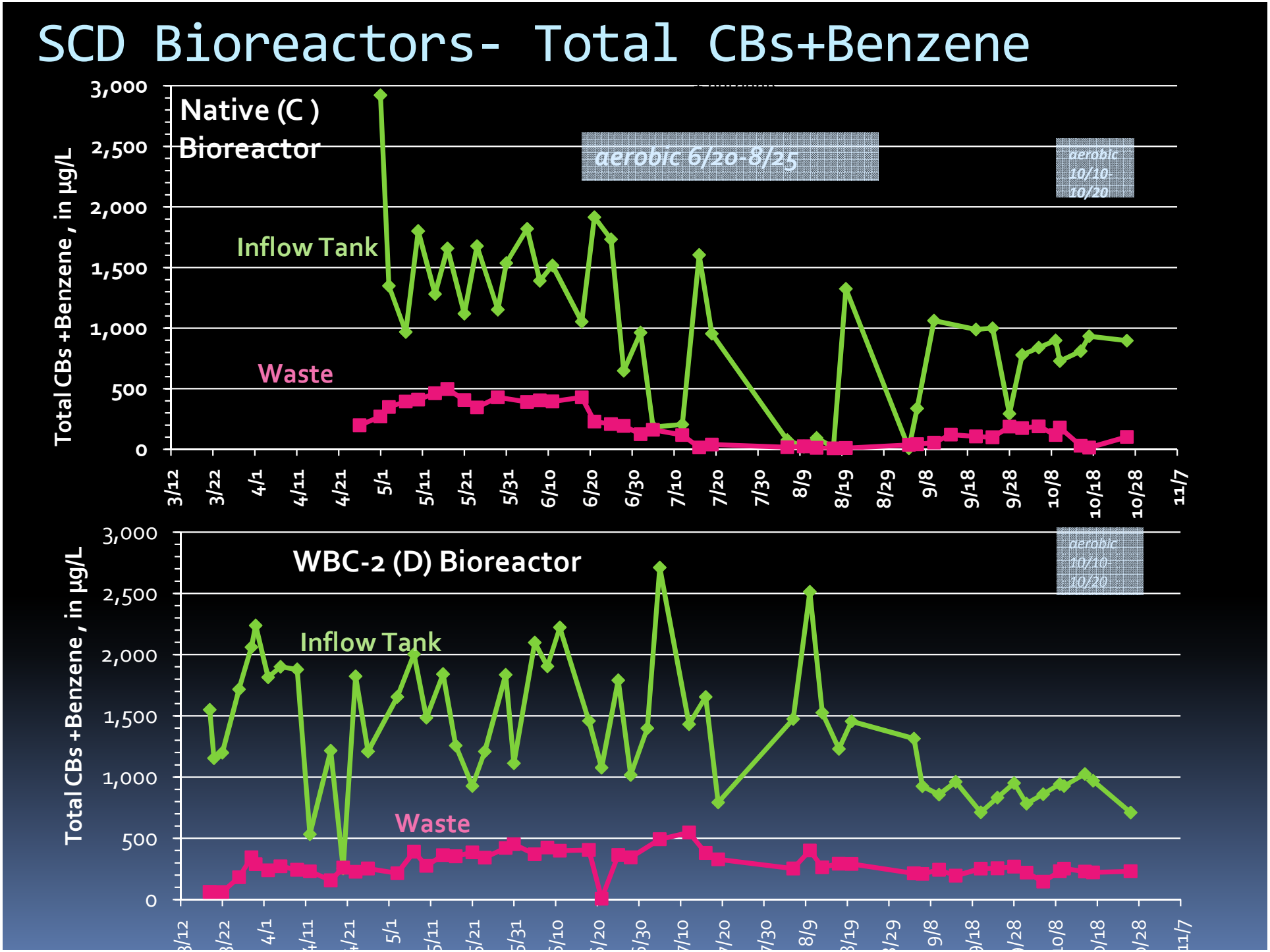
SCD Bioreactors- ORP

(median residence time~ 40 hr; pH~7.0-7.5)



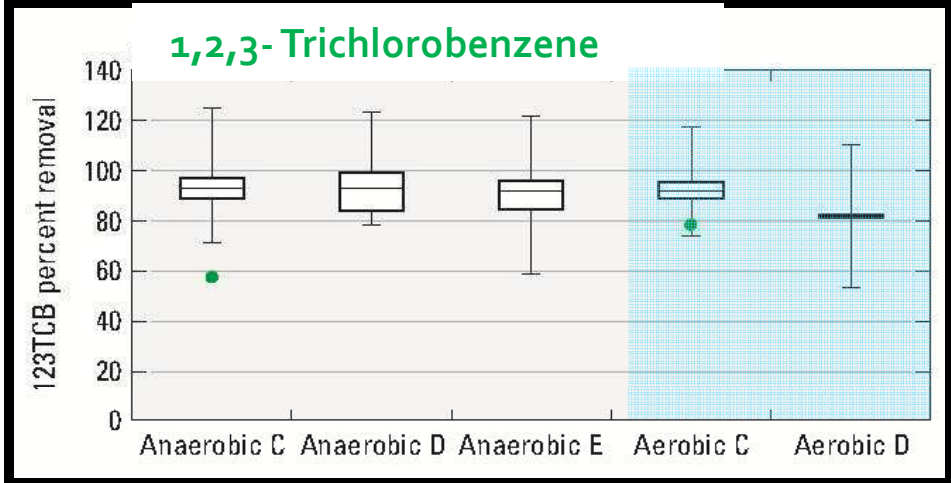


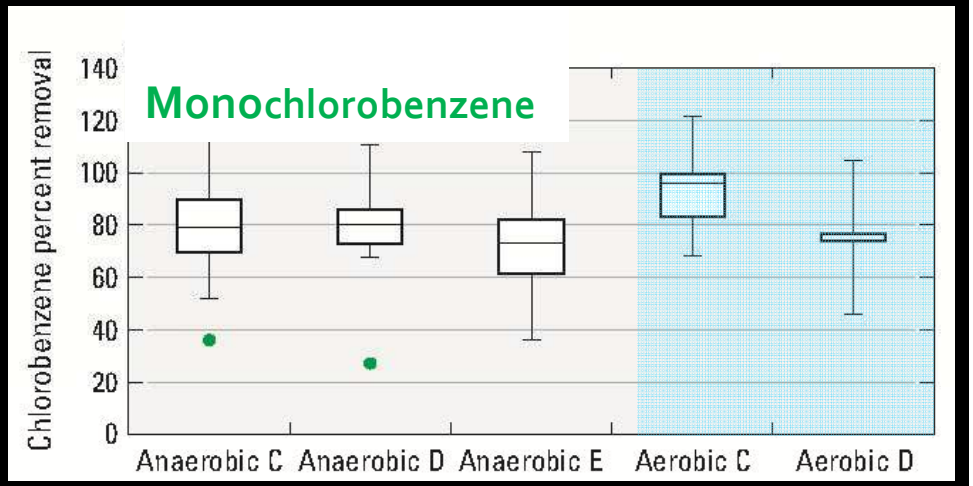
SCD Bioreactors- Total CBs+Benzene

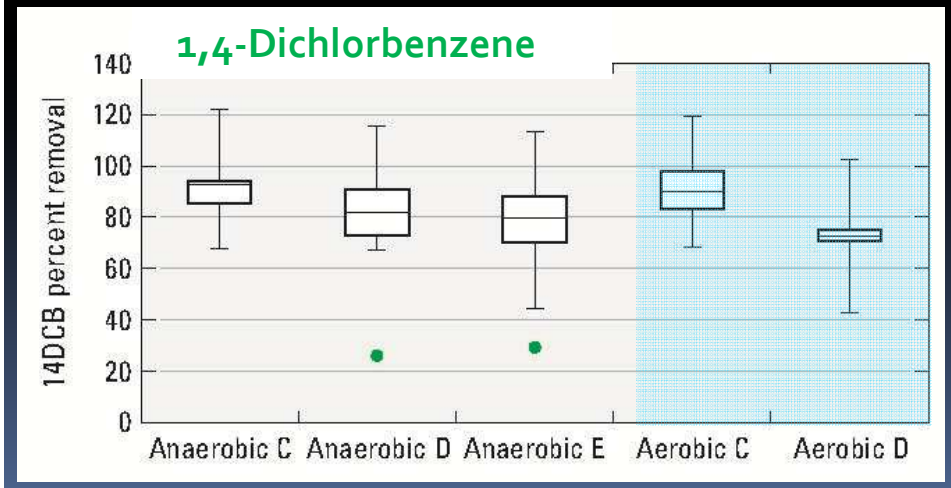


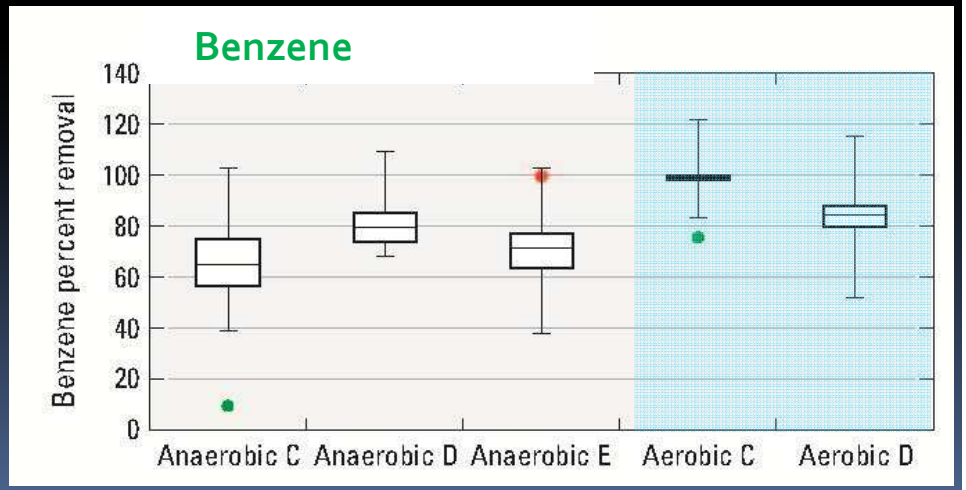
SCD Bioreactors- VOC Percent Removals

(median residence time~ 36 hr; pH~7.0-7.5)

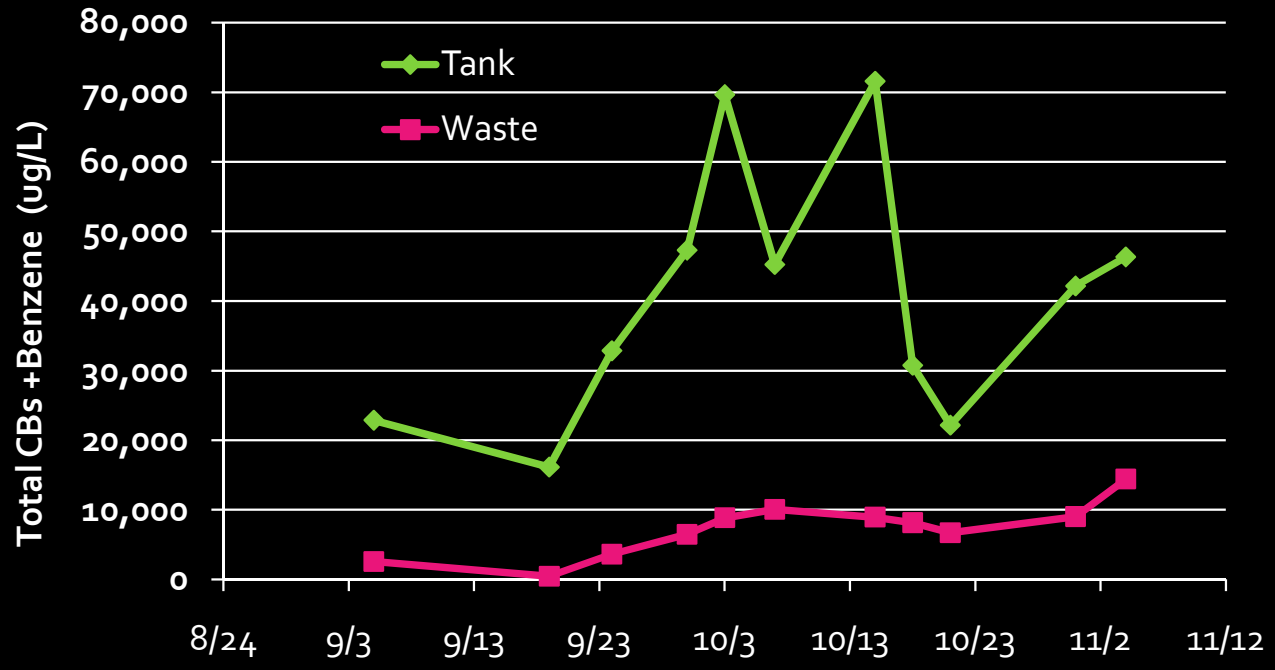


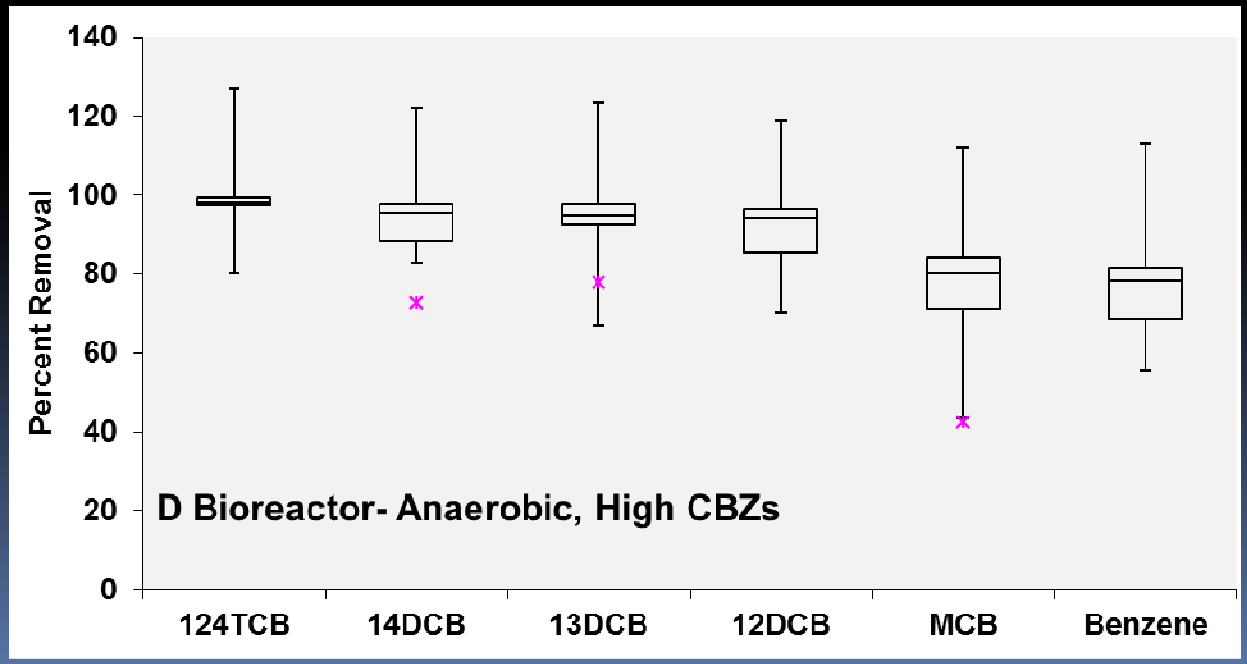






2013 SCD Bioreactors- High CBZs





MCB and benzene median removals = 80 % (about 85% at low initial total CBZ concentrations)

USGS Fate and Bioremediation Team

- Site characterization
- Feasibility evaluation
- Technology development
- Pilot test remediation

FAB Team:

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Mastin Mount
Jessica Thompson
Luke Myers
Roberto Cruz
Melody Flinchbaugh
Andrew Reid
Emily Majcher

CRADA Partner:

Geosyntec Consultants

http://md.water.usgs.gov/teams/fab/