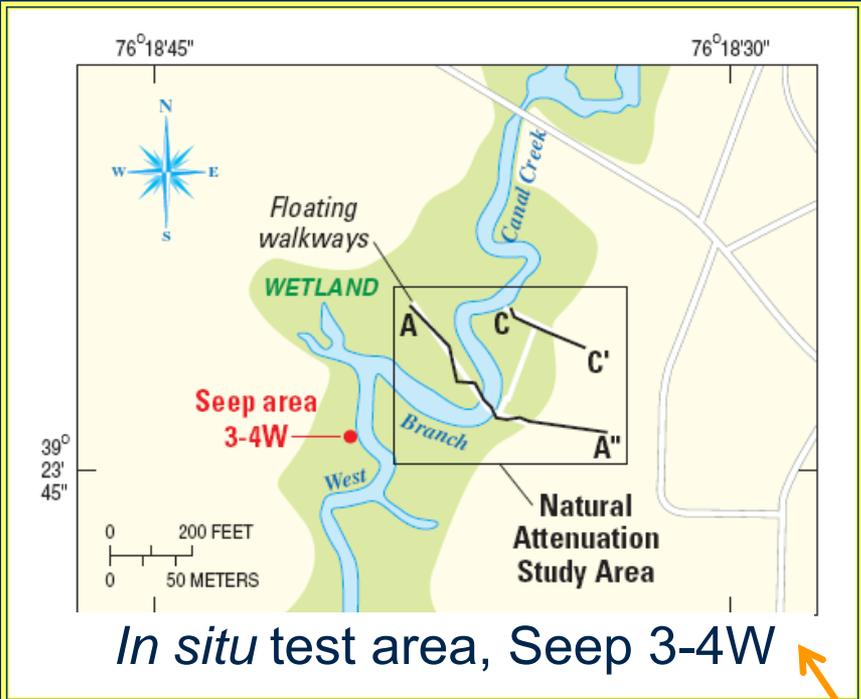


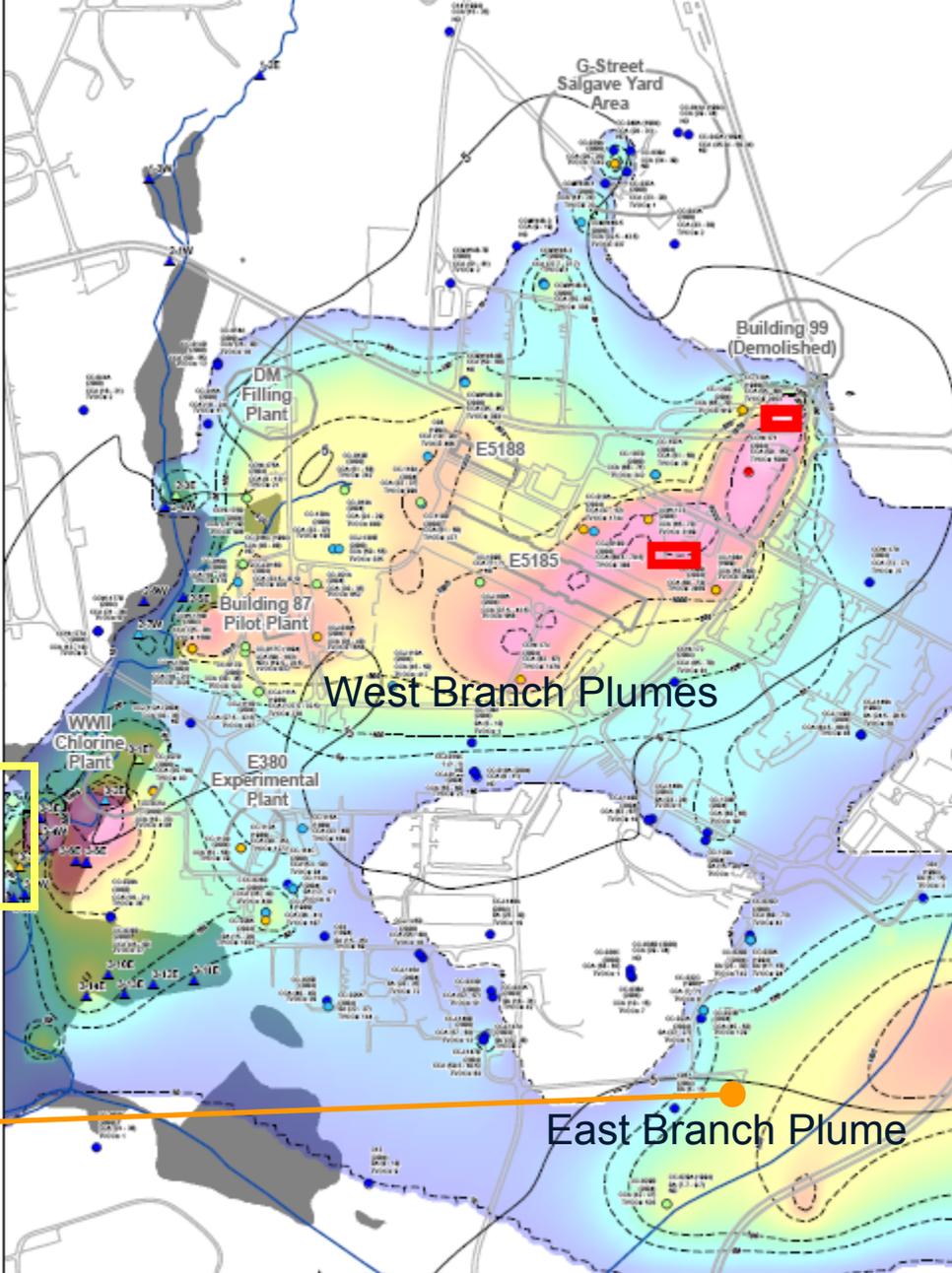
In Situ and *Ex Situ* Bioremediation Technologies for Groundwater Contaminated with Chlorinated Solvents

Michelle M. Lorah, U.S. Geological Survey
Emily Majcher , Duane Graves, Geosyntec Consultants
John Wrobel, Aberdeen Proving Ground





In situ test area, Seep 3-4W



Canal Creek Groundwater Treatment Plant- *Ex situ* test

Canal Creek Area, Aberdeen Proving Ground, Maryland

Legend

Wells (TVOCs µg/L):

- < 100
- 100 - 500
- 500 - 1000
- 1000 - 5000
- > 5000

Boys (TVOCs µg/L):

- ▲ < 100

Plume

Contour

Map TVOCs (µg/L)

LC50 Isoconcentration

Potential Source Area

Marsh

TVOCs (µg/L):

- 10000
- 5000
- 2000
- 1000
- 500
- 100
- 50
- 10

Water

1 The map overlaid on the Boys is that of the most recent sample.

2 The TVOCs concentration contour map overlaid from DPSCPT information along

WESTERN SYSTEMS

Coordinate System: UTM Zone 18 NAD83 feet

Graphic Scale

Figure 2
Total VOCs Distribution
Based on the Most Current
Data Available

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:

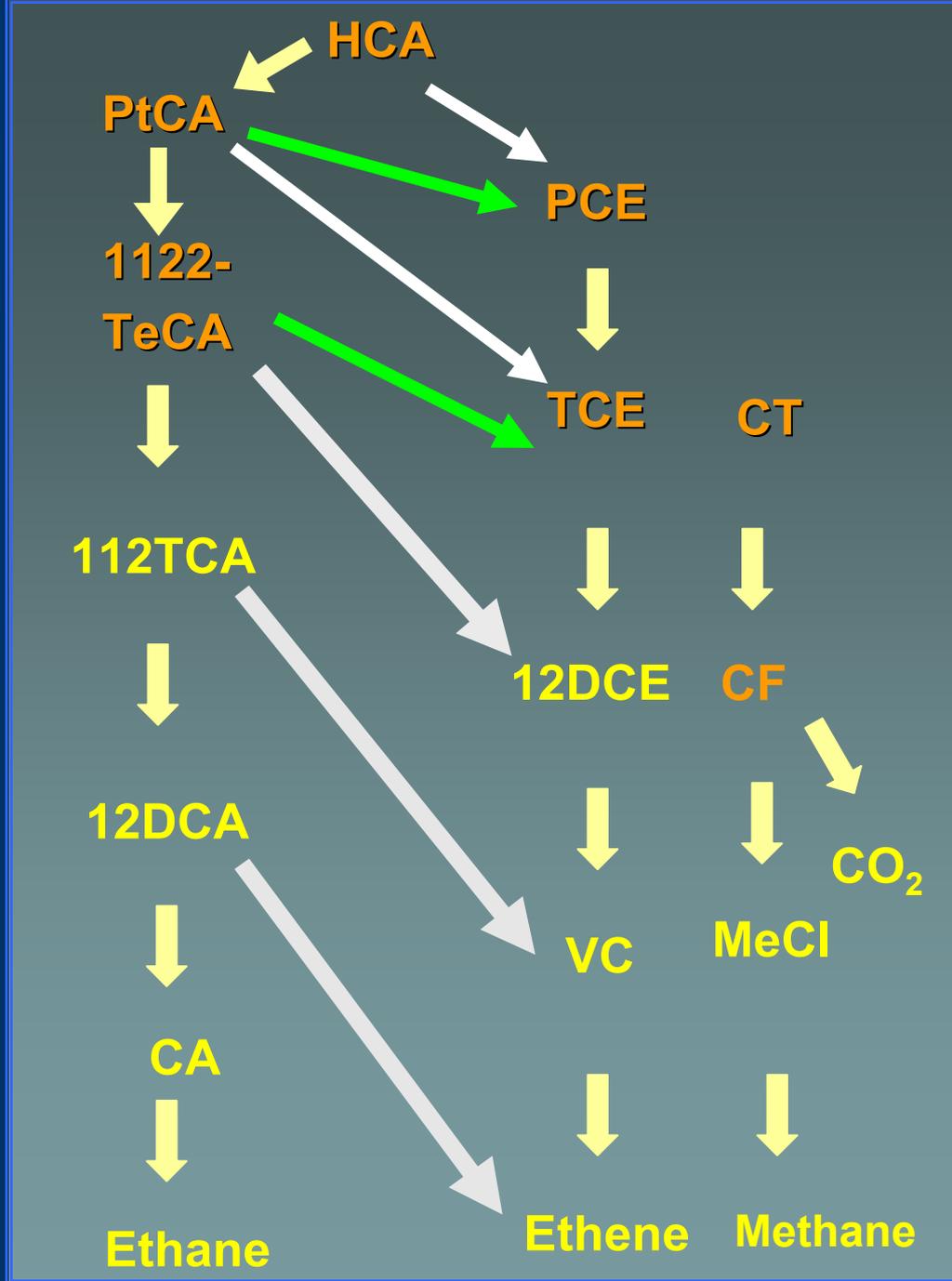
PCE= tetrachloroethene

TCE= trichloroethene

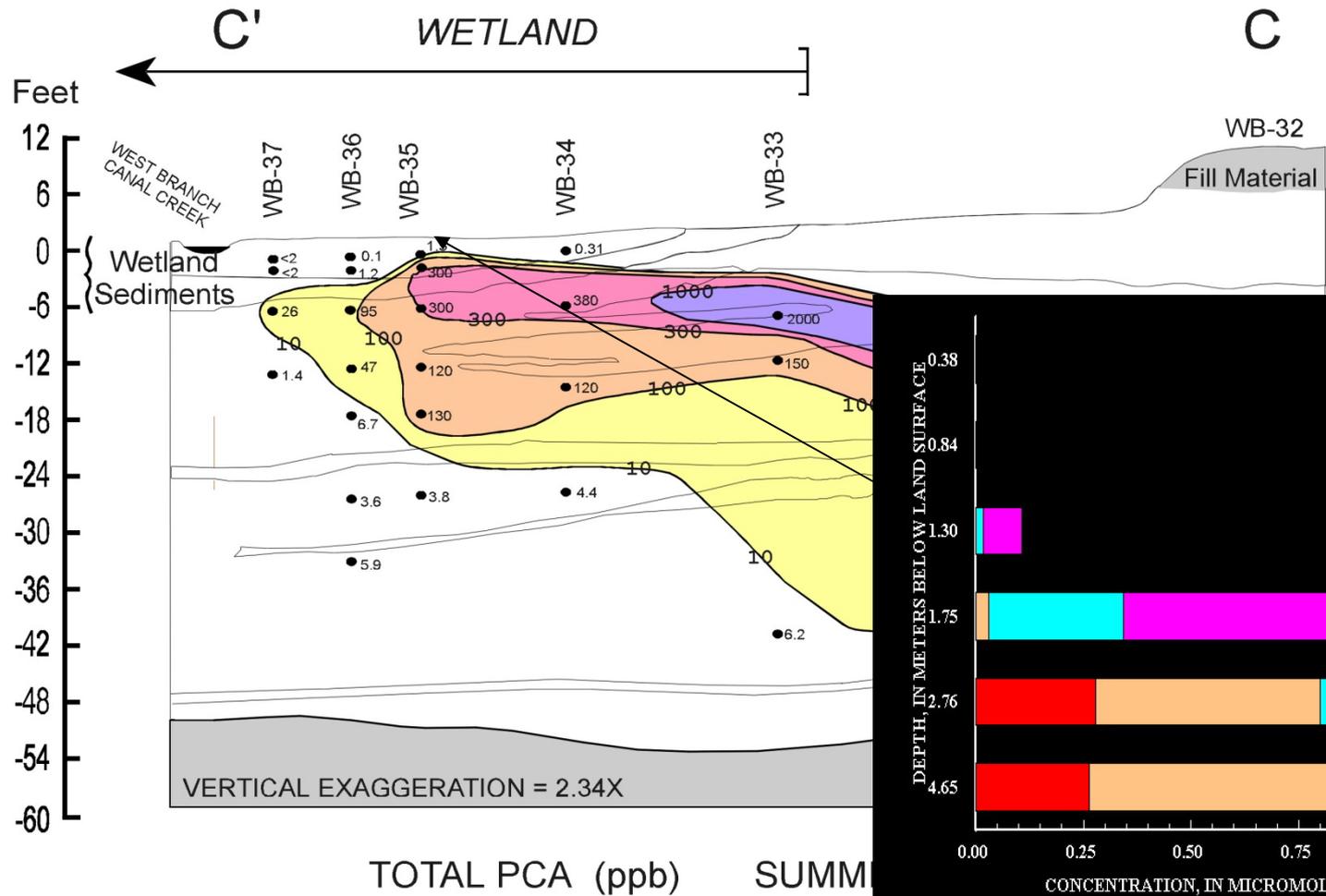
Chlorinated methanes:

CT= carbon tetrachloride

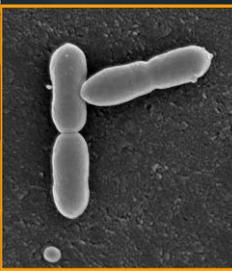
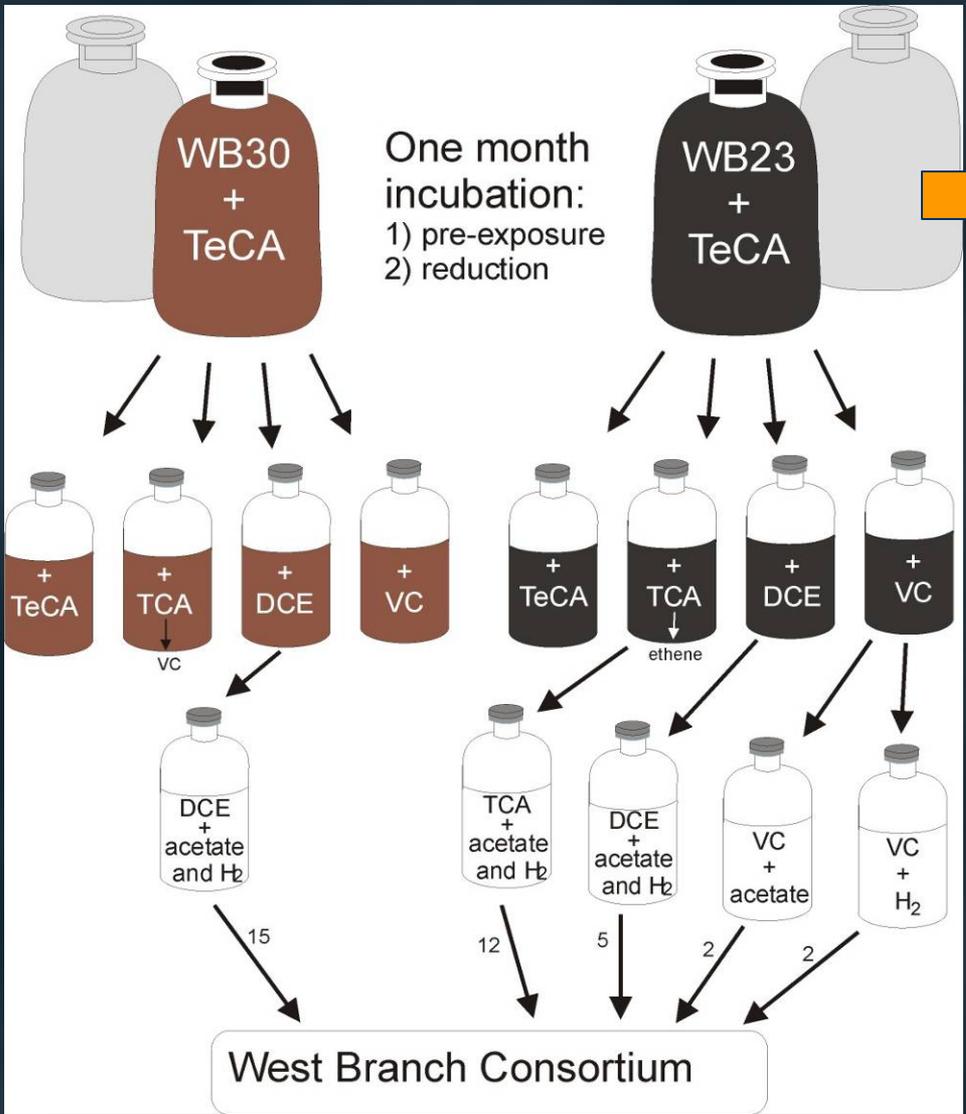
CF= chloroform



Natural Attenuation in Wetland



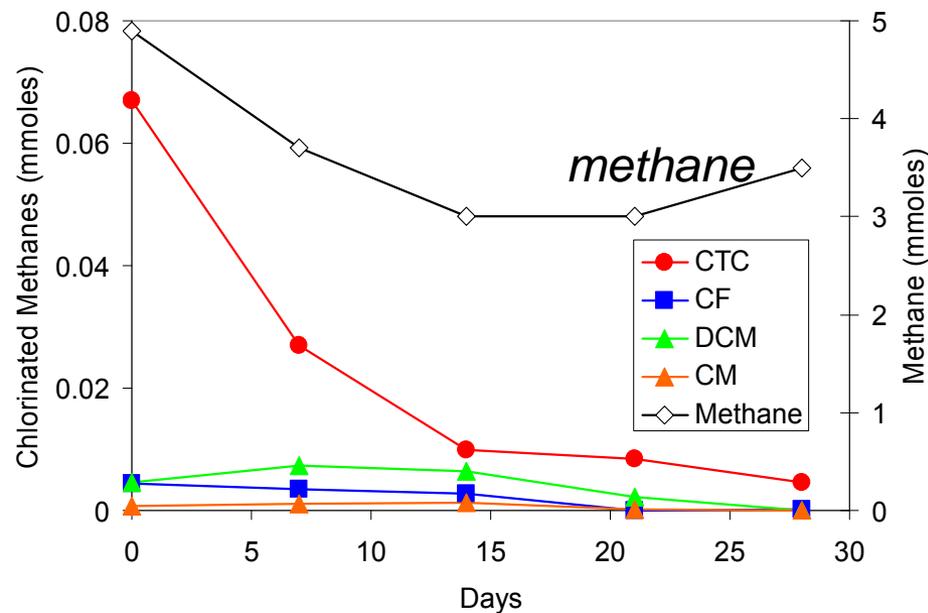
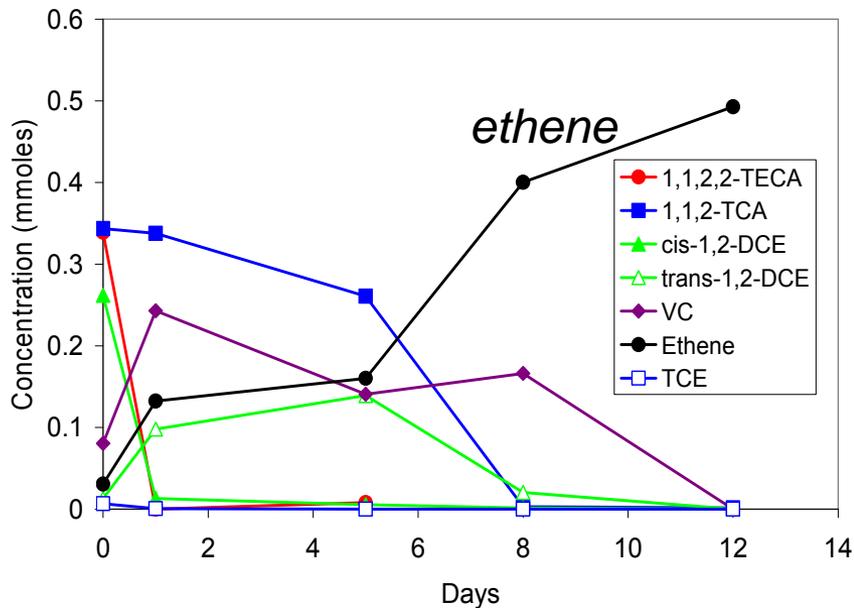
Development of WBC-2 Microbial Consortium





WBC-2 Substrate Range

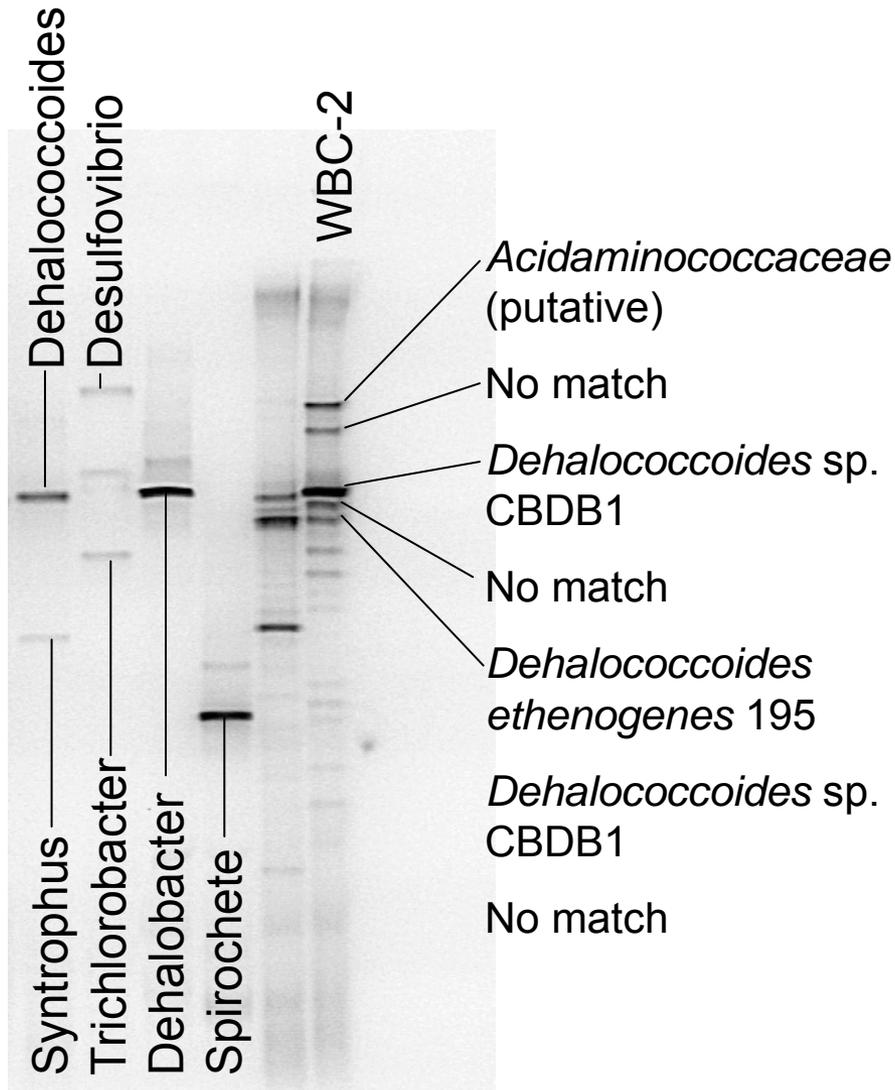
Chlorinated Ethanes, Ethenes, Methanes



- ▶ Sediment-free culture with consistent dechlorination ability
- ▶ Regularly fed 5 mg/L TeCA, 112TCA, cis12DCE, and lactate and ethanol (e^- donors)
- ▶ Degrades carbon tetrachloride and chloroethene/ethane degradation unaffected
- ▶ WBC-2 degradation stable since 2003

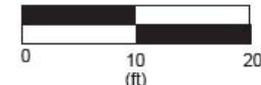


WBC-2 Microbial Composition



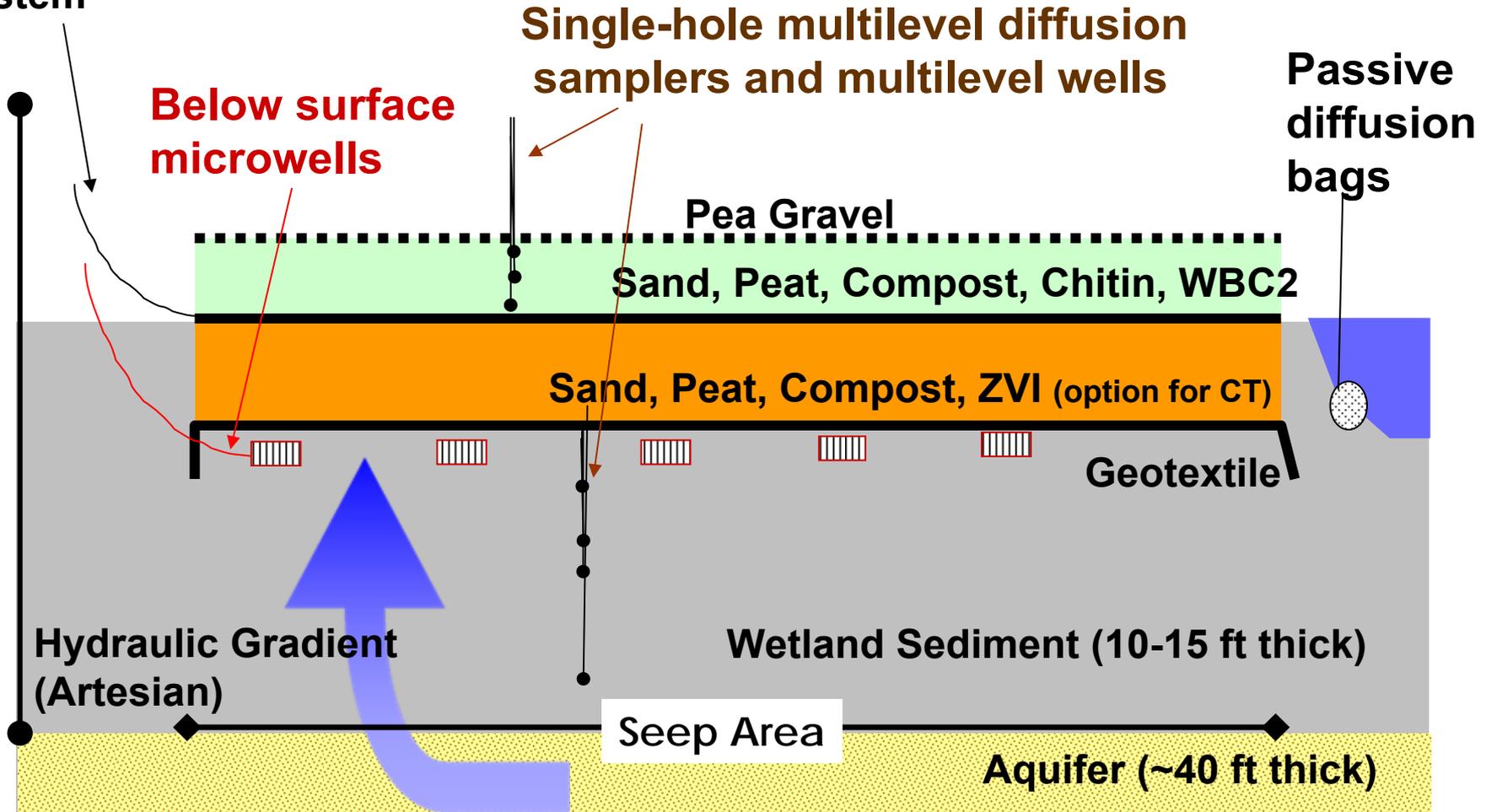
- ▶ Contains at least 17 and 21 distinct *Bacteria* phylotypes based on DGGE and clone library analysis, respectively
- ▶ *Acetobacterium* (40%), *Dehalobacter* (19%), and *Acidaminococcaceae* (9%) most prominent; *Dehalococcoides* 5%
- ▶ Diversity thought to support substrate range

Pilot-Test Area 3-4W



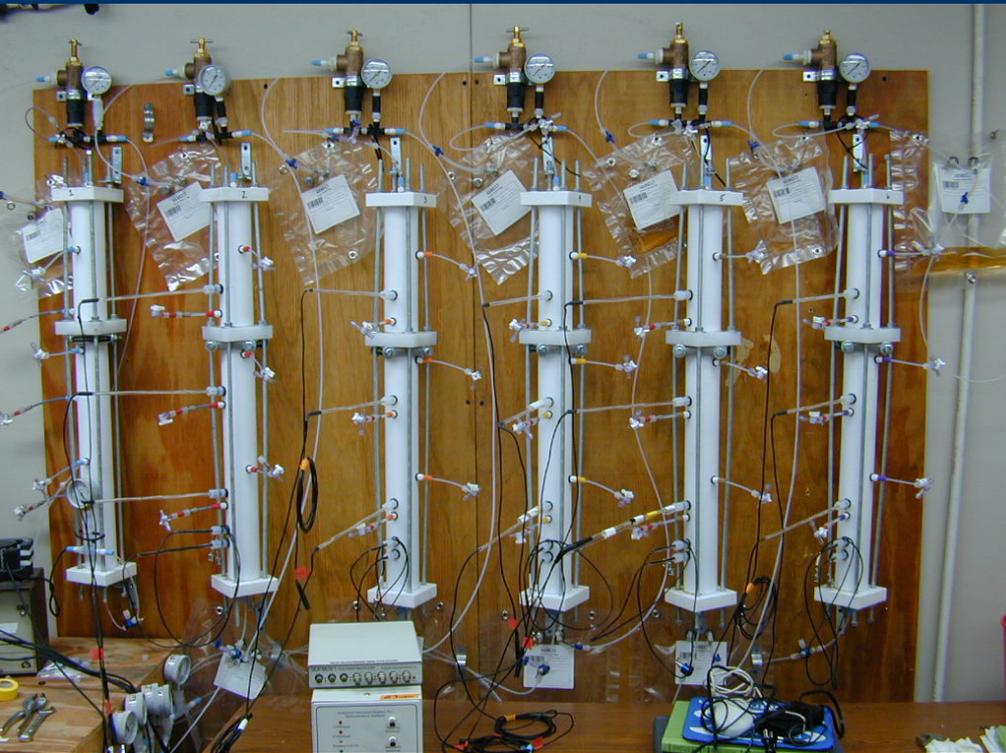
Reactive Mat Design and Monitoring

Re-amendment System



NOT TO SCALE

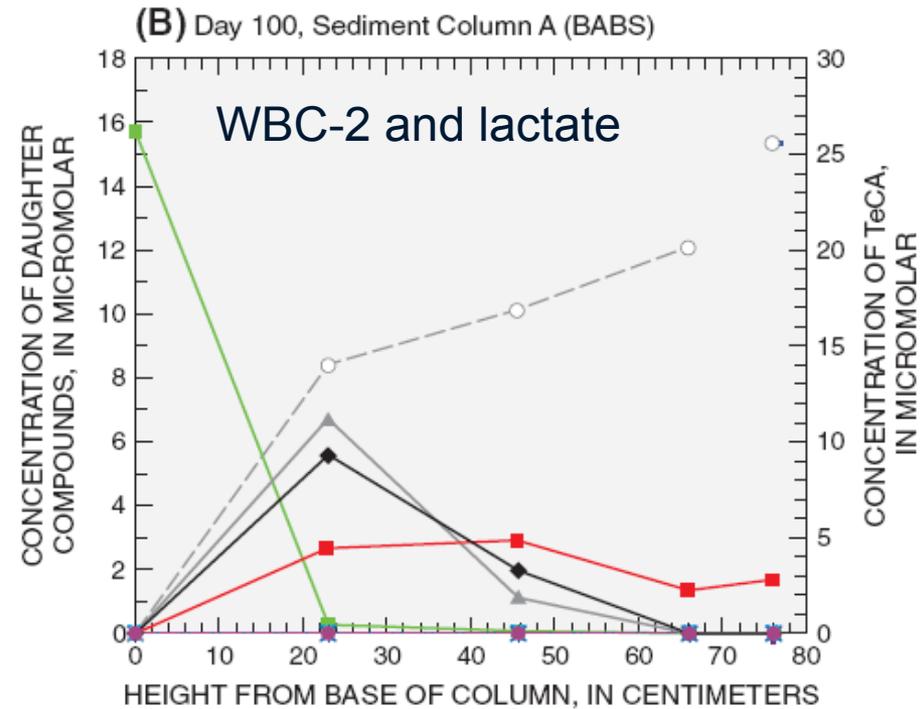
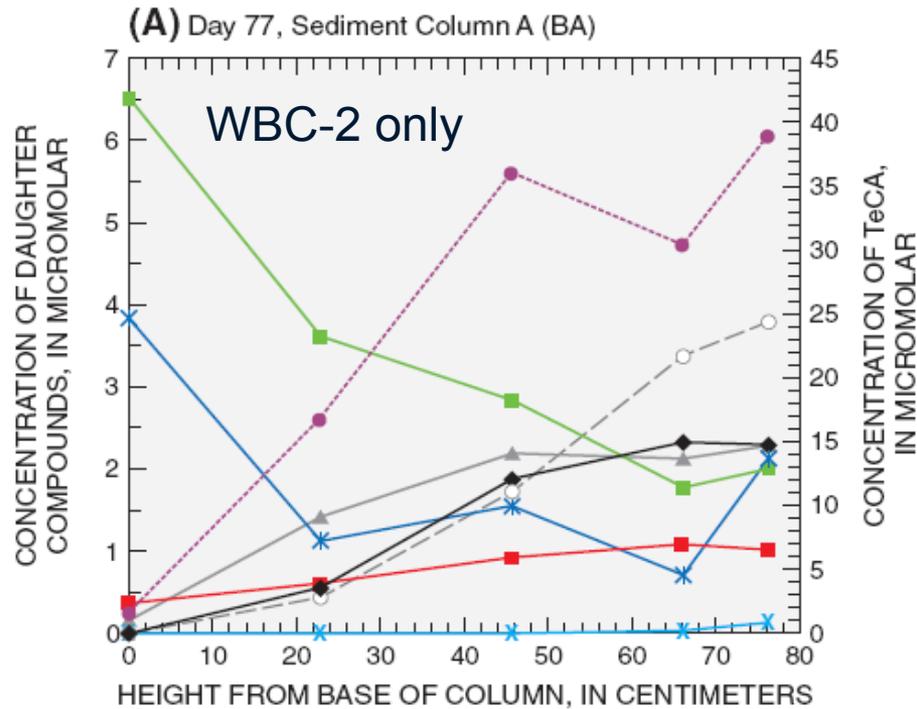
Flow-Through Column Tests - Biomat



Simulate biomat layers

- Continuous upflow columns
- Establish similar discharge rates/concentrations to field
- Evaluate sediment only, compost/peat mix, and iron layer before compost/peat mix
- Measure VOCs, redox, culture behavior, hydraulic properties

Degradation of VOCs by WBC-2 seeded sediment in columns

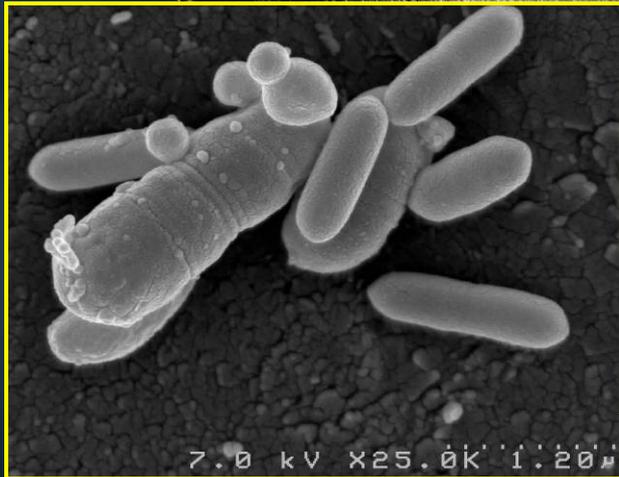
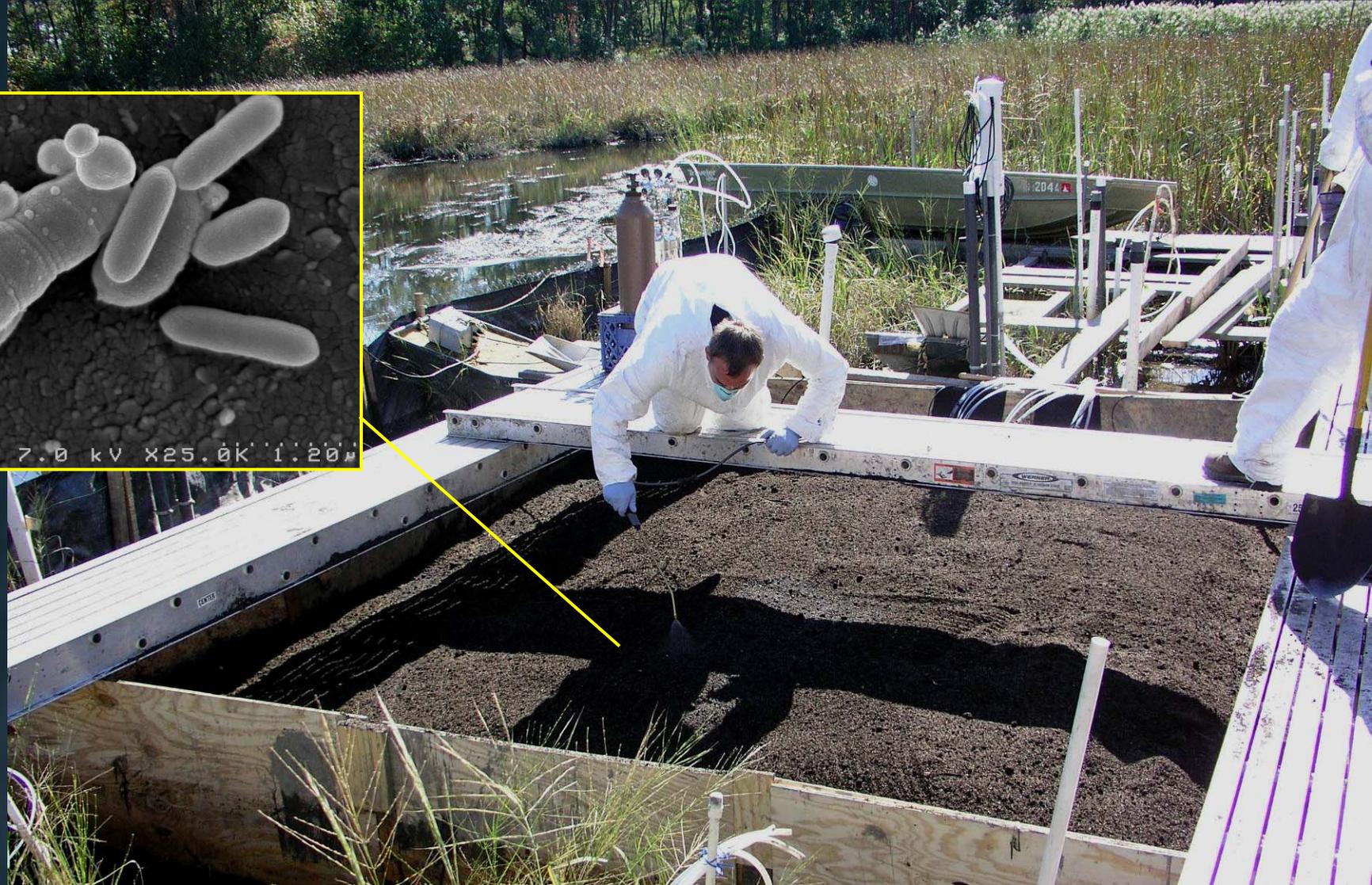


EXPLANATION

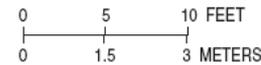
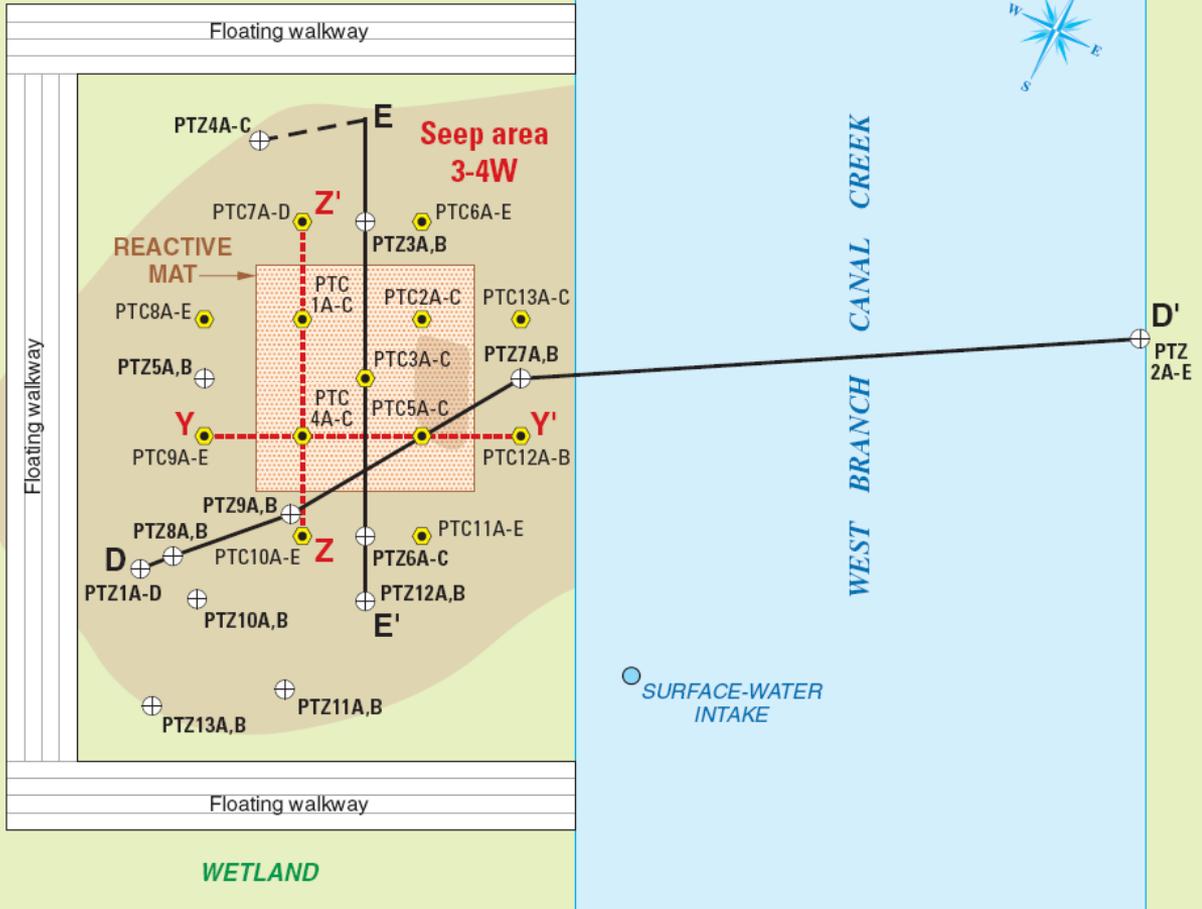
- ◆—◆ VC (vinyl chloride)
- *trans*12DCE (*trans*-1,2-dichloroethene)
- ▲—▲ *cis*12DCE (*cis*-1,2-dichloroethene)
- ×—× 12DCA (1,2-dichloroethane)
- *—* TCE (trichloroethene)
- 112TCA (1,1,2-trichloroethane)
- TeCA (1,1,2,2-tetrachloroethane)
- ethene

Bioreactive Mat Construction

Sprayed WBC2 between each wheelbarrow load of material



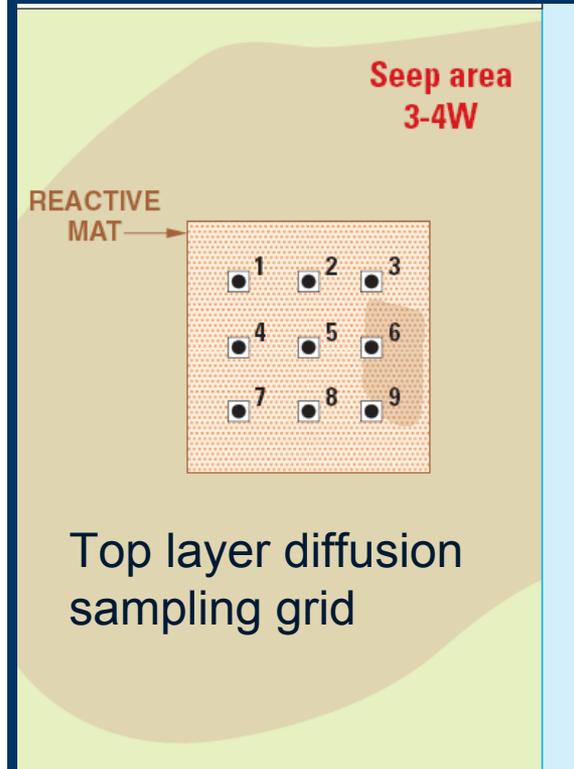
WETLAND



EXPLANATION

- REACTIVE MAT
- WETLAND AREA
- HIGHLY SATURATED AREA
- PTC7A-E CMT PIEZOMETER AND IDENTIFIER
- PTZ5A,B PIEZOMETER NEST FOR WATER-LEVEL MEASUREMENT AND IDENTIFIER
- SURFACE-WATER INTAKE

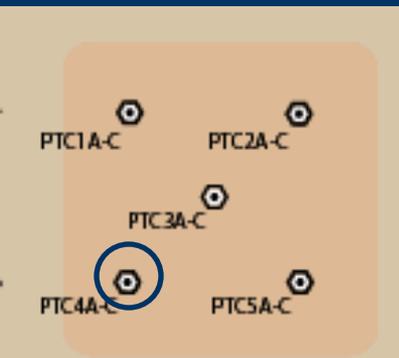
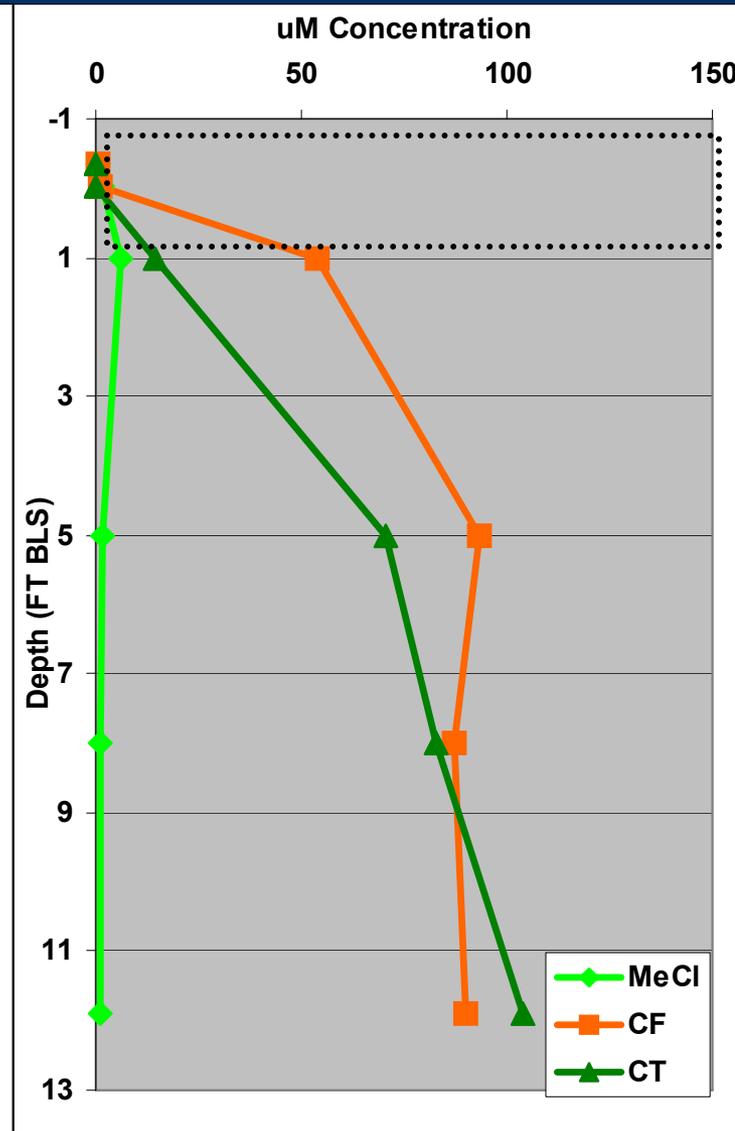
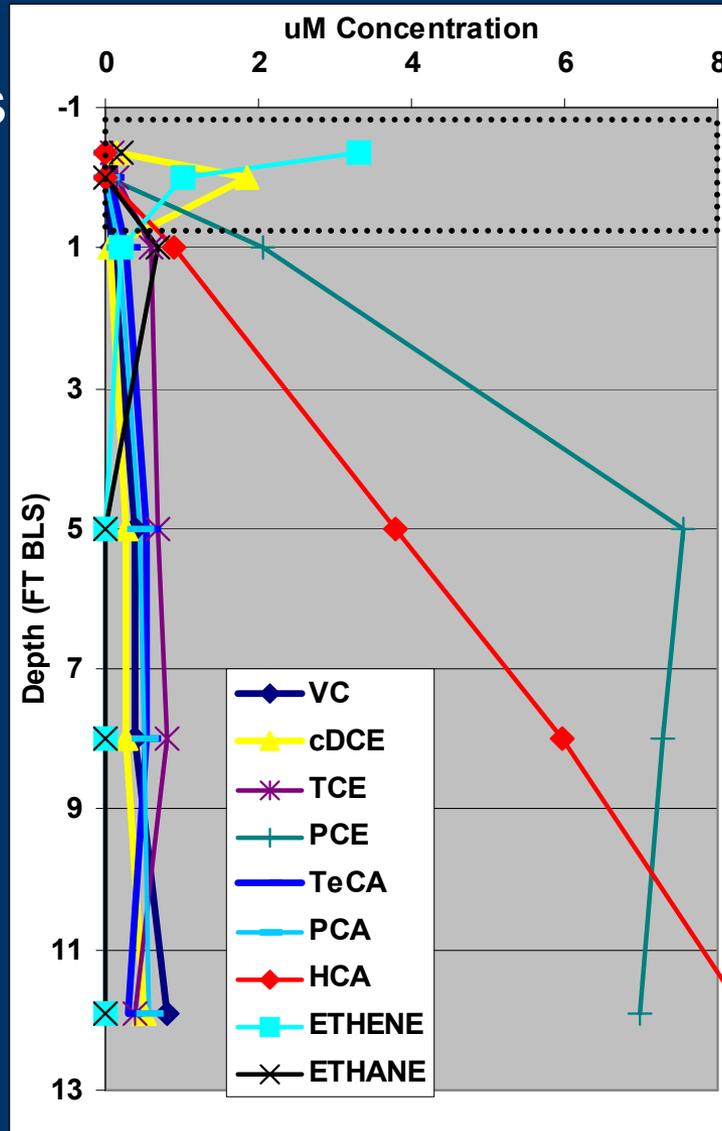
Reactive Mat Location and Monitoring Network



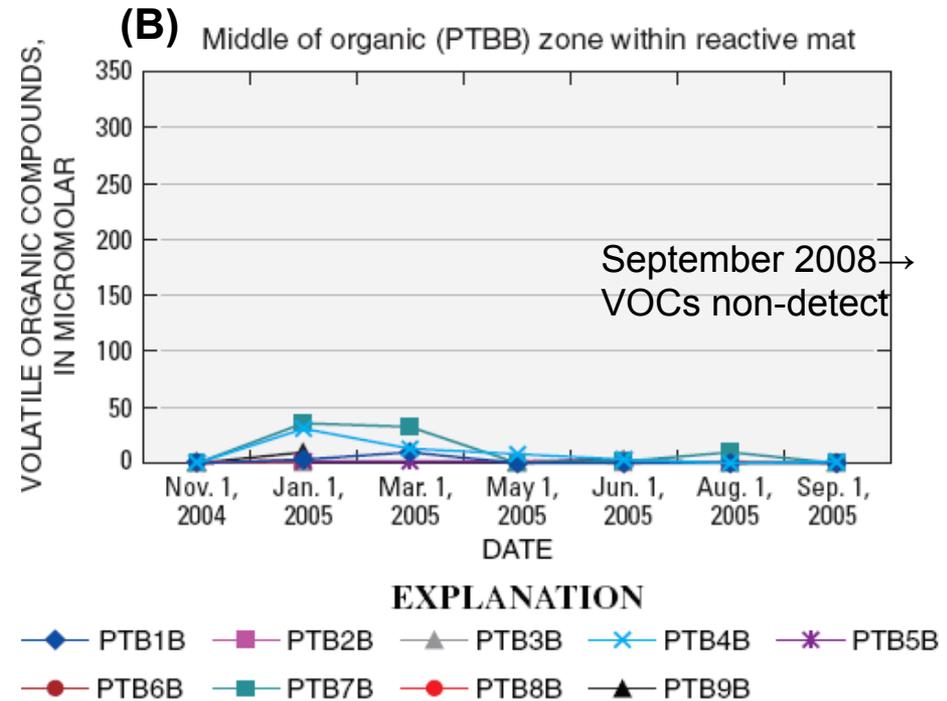
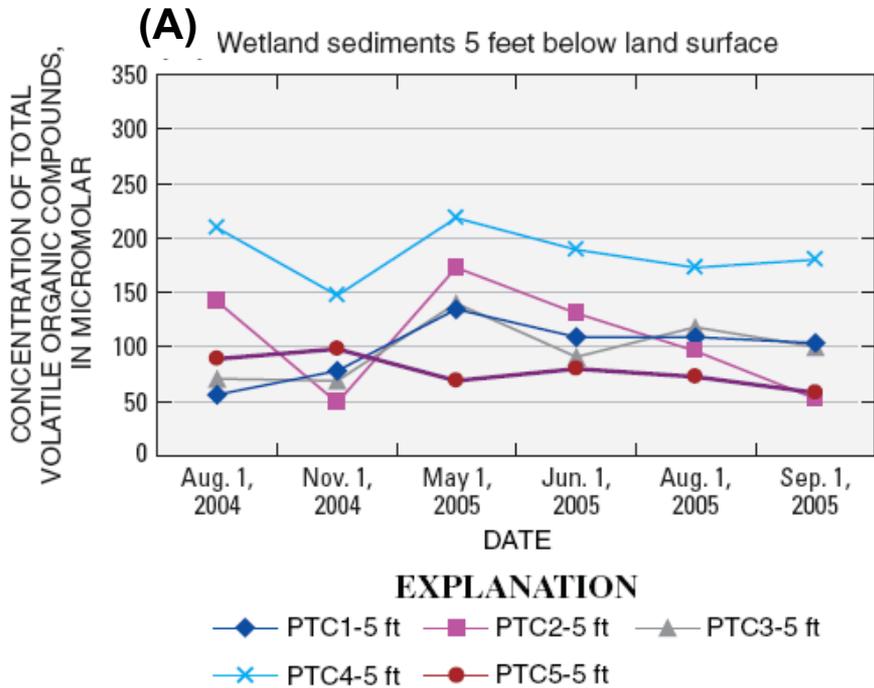
Top layer diffusion sampling grid

Reactive Mat – VOC Removal

- Consistent vertical profiles of VOC reduction through mat, increased ethene/ethane
- 95 to 99% mass removal



Sustainability of Degradation



(A) Consistent upward flow of VOC to mat over 1 year monitoring period

(B) Consistent VOC degradation within reactive mat over 1 year monitoring period

October 2008 sampling- still effective 4 years after emplacement.

Application of WBC-2 in an Anaerobic Bioreactor for the Canal Creek Groundwater Treatment Plant



Advantages of Fixed Film Anaerobic Bioreactor System

- Mechanically simple with low energy costs and maintenance
 - Very low production of waste solids (sludge)
 - Highly resistant to upsets and toxic shock
 - Insignificant pretreatment of water (no bag filters needed)
-
- ❖ *An anaerobic culture is available that can degrade the suite of chlorinated VOCs in the treatment plant influent*
 - ❖ *WBC-2 has been grown previously on a common bioreactor support medium in a static batch, where it retained its full dechlorinating ability*
 - ❖ *Extensive testing of WBC-2 in lab and field has shown its robustness and ability to obtain high rates of degradation*

Treatment Plant Influent

| Contaminant | ($\mu\text{g/L}$) | (μM) |
|--|-------------------------------------|-----------------------------------|
| 1,1,2,2-tetrachloroethane (TeCA) | 190 | 1.13 |
| 1,1,2-trichloroethane (112TCA) | 4.7 | 0.04 |
| 1,,2-dichloroethane (12DCA) | 4.2 | 0.04 |
| Carbon tetrachloride (CT) | 15 | 0.10 |
| Chloroform (CF) | 5.6 | 0.05 |
| Tetrachloroethene (PCE) | 2.8 | 0.02 |
| Trichloroethene (TCE) | 130 | 0.99 |
| Vinyl chloride (VC) | 71 | 1.14 |
| <i>cis-</i> and <i>trans</i> -1,2-Dichloroethene (12DCE) | 167 | 1.72 |
| Total VOCs | 590 | 4.5 |
| <i>Maximum Total VOCs</i> | <i>1,000</i> | <i>7.6</i> |

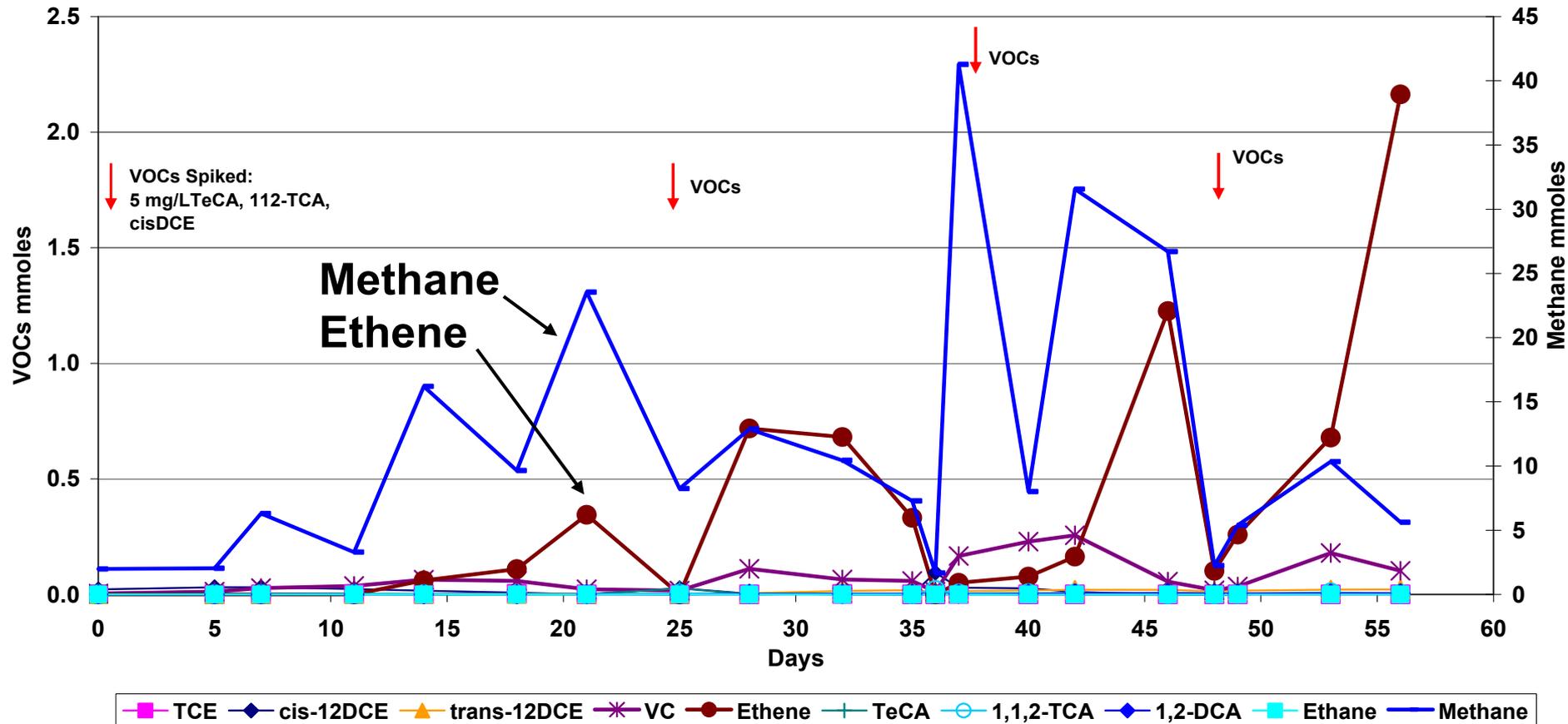
Degradation rates in mat columns-

Rates for initial VOC= 40 μ M

| Contaminant | Mean rate Constant (day ⁻¹) | Half-Life (hour) | Rate (μ M/day) |
|----------------------------------|---|------------------|---------------------|
| 1,1,2,2-tetrachloroethane (TeCA) | 3.43 | 4.85 | 140 |
| Chloroform | | 7.20 | 92 |
| Carbon tetrachloride | | 5.88 | 113 |
| Tetrachloroethene (PCE) | 1.40 | 11.9 | 56 |
| Trichloroethene (TCE) | 3.04 | 5.47 | 122 |

More than 4 times the degradation rate in static culture vessel

WBC-2 20L Vessel Filled with EXCEED Polyurethane Foam



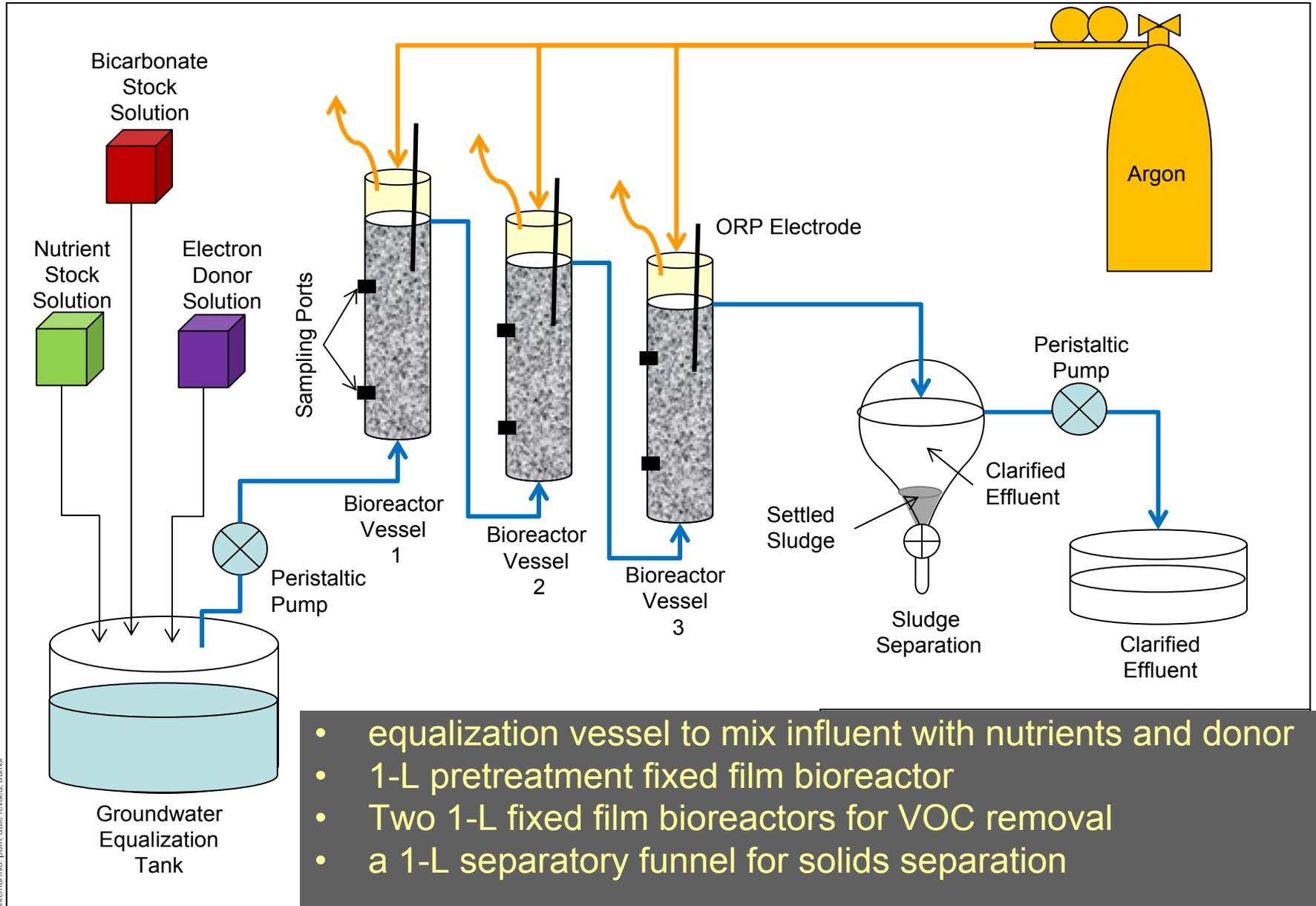
❖ *WBC-2 has been grown previously on a common bioreactor support medium in a static batch, where it retained its full dechlorinating ability*

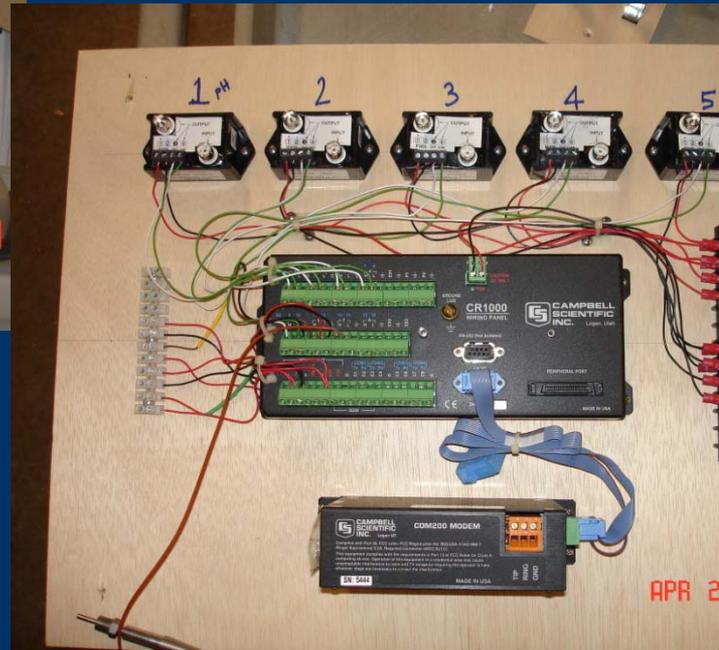
Bioreactor Study Objectives

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

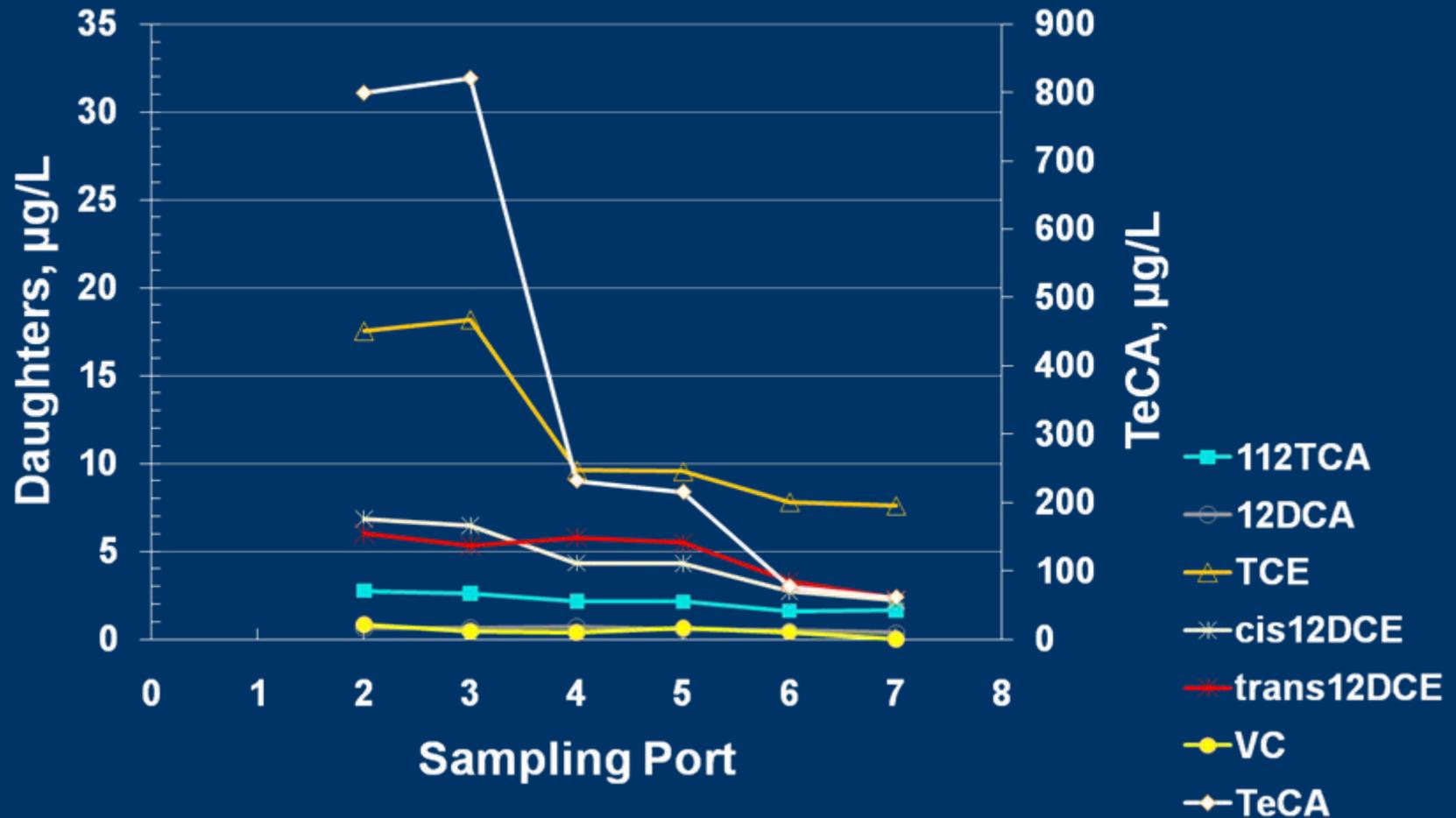
- optimal hydraulic retention time to achieve efficient VOC degradation and meet discharge criteria
- optimal electron donor
- nutrient and electron donor utilization rates
- oxygen consumption rate and design constraints to maintain anaerobic conditions in the bioreactor
- typical equilibration/growth rate for WBC-2 following a change in flow or upset to the system
- sludge production rates and handling requirements

Bench Test Bioreactor

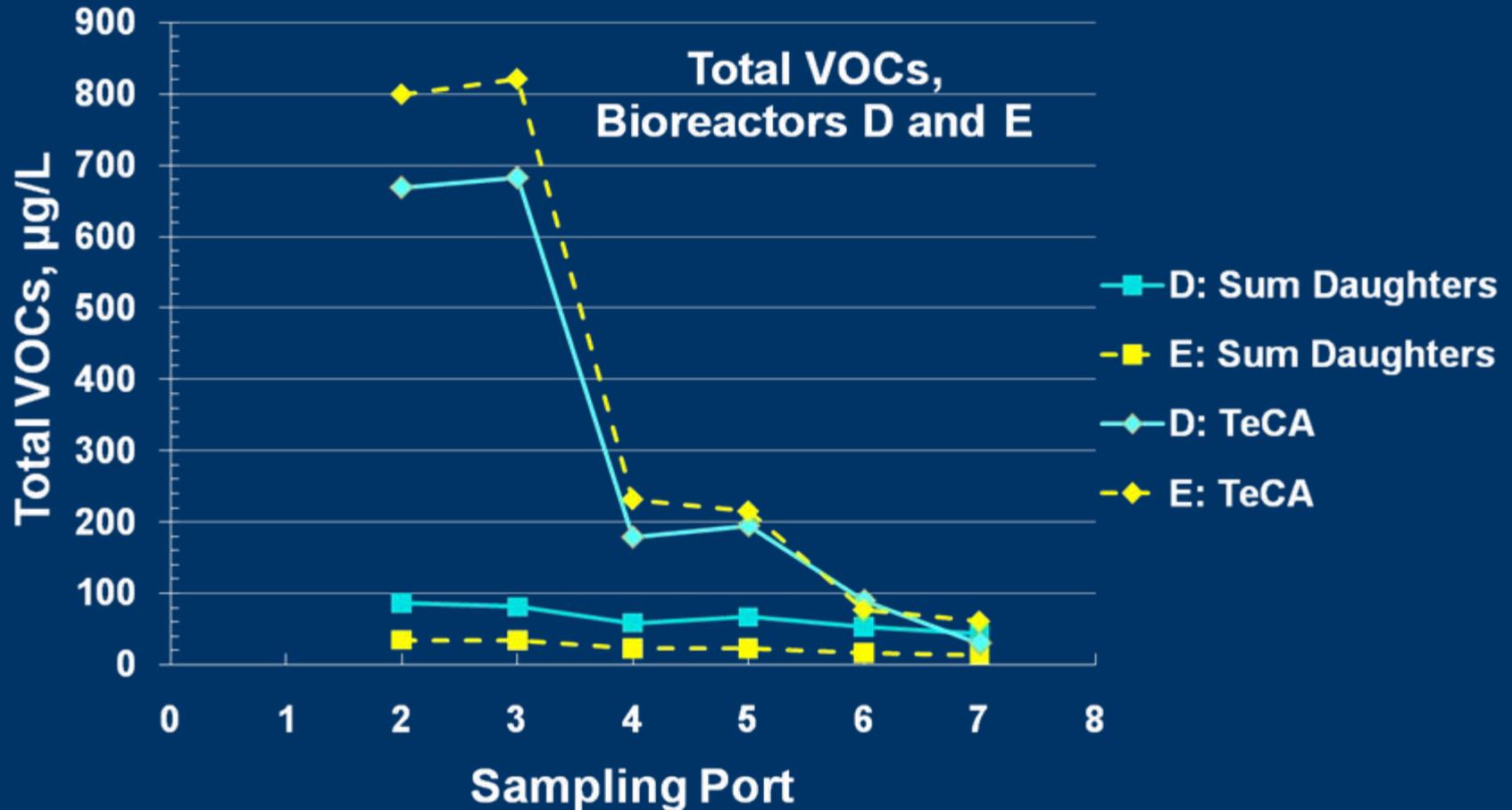




Bioreactor Bench Test Results

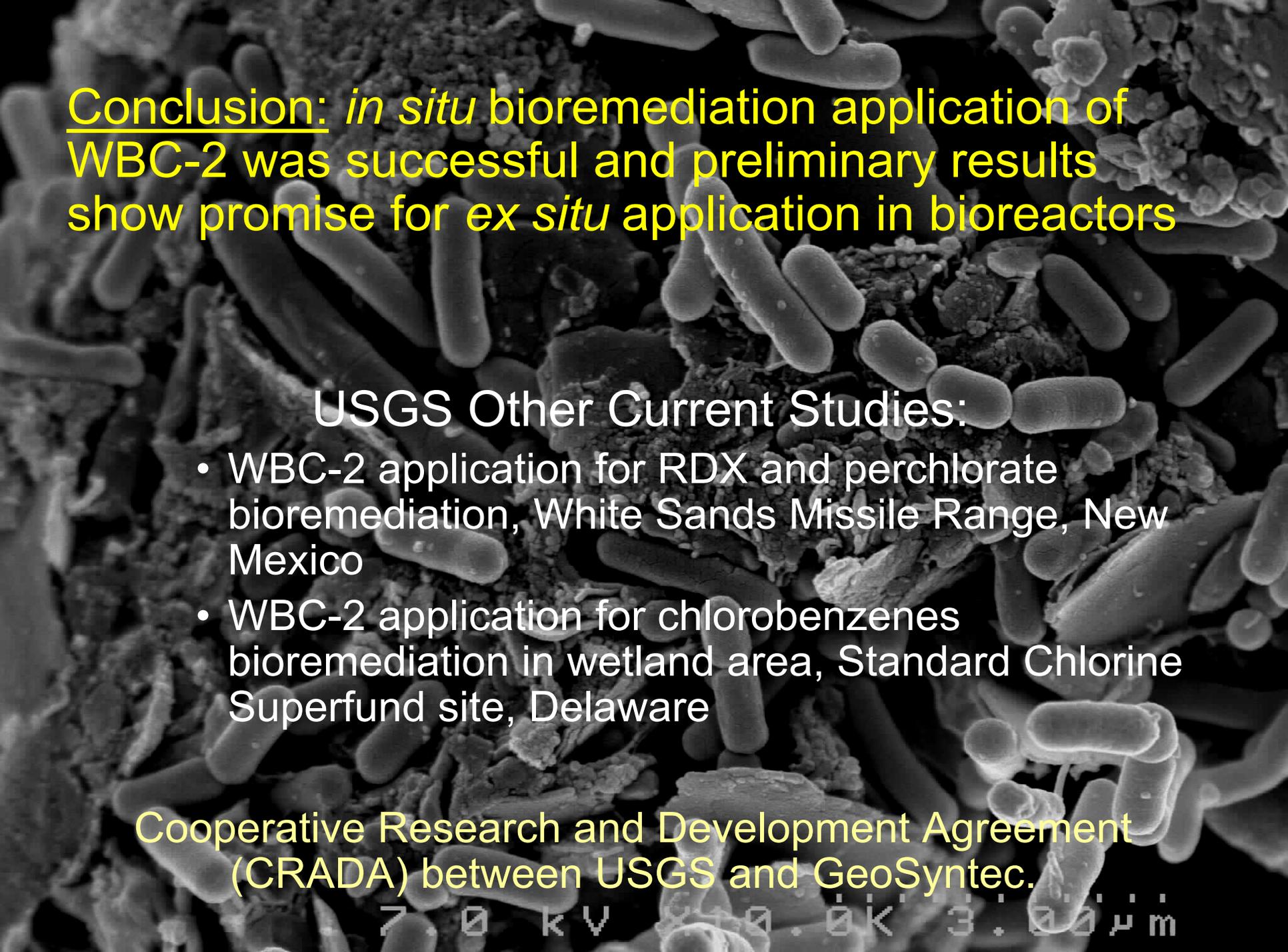


Bioreactor Bench Test Results



Bioreactor: Donor Testing

- Microcosms show dissolvable packing peanuts (corn starch) and corn syrup are inexpensive possibilities
- Currently testing a lower grade lactate
- Small-scale hydrogen generators (electrolysis cells) have been made and will be placed in-line in one of the bioreactor bench tests



Conclusion: *in situ* bioremediation application of WBC-2 was successful and preliminary results show promise for *ex situ* application in bioreactors

USGS Other Current Studies:

- WBC-2 application for RDX and perchlorate bioremediation, White Sands Missile Range, New Mexico
- WBC-2 application for chlorobenzenes bioremediation in wetland area, Standard Chlorine Superfund site, Delaware

Cooperative Research and Development Agreement (CRADA) between USGS and GeoSyntec.

7.0 kV X10.0k 3.00um

Questions?



APG - Installation Restoration Program

