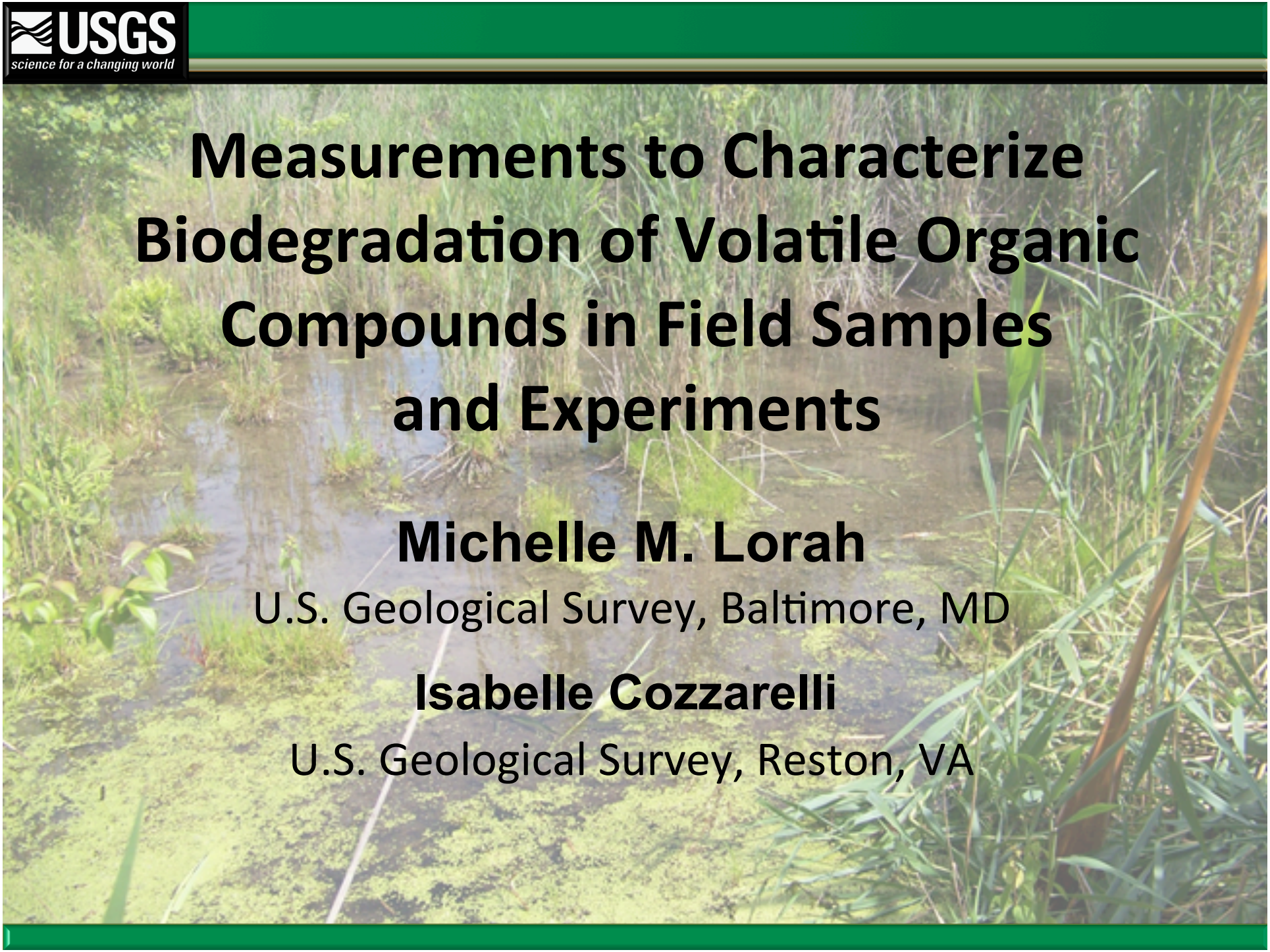

Measurements to Characterize Biodegradation of Volatile Organic Compounds in Field Samples and Experiments

Michelle M. Lorah
U.S. Geological Survey, Baltimore, MD

Isabelle Cozzarelli
U.S. Geological Survey, Reston, VA

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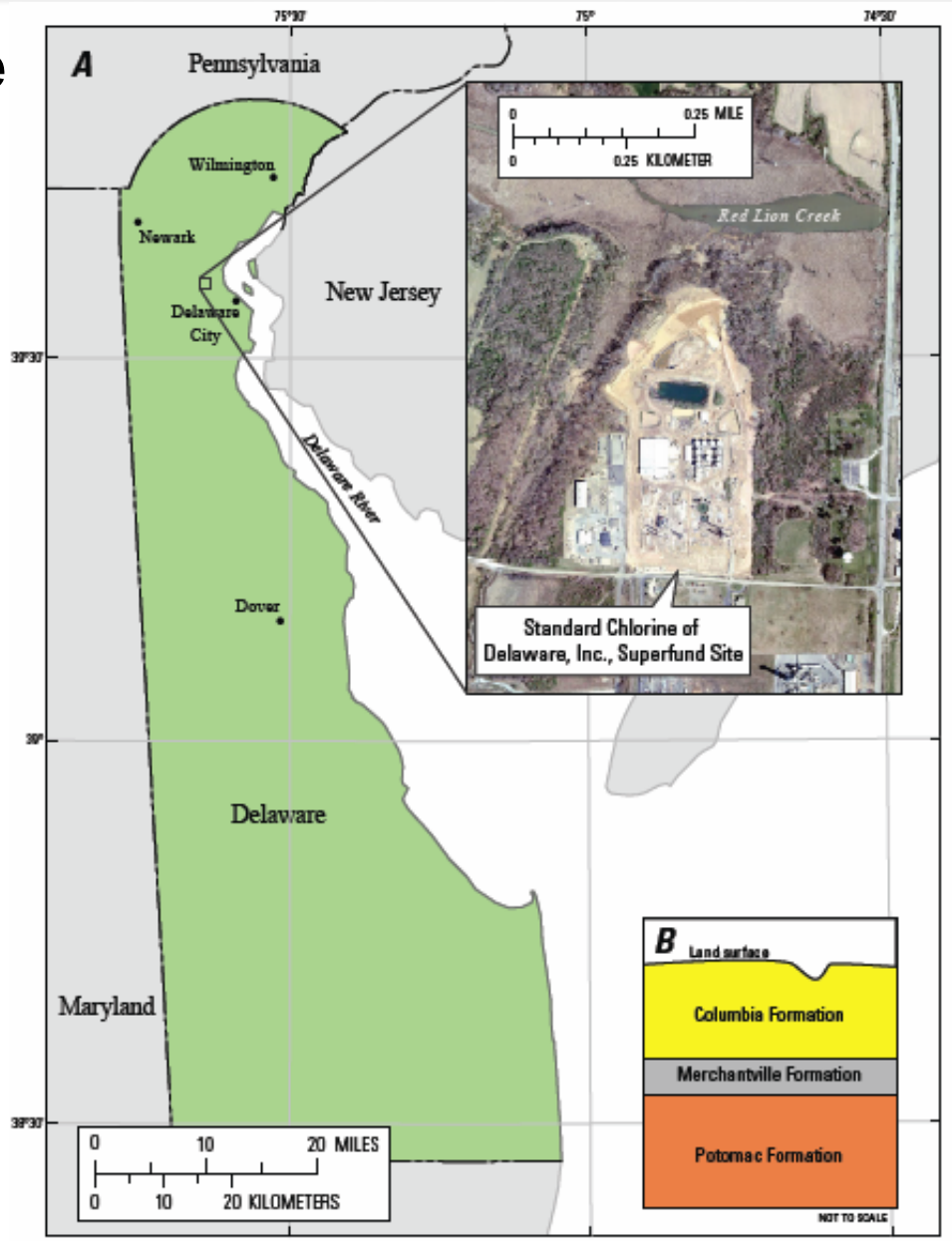
Standard Chlorine of Delaware

- Chemical plant 1966-2002; EPA Superfund site since 2002
- Major spills:
  - 1981- 5,000 gal CB
  - 1986 storage tanks- 579,000 gal 14DCB and TCBs
- Substantial containment and treatment in uplands, but not in wetlands



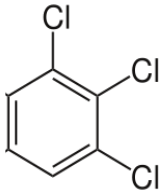
Biodegradation Pathways

Anaerobic (reductive dechlorination)

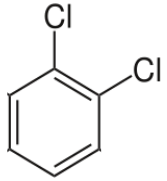
- Contaminant used as e^- acceptor
- rate slows with decreasing Cl

Aerobic (oxidation)

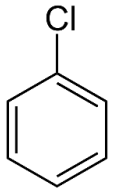
- O_2 used as e^- acceptor
- rate faster with decreasing Cl



70 (124TCB)



75 (14DCB)



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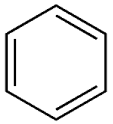


5

Drinking Water MCL µg/L

Trichlorobenzenes*
135TCB,124TCB, 123TCB

Dichlorobenzenes*
14DCB, 13DCB, 12DCB

Chlorobenzene*

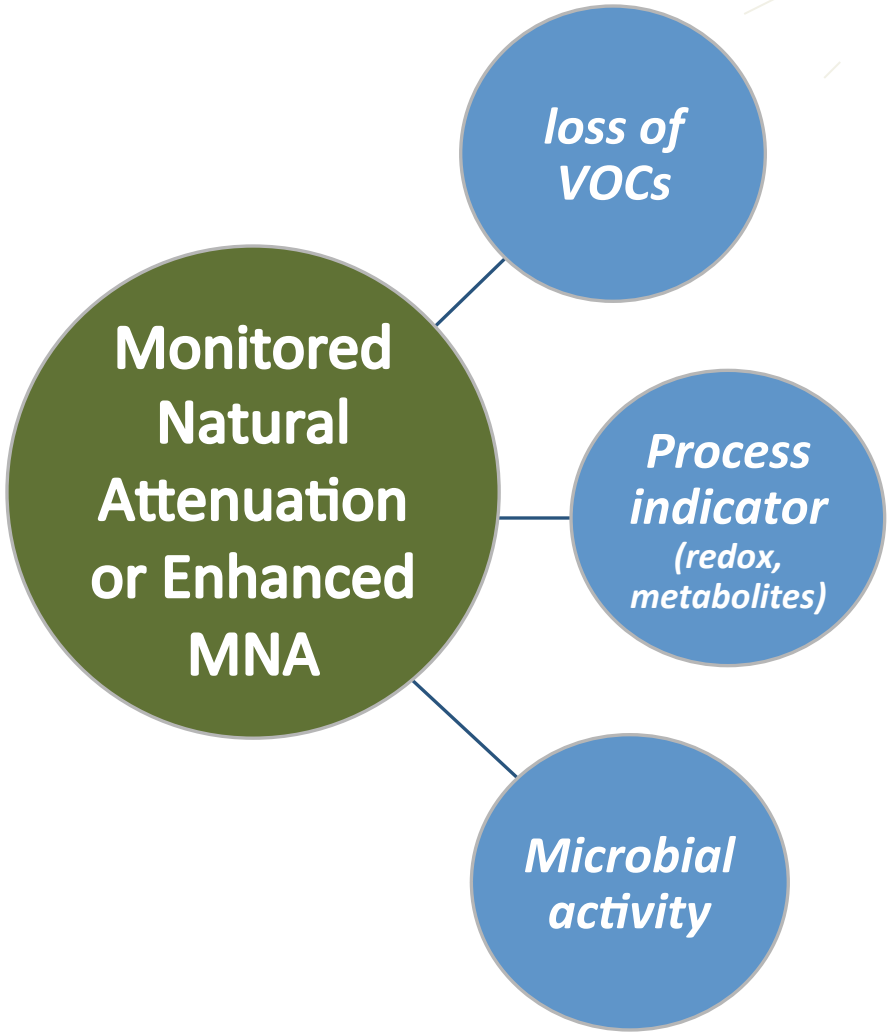
Benzene *

CO_2, CH_4

Aerobic CO_2, HCl

* Parent contaminant

Three Lines of Evidence for Biodegradation



Challenges:

- Spatial and temporal variability
- Volatile and oxygen-sensitive constituents
- Metabolites non-specific and/or difficult to analyze
- Multiple microbial populations involved

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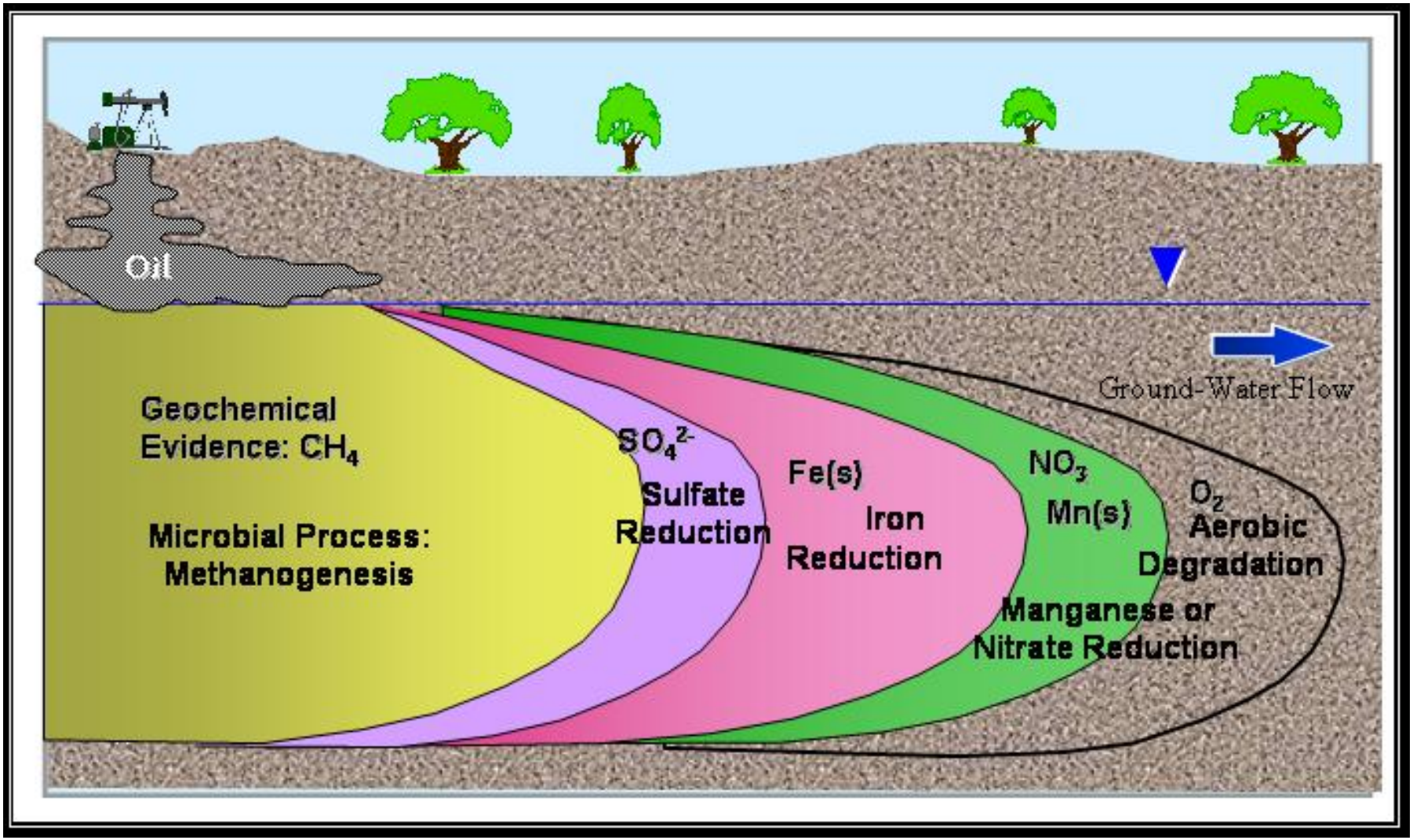
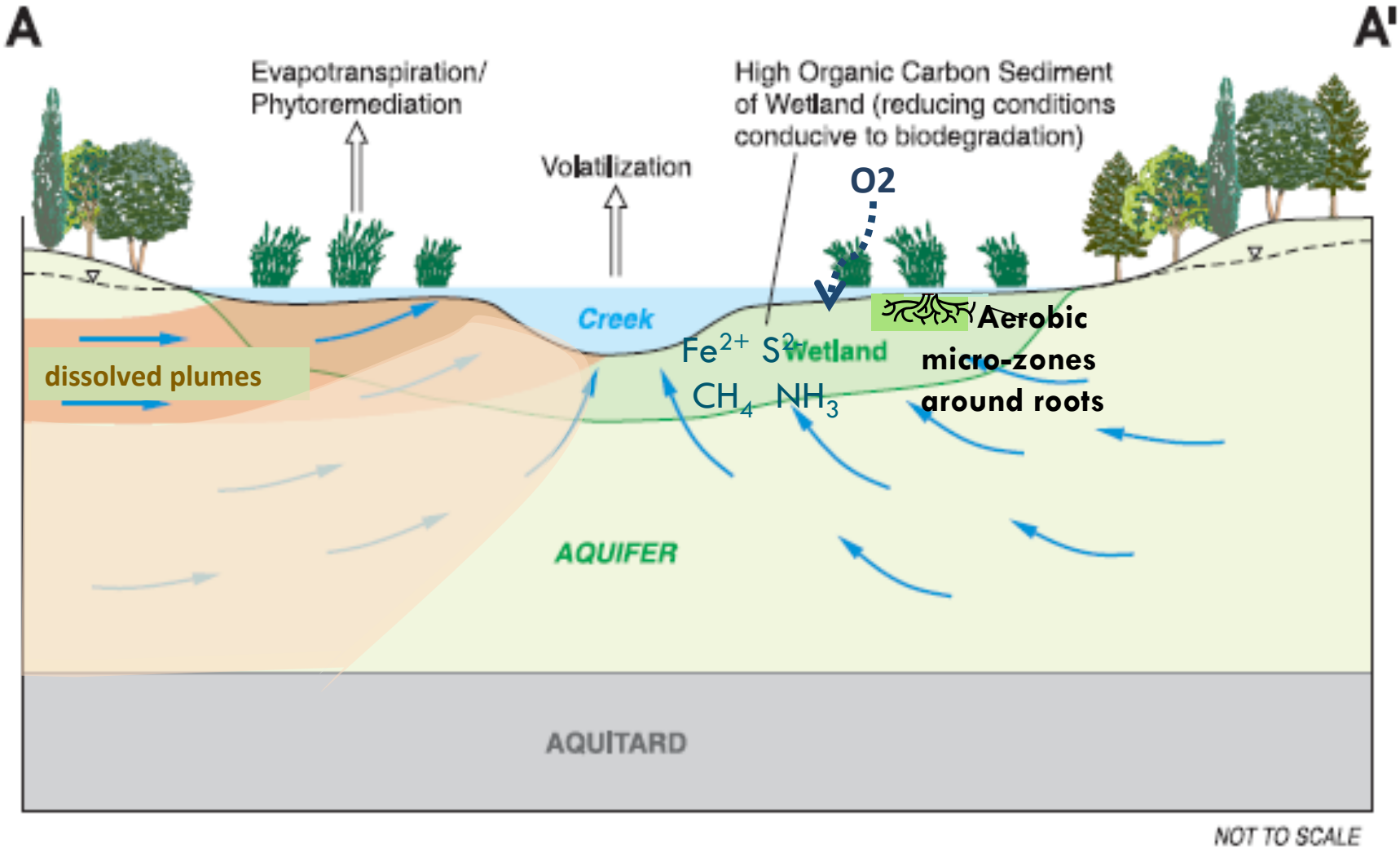
Redox conditions are altered by contaminants and affect biodegradation



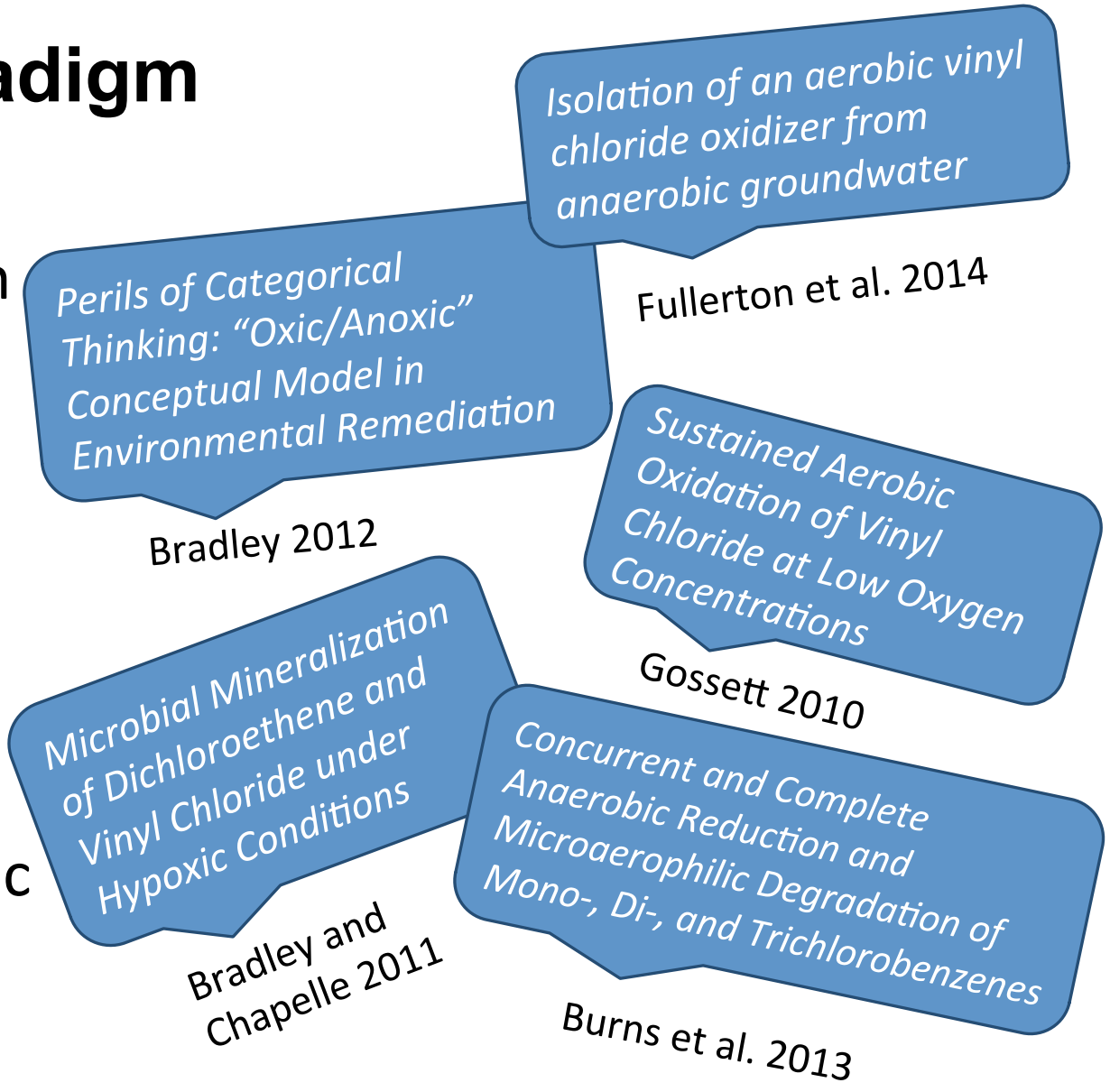
Conceptual Model for Wetland



Changing Paradigm

Previously:

- Aerobic oxidation requires measurable oxygen
- Anaerobic oxidation responsible for losses of lower VOCs at anaerobic plume fringes



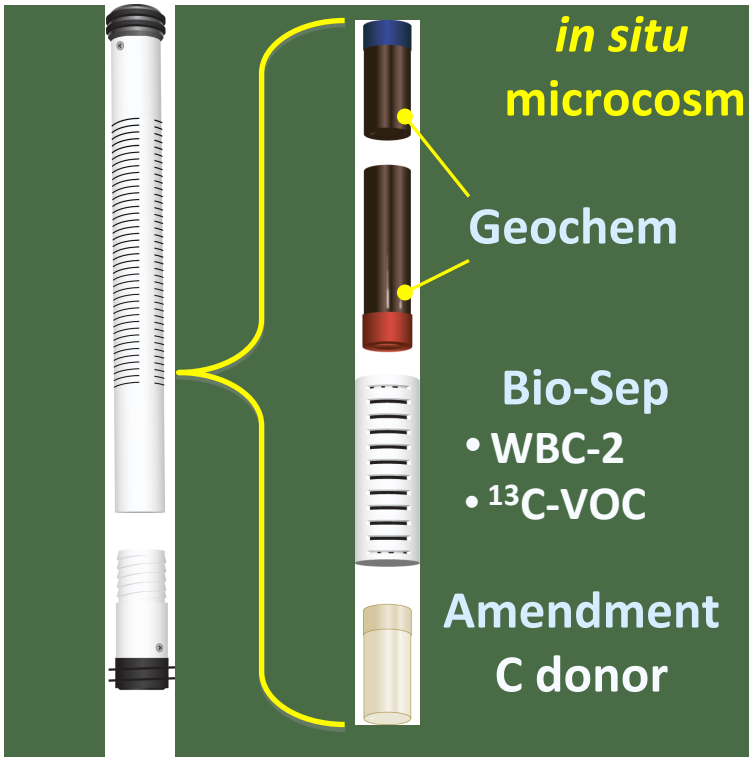
Chemical Analyses- Field and Lab

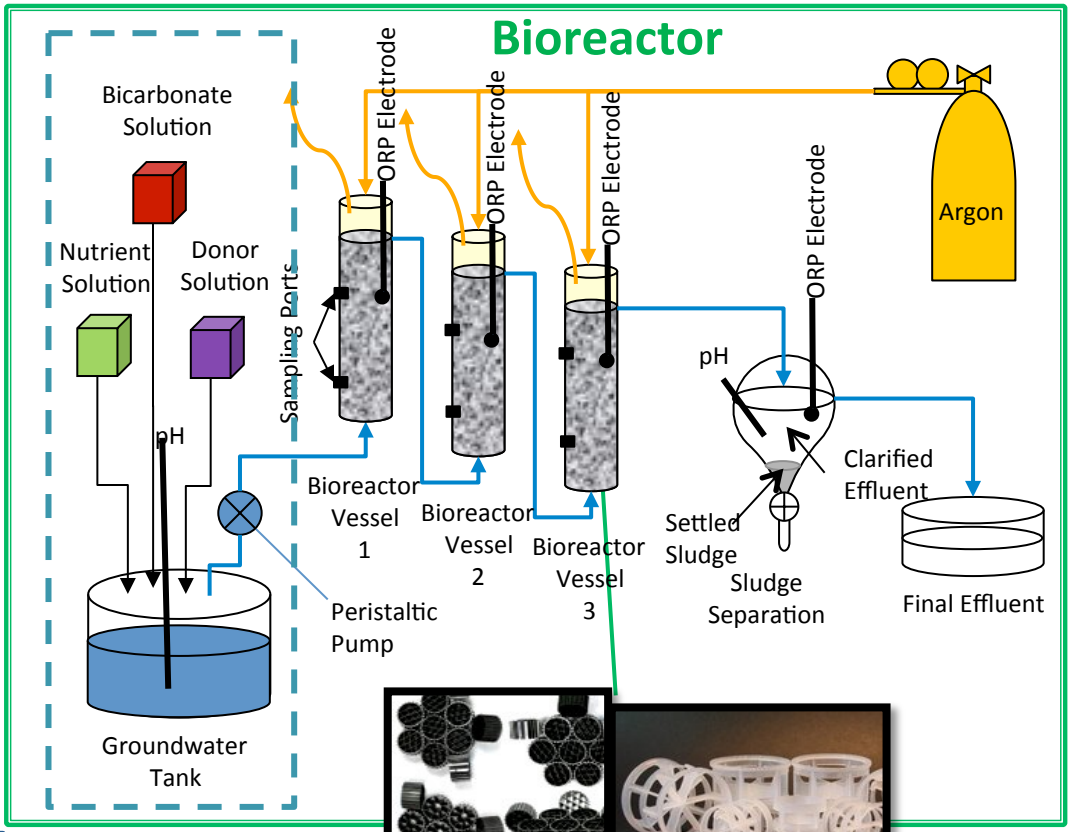
- pH, Eh, specific conductance, temperature
- Volatile organic compounds (VOCs)
- Redox-constituents (nitrate, ammonia, ferrous and total dissolved iron, sulfate, sulfide, methane)
- Major anions and cations (chloride as indicator)
- Volatile fatty acids and dissolved organic carbon

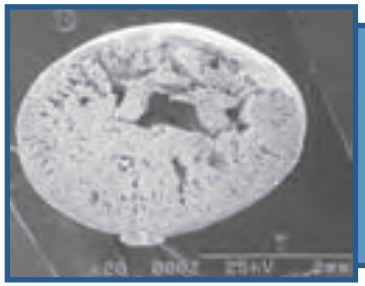
Methods- Field Sampling

- Passive diffusion bags (PDBs) and dialysis samplers
- 2 inch drivepoint piezometers
- 4-ft long porous membrane samplers (peepers) at 6 sites

Methods- Field and Laboratory Experiments







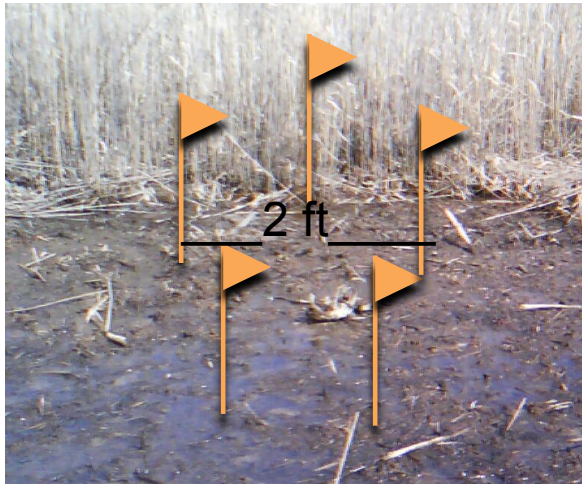
Bio-Sep® beads provide a large surface area for microbial attachment

Polyethylene and polyurethane support matrix seeded with native microorganisms or WBC2 culture

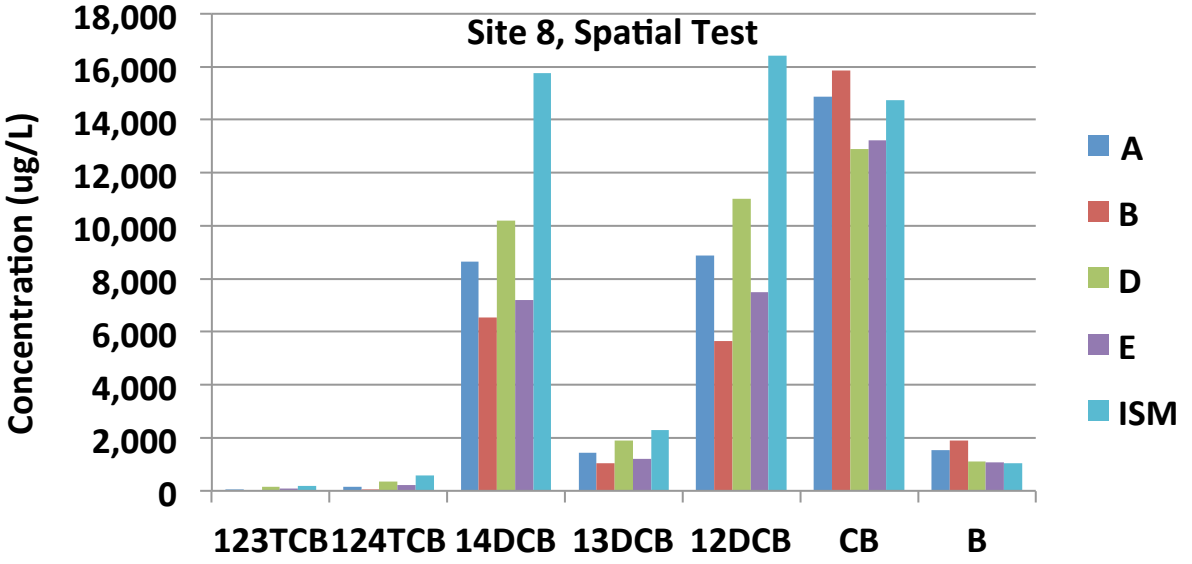
Field Sampling and Analysis

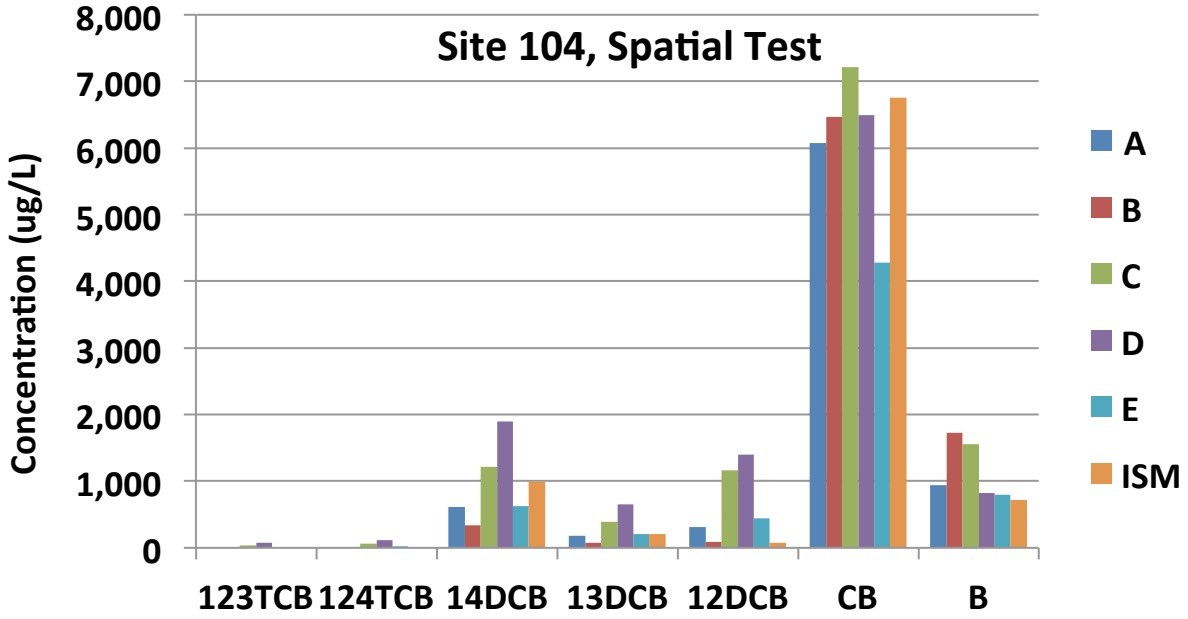
- Spatial Heterogeneity- lateral and vertical
- Temporal variability
- Sampling method

Lateral Heterogeneity- VOC concentration

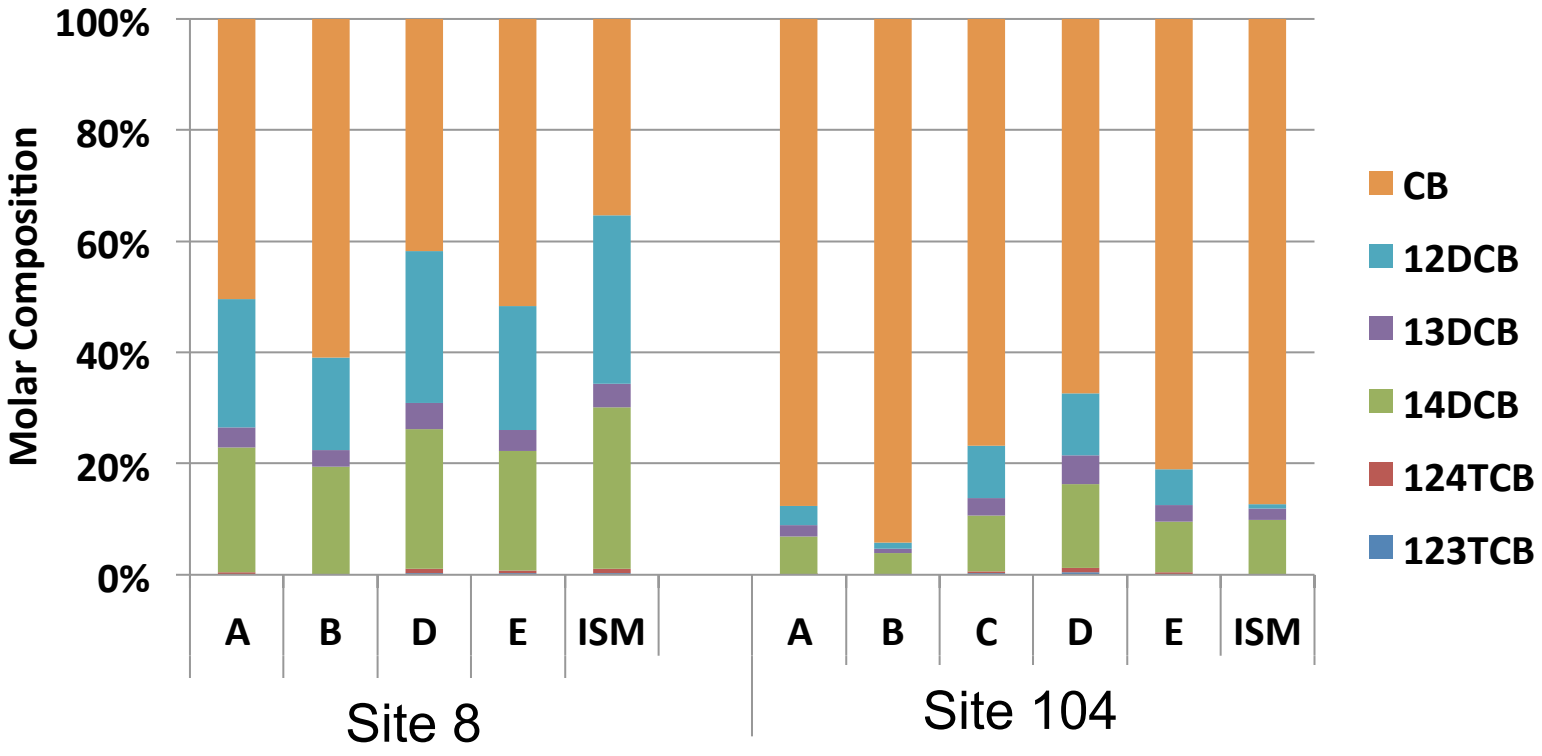


5 PDBs in 2 ft diameter

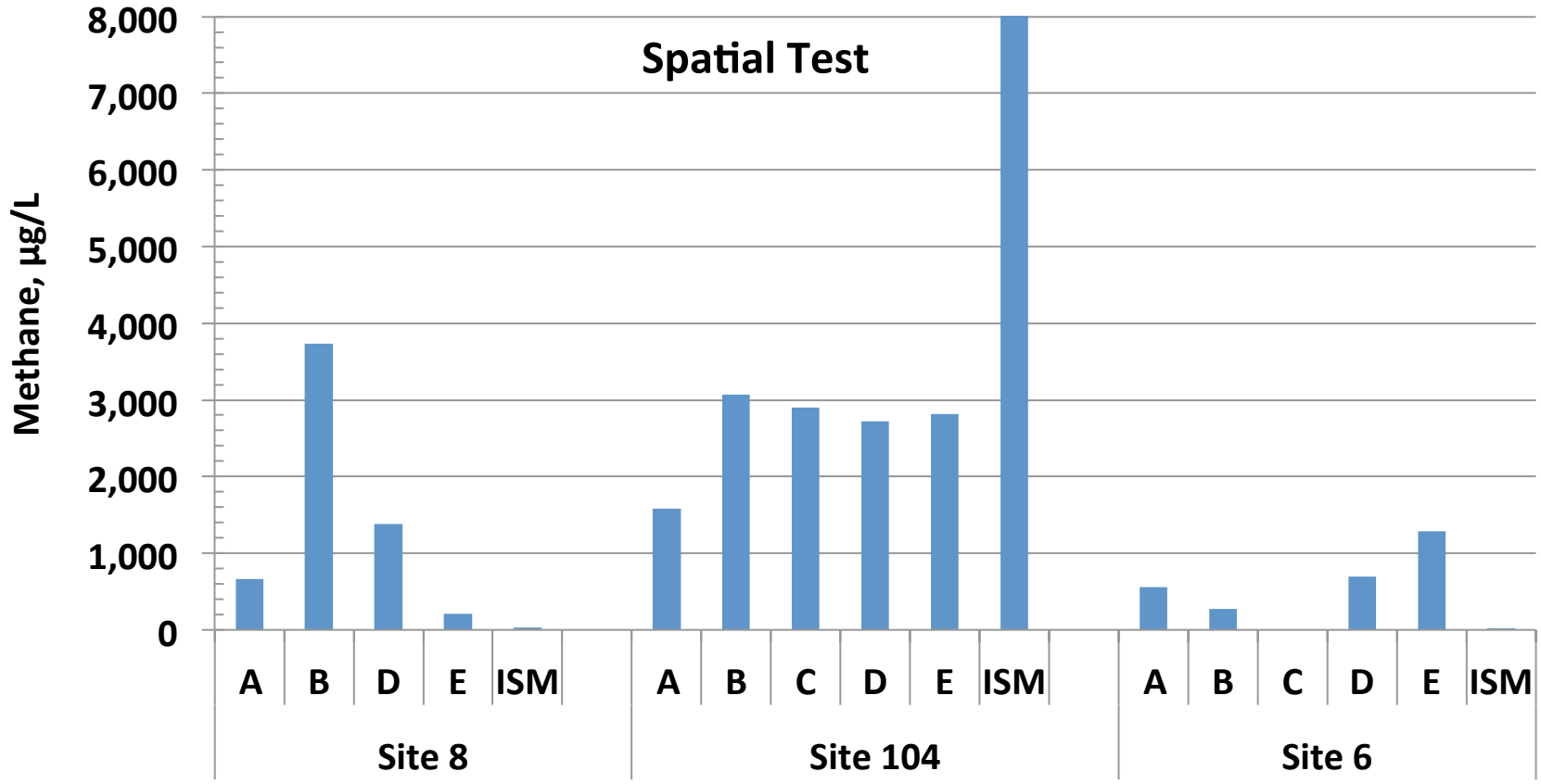




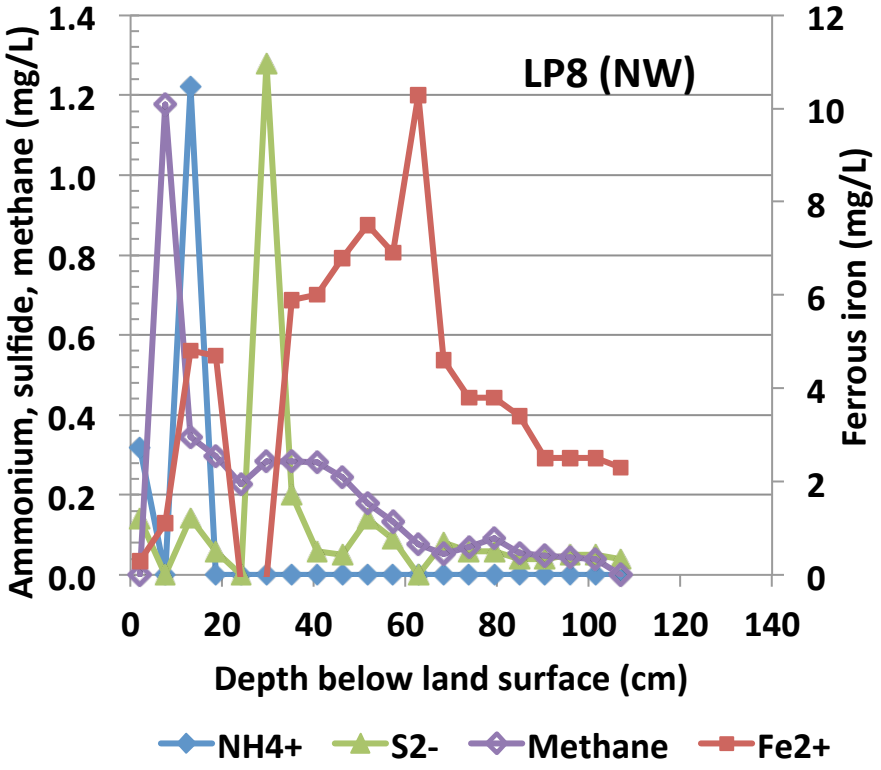
Lateral Heterogeneity- VOC molar ratio

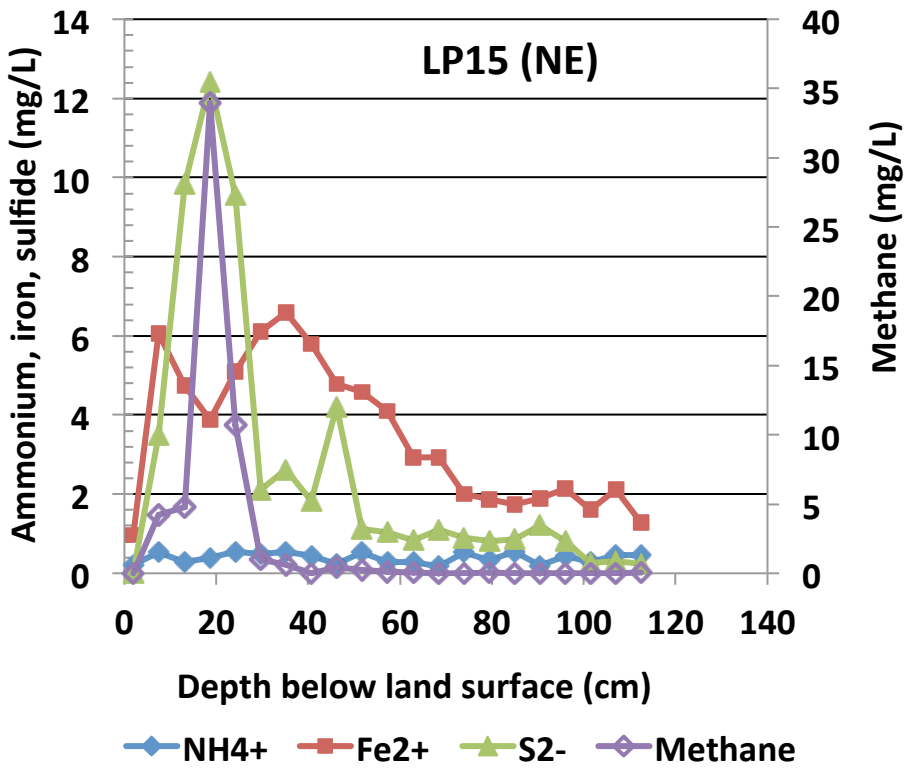


Lateral Heterogeneity- Methane

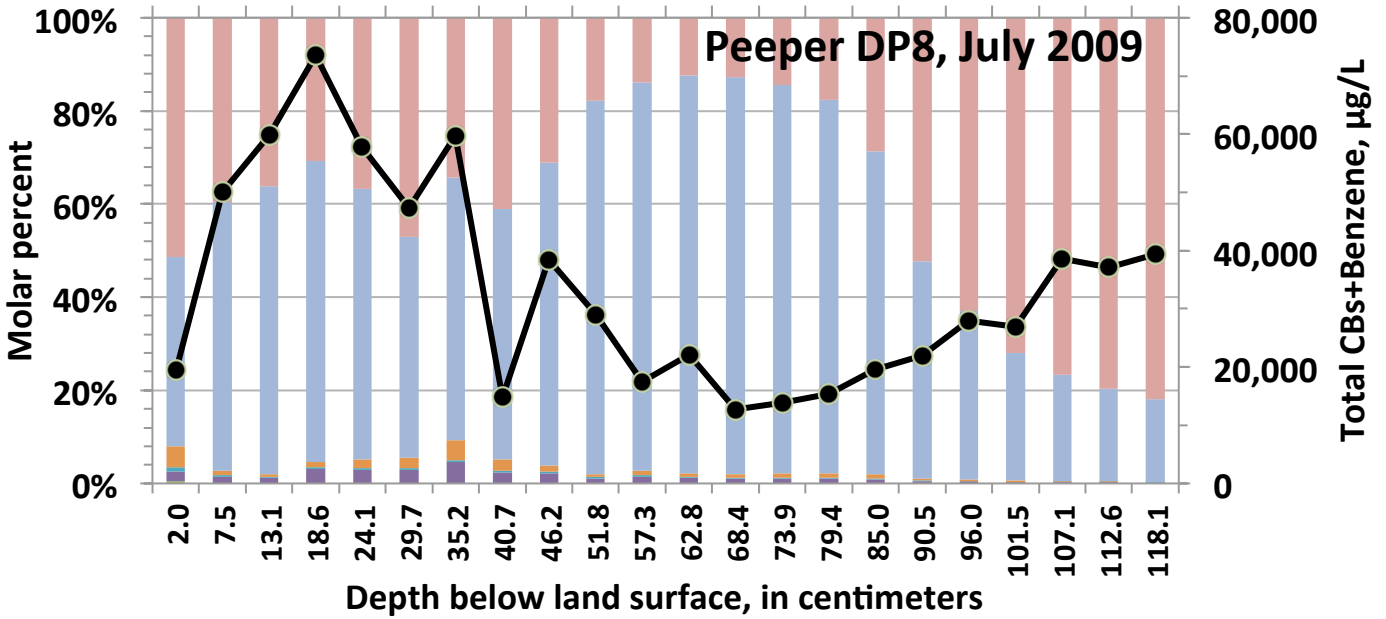


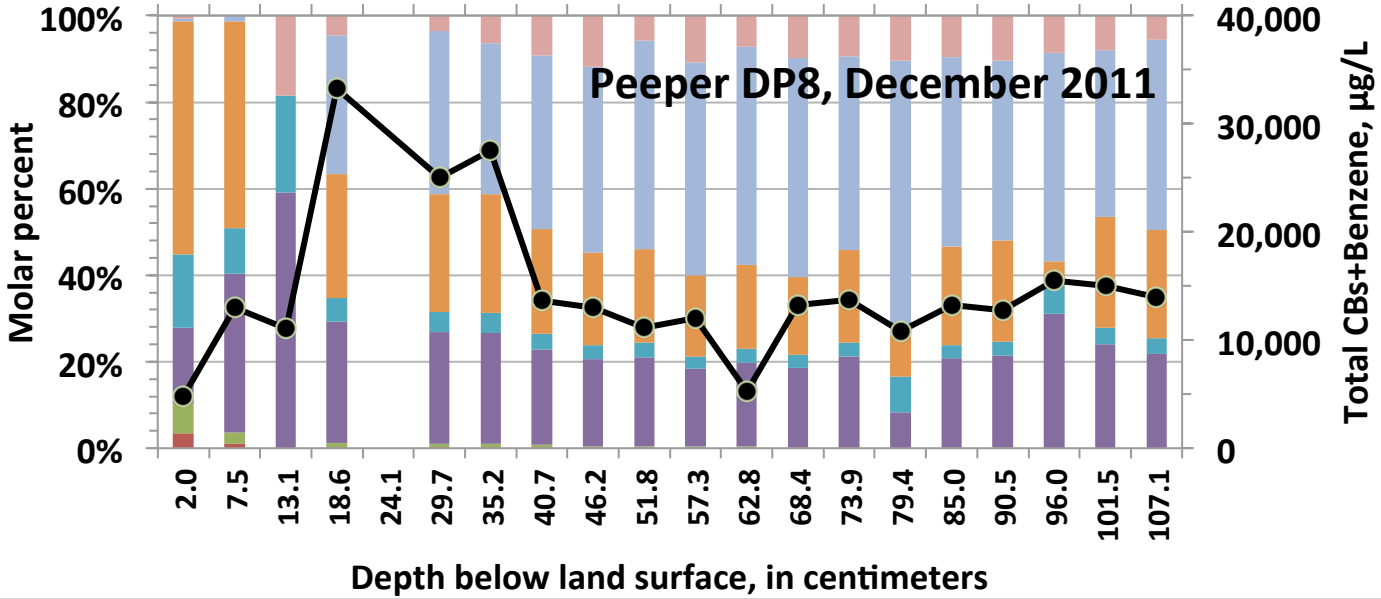
Vertical Heterogeneity- Redox





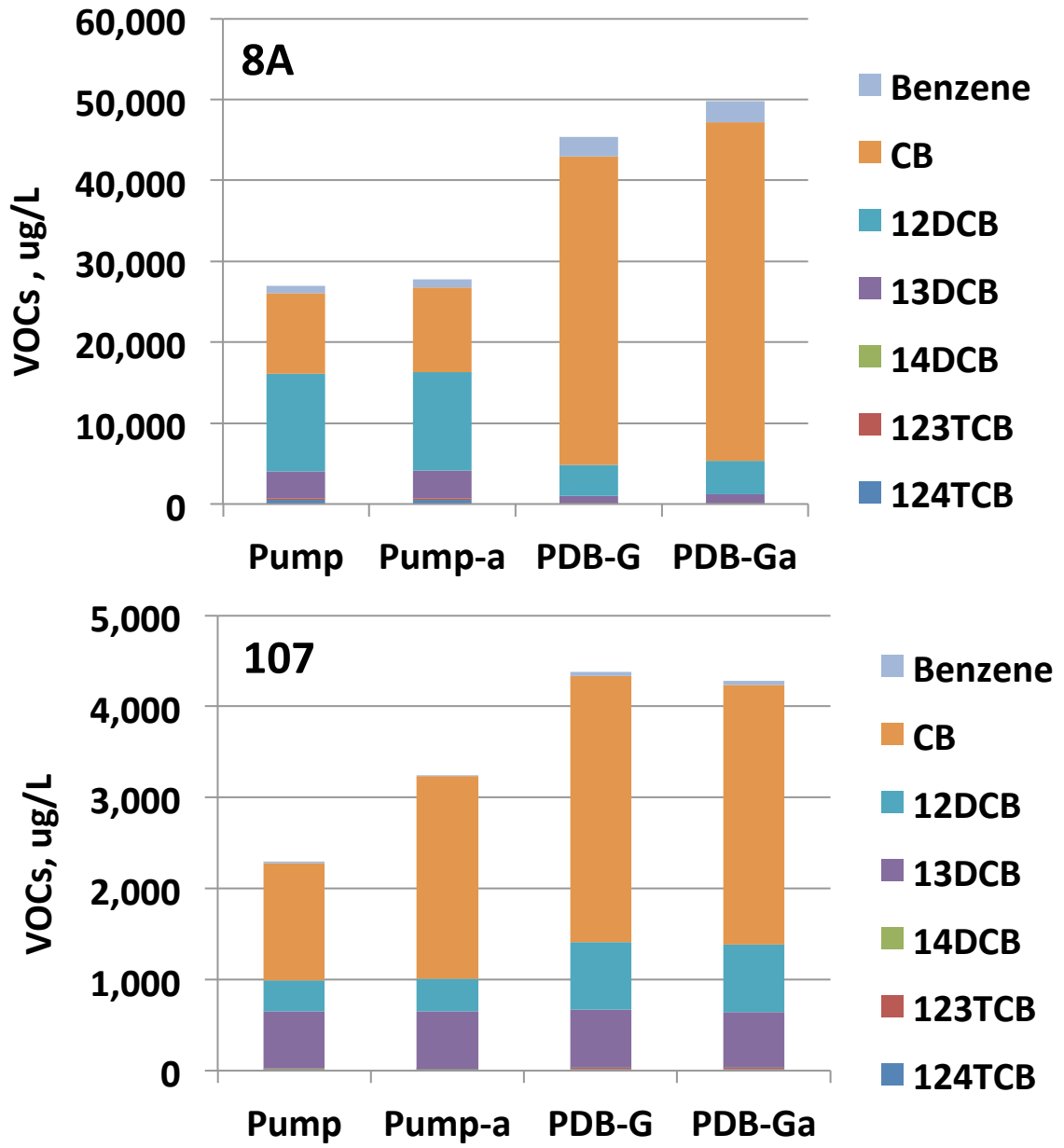
Vertical and Temporal-VOCs, Site 8 Peepers





Field Sampling Method

Passive diffusion bag in ground versus piezometer peristaltic pump purge and syringe sampling



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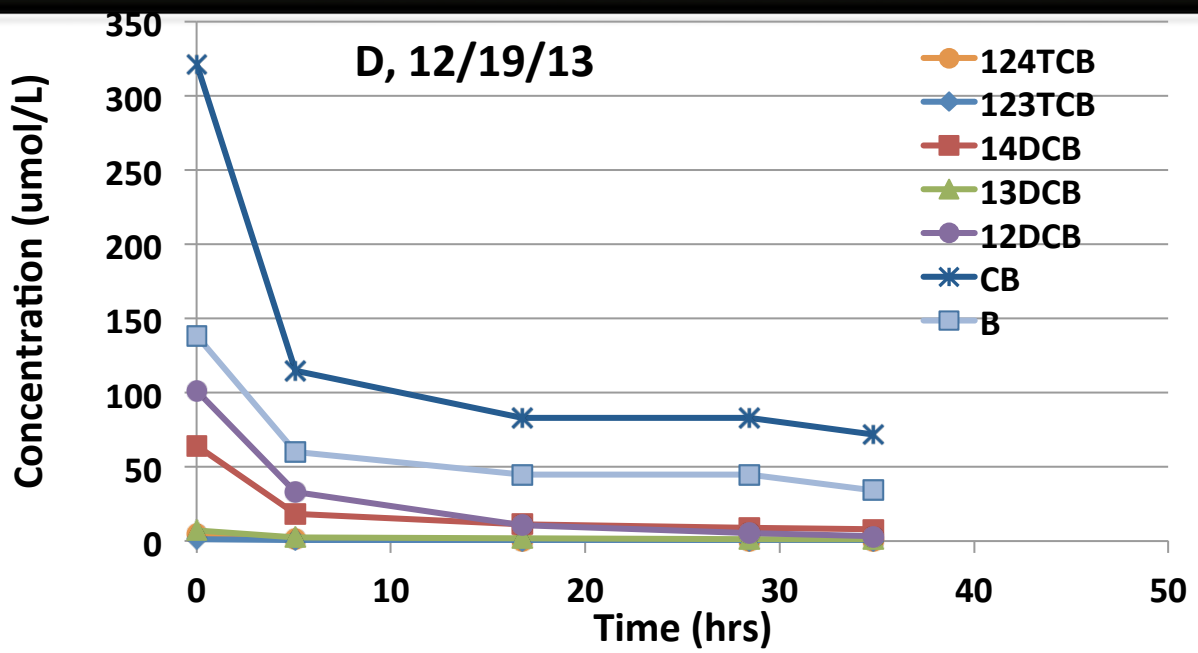
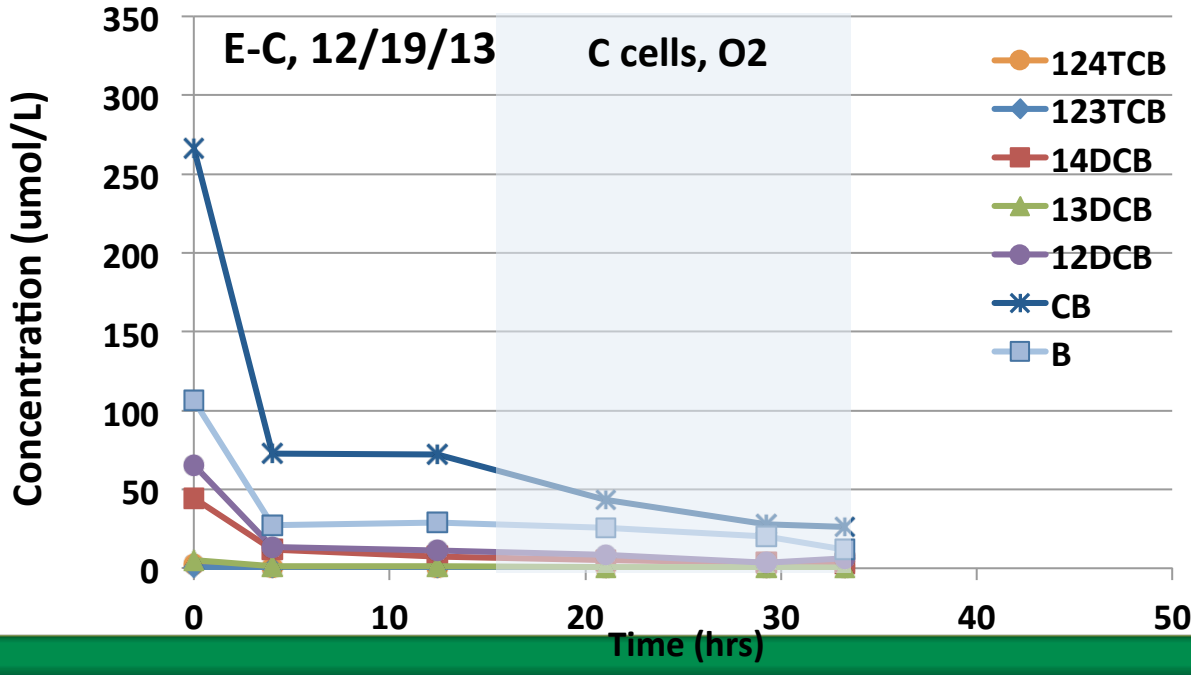
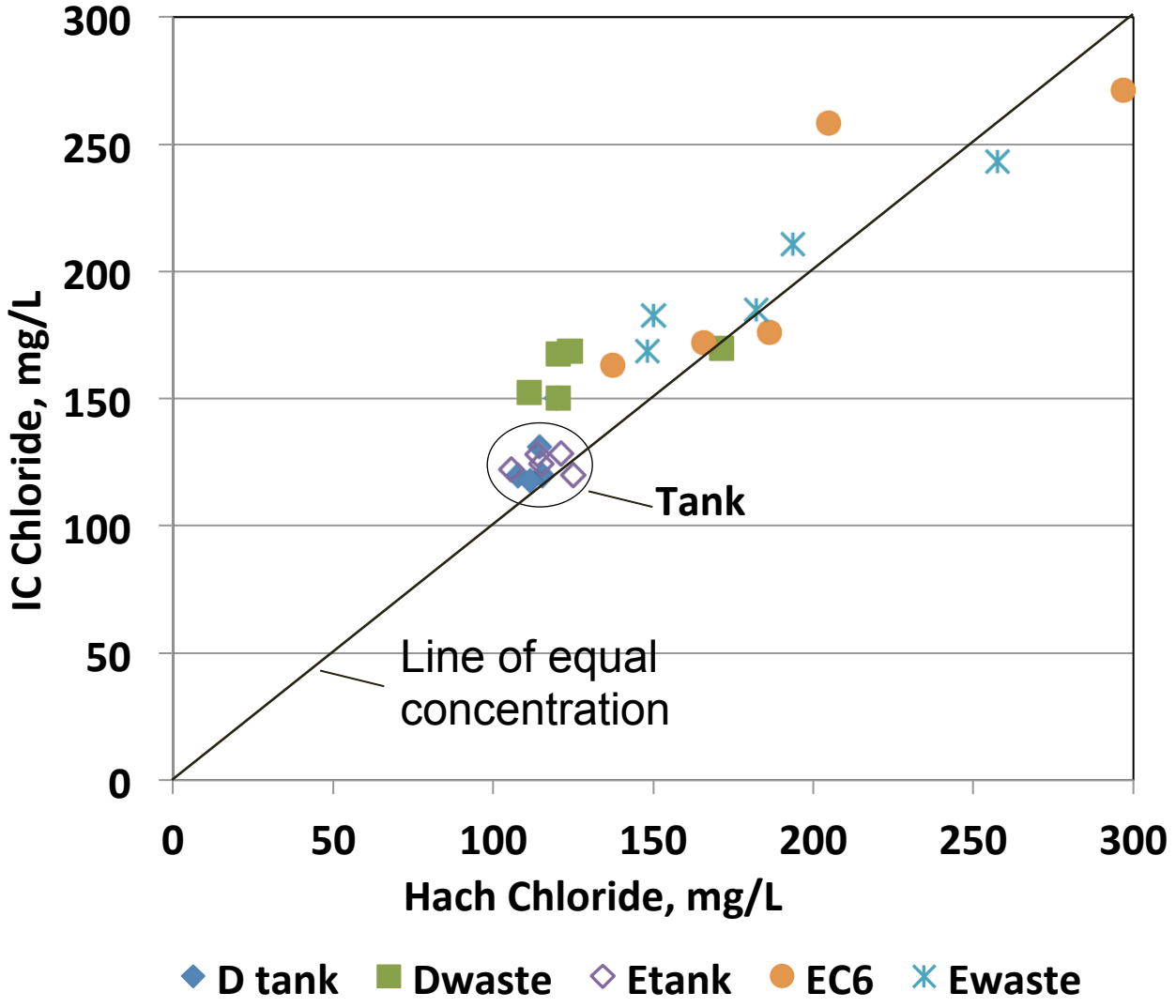
Bioreactor Experiments



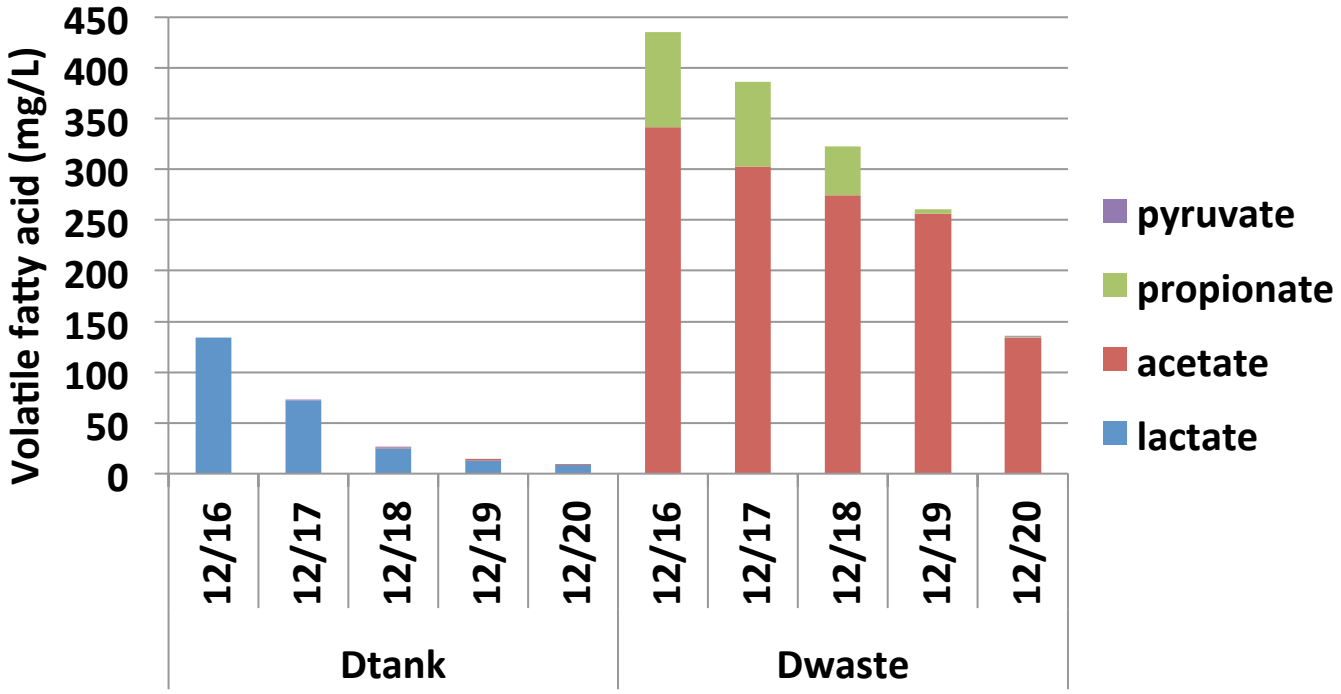


Chloride- Bioreactors

- Chloride important as a measure of overall amount of VOC dechlorination
- Noticed difference between two methods of chloride and sulfate analysis



VFAs in Bioreactor Tests- lactate and corn syrup amended to tank



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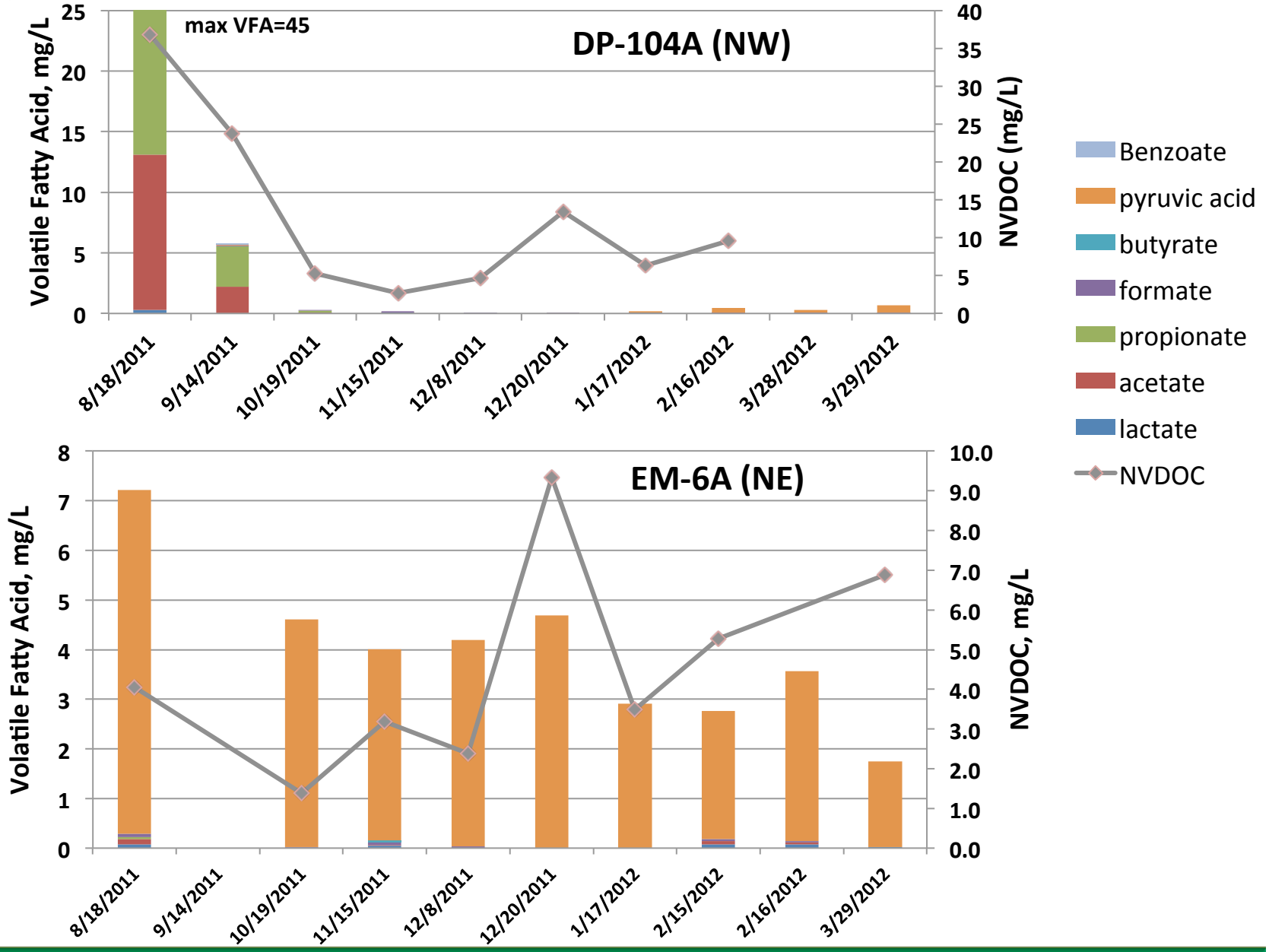
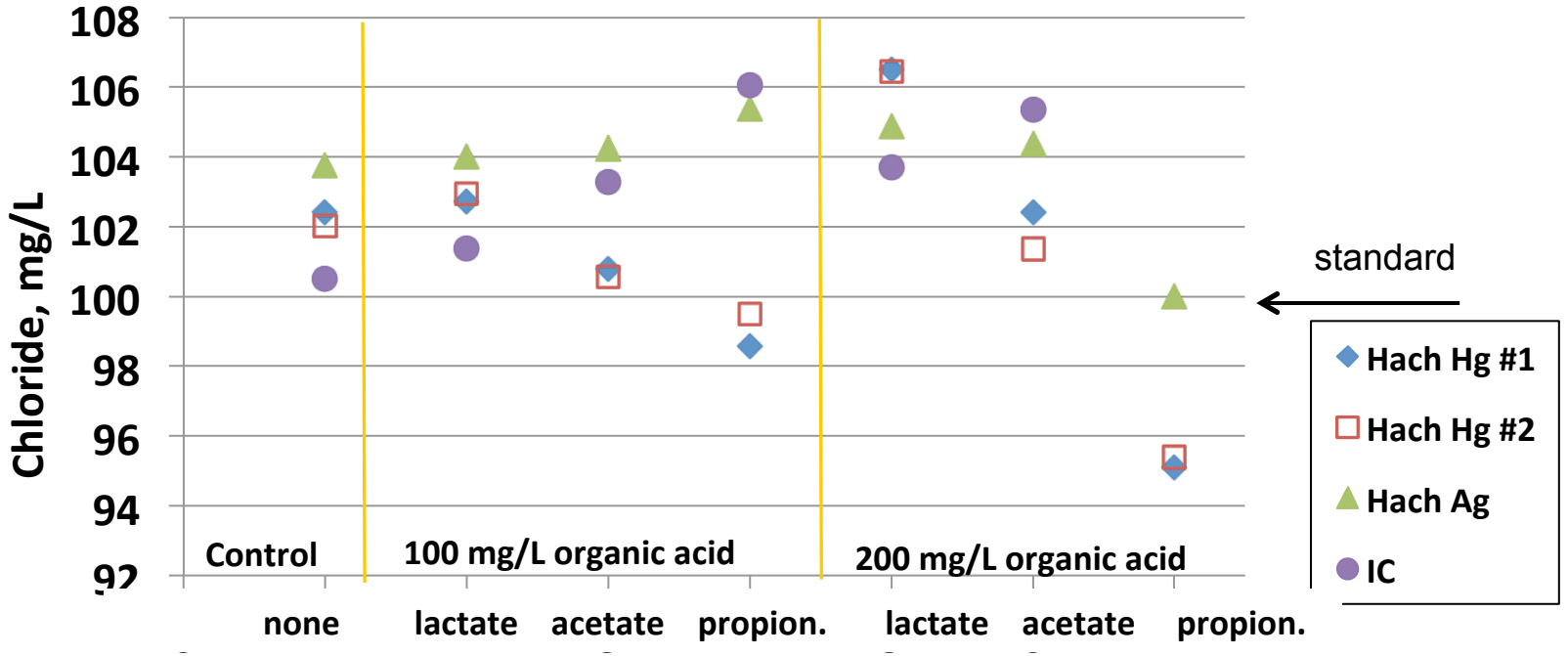
DOC, VFAs in wells

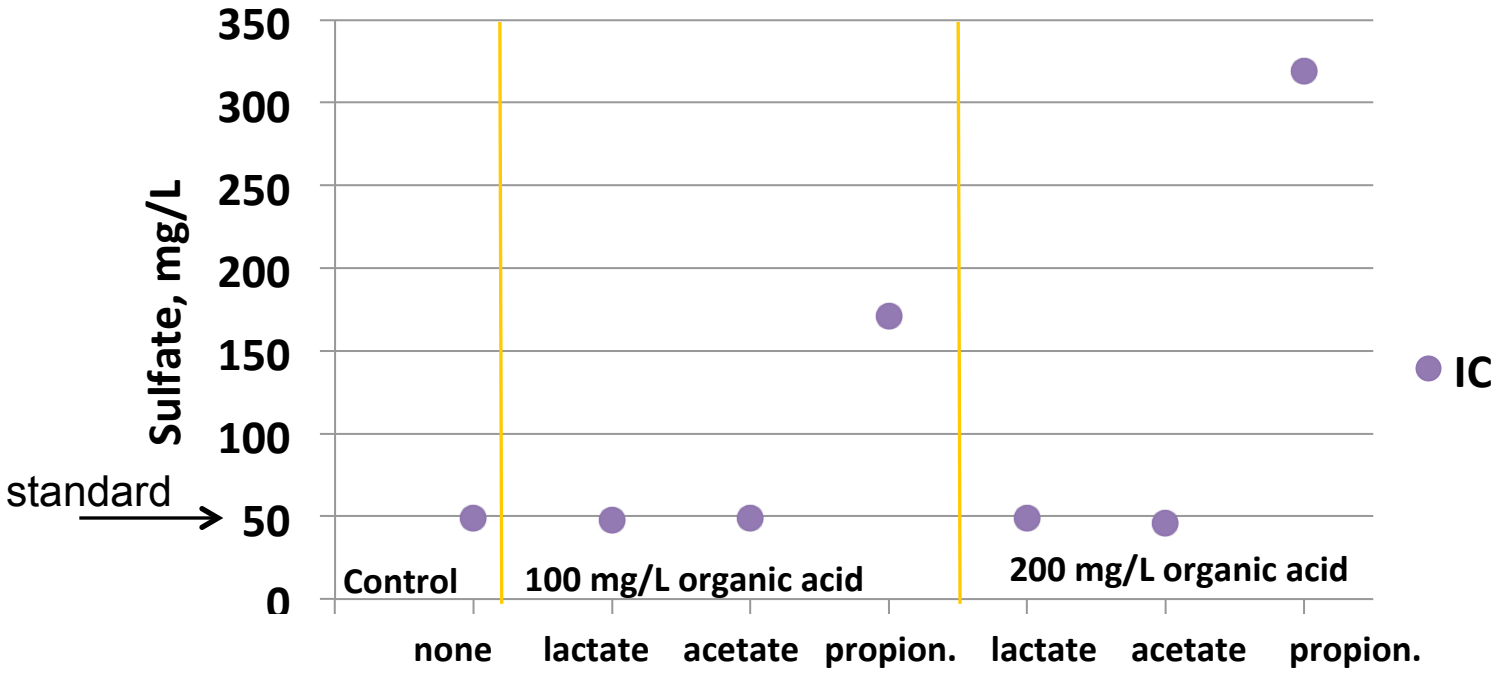


Chloride analysis- organic acids interference



- IC lowest error for control (100 mg/L) concentration
- IC and Hach silver nitrate show similar bias high (4-6 %)
- IC had peak interference with 200 mg/L propionate
- Hach mercuric chloride method (Hg) showed lowest error, except with 200 mg/L lactate and propionate

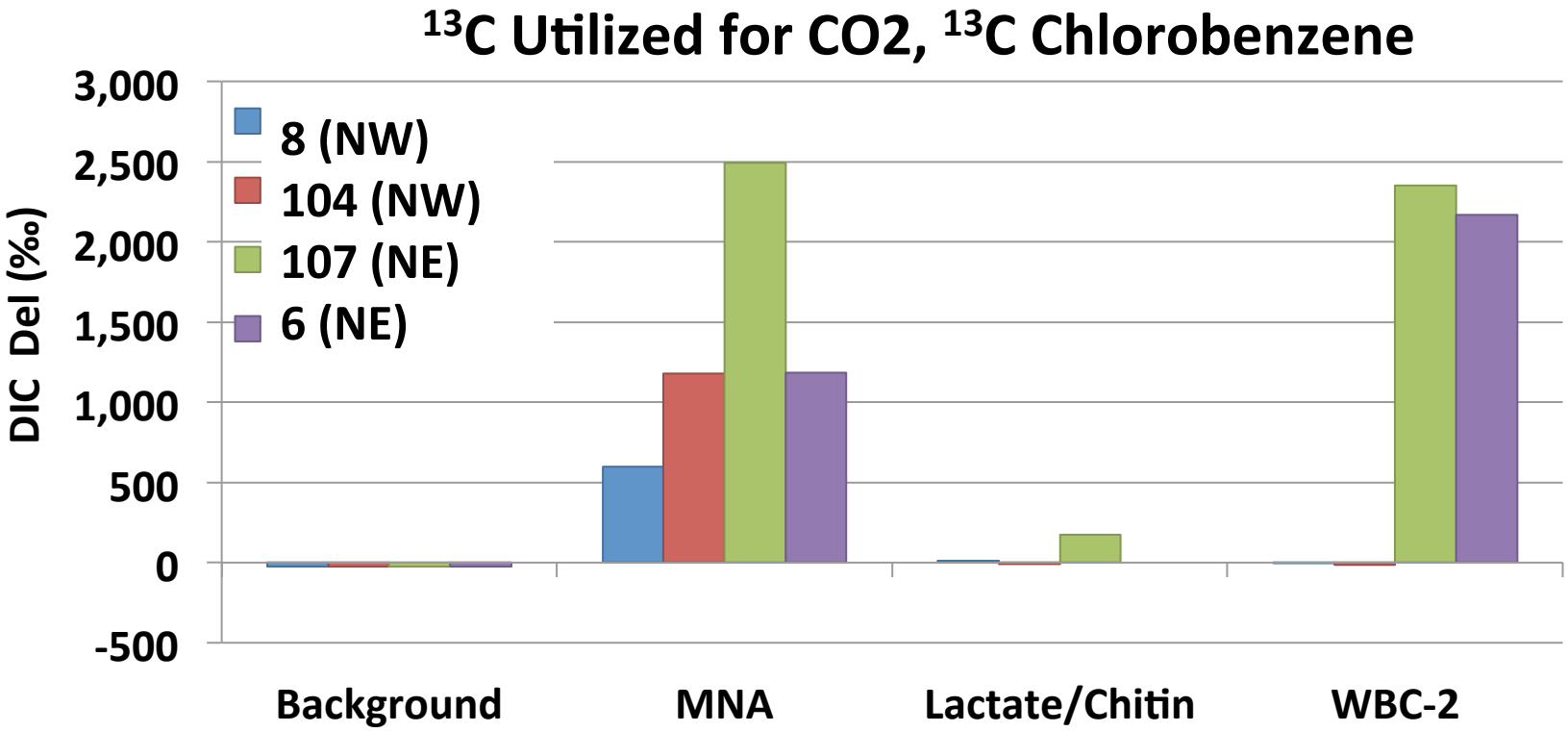
Sulfate analysis- organic acids interference



- IC low error in control (50 mg/L) concentration and lactate and organic acid solutions
- IC showed very high error with 100 or 200 mg/L propionate
- Sulfate measurement error doubled with doubling in propionate concentration

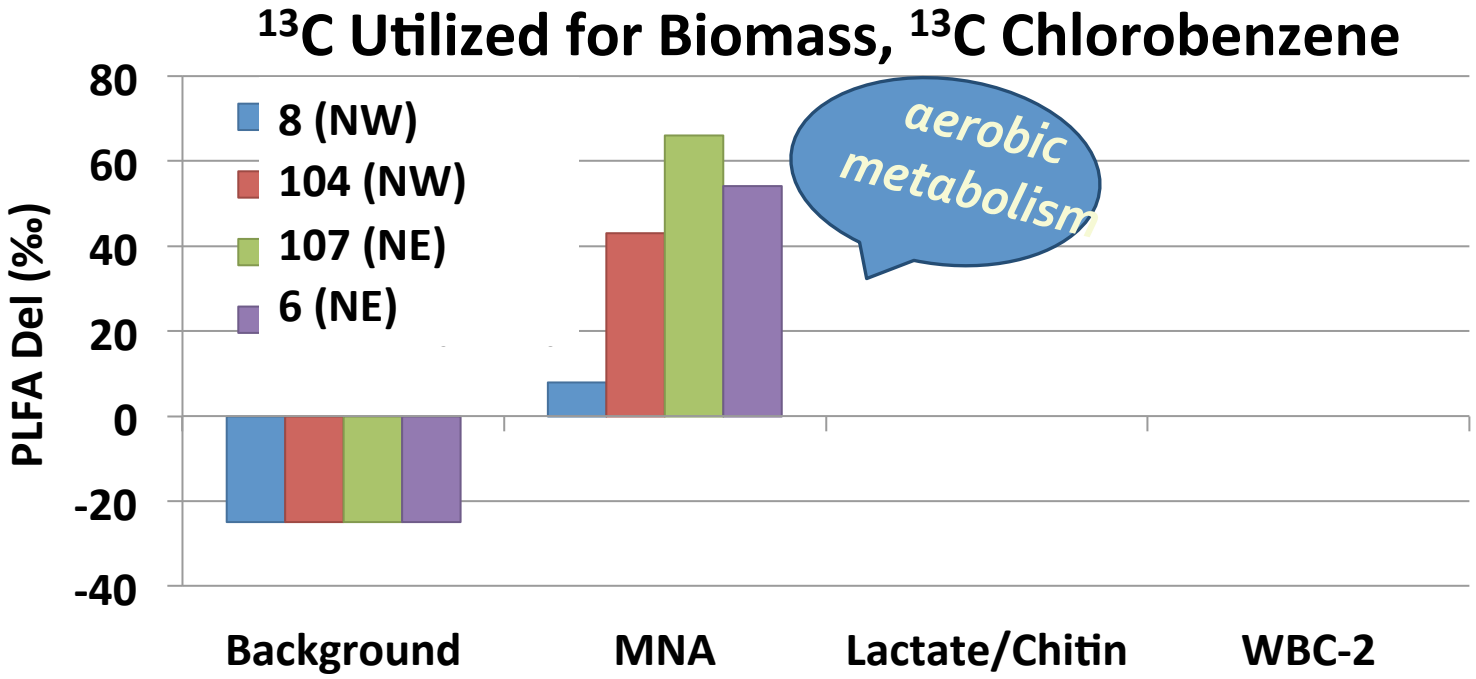
In Situ Microcosms with Bio-Traps

- Field experiments with stable carbon isotopes and microbial community analyses provide additional biodegradation evidence
- Three treatments:
  - MNA, no amendment
  - Lactate, biostimulated
  - WBC-2, anaerobic culture added



Bio-Traps:

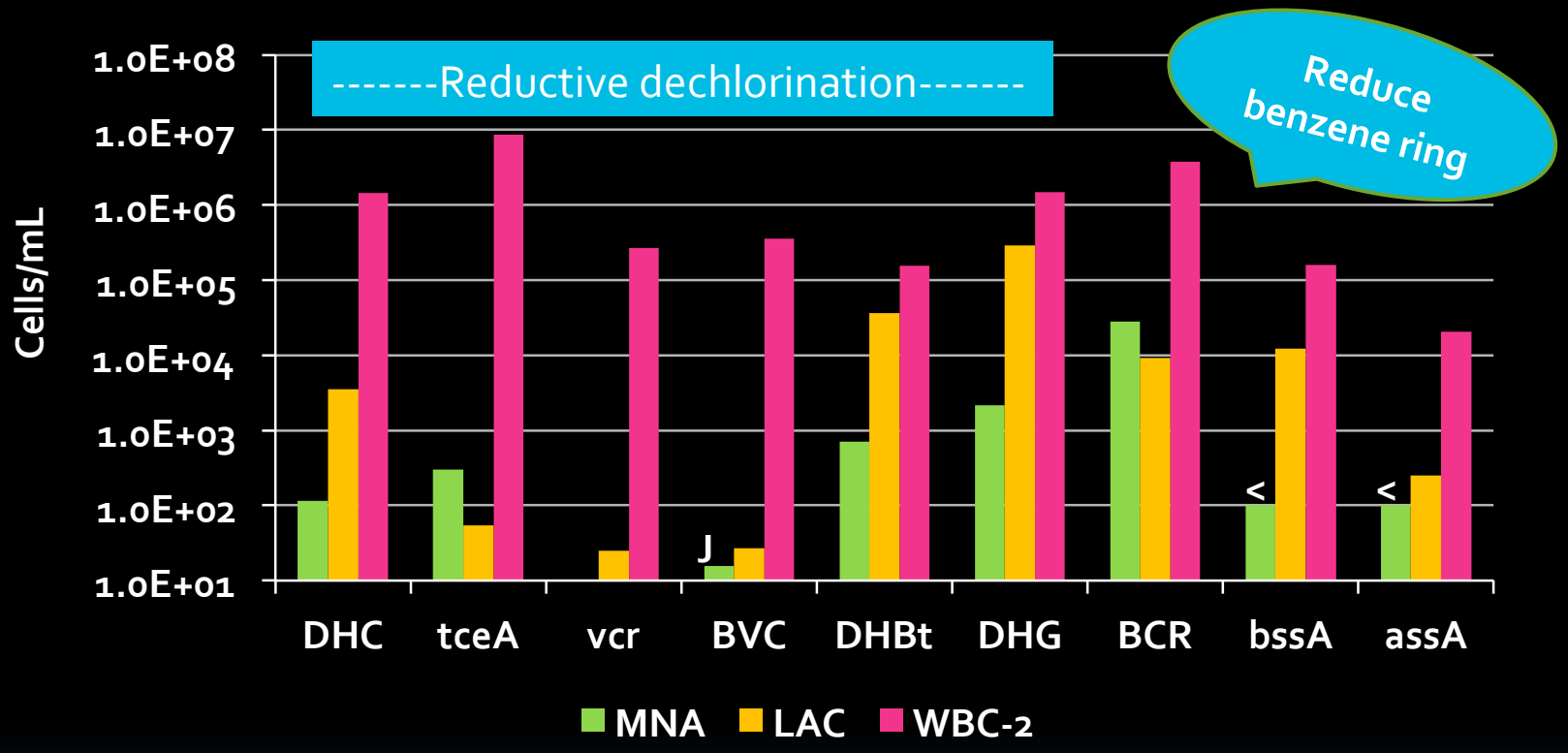
^{13}C-labeled chlorobenzene incorporated in inorganic carbon (CO_2) indicates complete mineralization



Bio-Traps:

^{13}C-labeled chlorobenzene incorporated in phospholid fatty acid (cell membrane material) indicates aerobic oxidation

QuantArray Microbial Analysis- Anaerobic



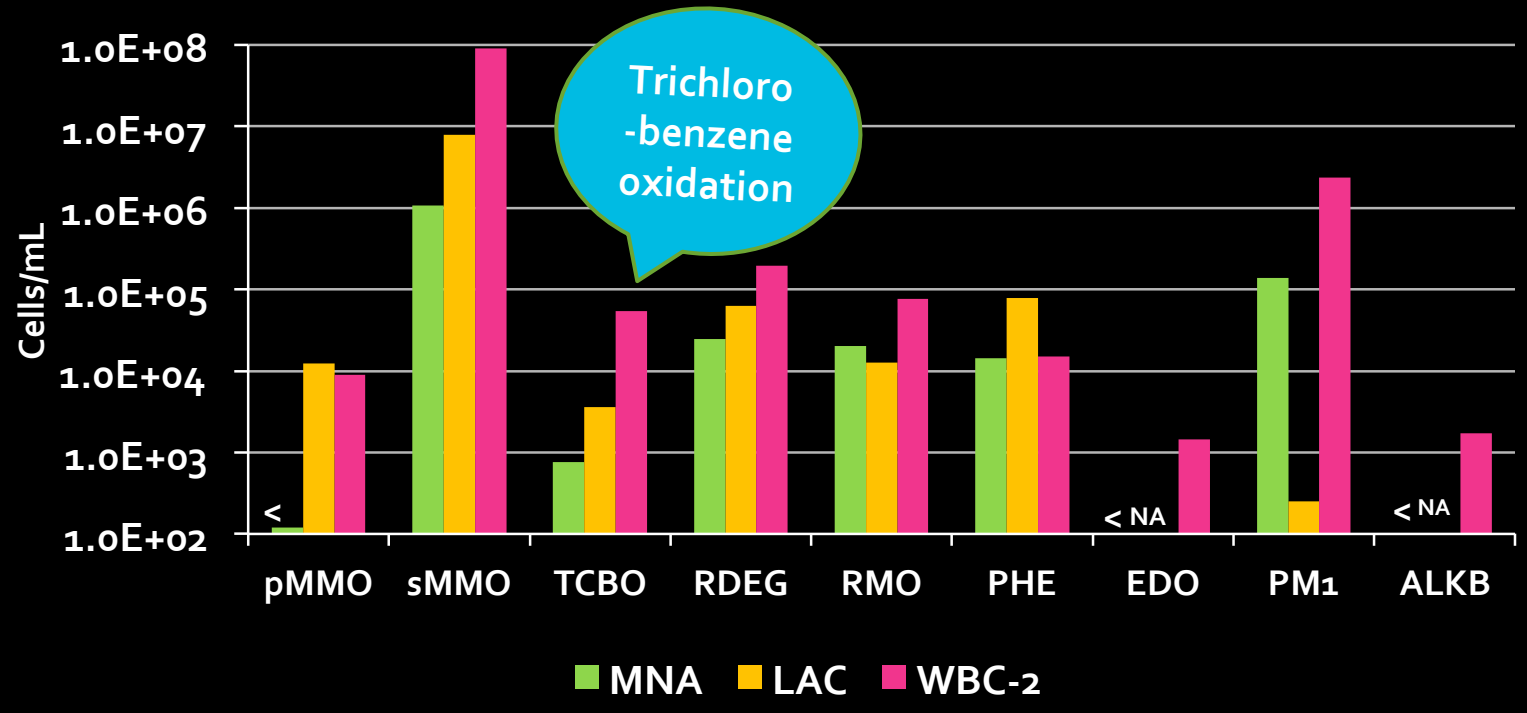
Reductive dechlorination:

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

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

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Luke Myers

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USEPA Region III

Toxic Substances Hydrology Program

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Questions?