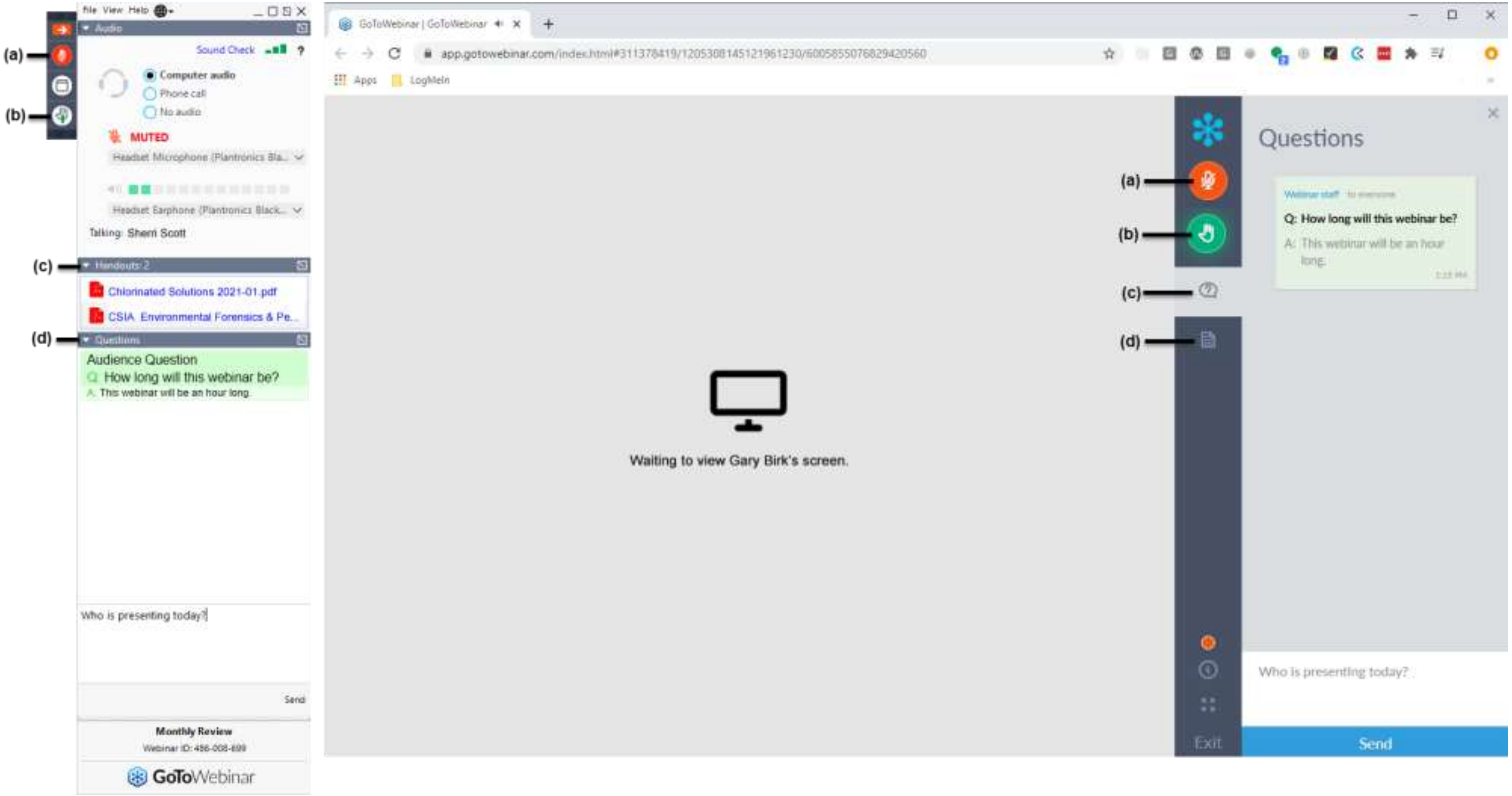
Remediation Seminar

Performance Monitoring to Assess Remediation Effectiveness

Thu, March 18, 2021 1:00 PM - 2:00 PM EST

User Dashboard



Remediation Seminar

Today's Speakers

- David Alden
- Tersus Technical Support

Remediation Seminar

Today's Speakers

- Daniel Bouchard, Ph.D.

Remediation Seminar

Today’s Speakers

- Brent G. Pautler, Ph.D.
- Customer Service Coordinator
- SiREM, Guelph, ON

Remediation Seminar

For Upcoming Events, Visit

www.RemediationSeminar.com

Remediation Seminar

SiREM
Leading Science · Lasting Solutions

Performance Monitoring for Enhanced Reductive Dechlorination

Brent G. Pautler, Ph.D.
Chemistry Services Manager

The Basics of Enhanced Bioremediation

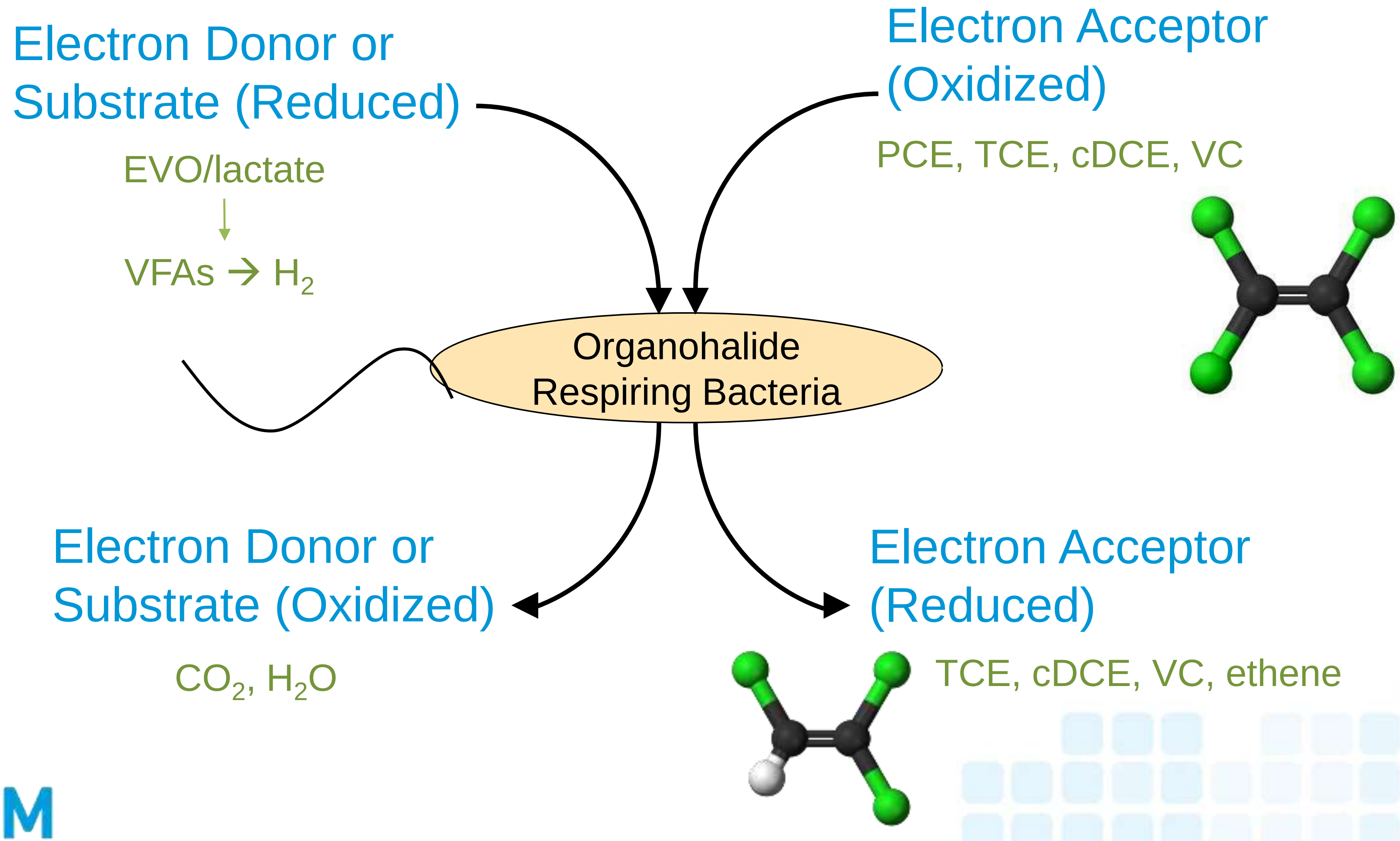
- **Biostimulation:** The addition of nutrients to stimulate microbial activity (e.g., electron donors)
- **Bioaugmentation:** The addition of beneficial microorganisms to improve the rate or extent of biodegradation
- **SiREM bioaugmentation cultures:** for remediation of chlorinated volatile organic chemicals and benzene

Injection of KB-1® each liter has ~100 billion Dhc cells

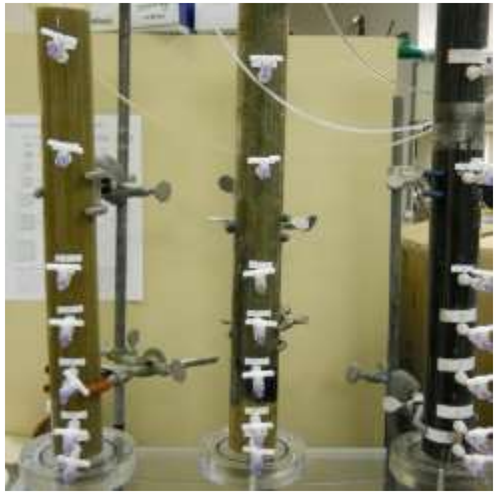
KB-1® KB-1plus® DGGB™

SiREM

Chlorinated VOCs and Molecular Metabolism



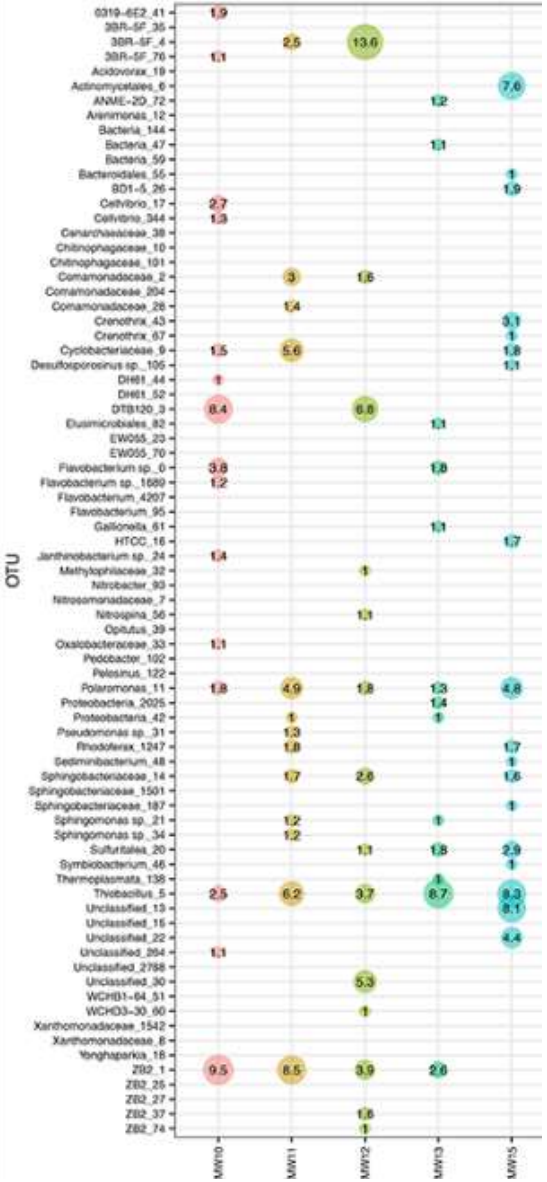
Pre-Implementation: Treatability Testing



Bioremediation Pre-implementation Monitoring

gene trac

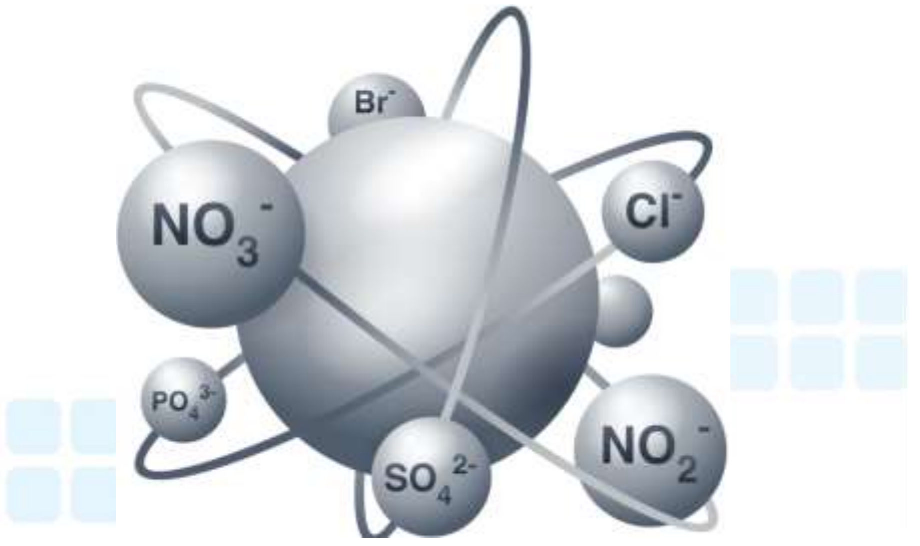
- Determine need for bioaugmentation vs. biostimulation
- Predict if intermediates such as cDCE or VC are likely to accumulate
- Characterize microbial community spatial and temporal variability
- Consider Next Generation Sequencing for non-targeted insight into community function and dynamics



analytical testing

Anions Analysis

- Determine concentrations of redox-sensitive anionic species
- Confirm onset of suitable reducing conditions required for reduction of COCs
- Determine groundwater velocity and flow path using stable anionic tracers



SiREM

Implementation: Cultures and Electron Donors

EVO (EDS-ER™, EDS-QR™)

Commercially Available Cultures

KB-1® KB-1 plus® DGG B™

Anaerobic Injection Water Preparation

SiREM

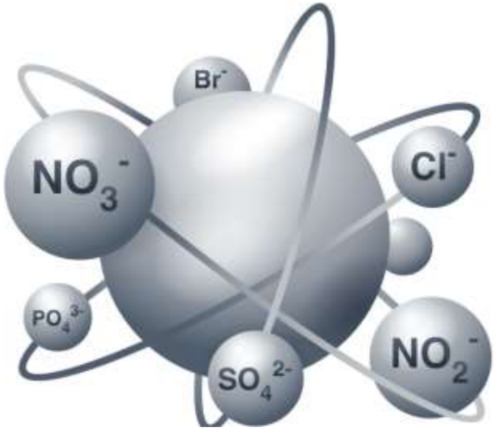
Bioremediation Performance Monitoring

gene trac

- Quantify microbial biodegraders (qPCR)
- Determine impact of site amendments including electron donor/acceptors on microbial community
- Monitor progress and validate performance of bioremediation

Anions Analysis

- Monitor Cl^- released during reductive dechlorination
- Monitor competing electron acceptors, e.g., nitrate/sulfate

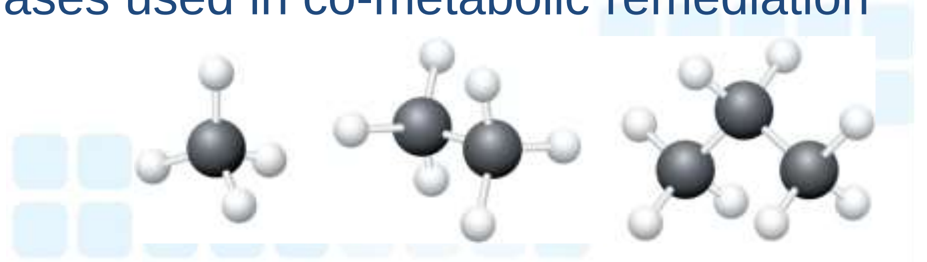


Volatile Fatty Acids

- Confirm fermentation of slow release and soluble electron donors
- Map fermentation pathways
- Determine the need for additional electron donor

Dissolved Hydrocarbon Gases

- Confirm complete dechlorination of chlorinated ethenes, ethanes and propanes
- Quantify methanogenesis
- Quantify gases used in co-metabolic remediation

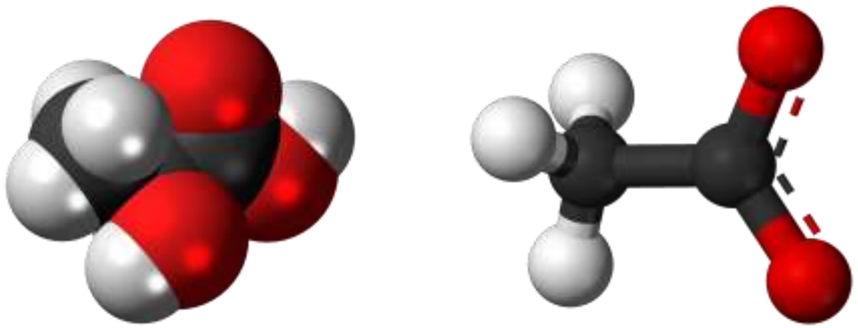


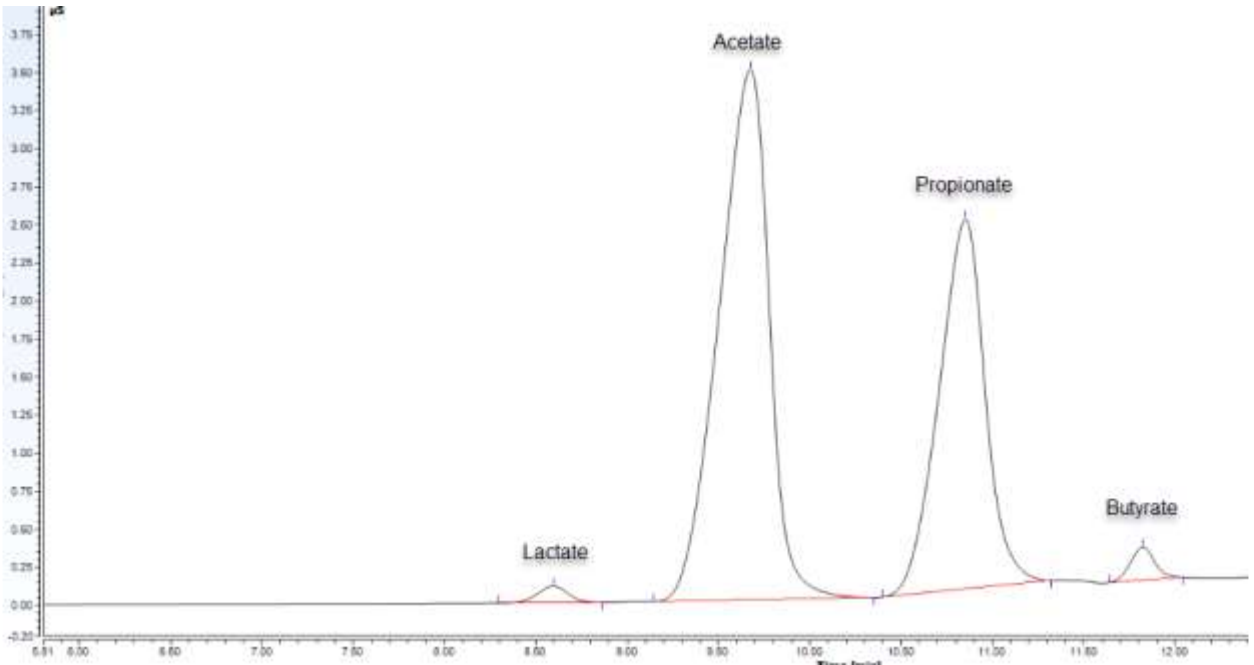
SiREM

Bioremediation Performance Monitoring

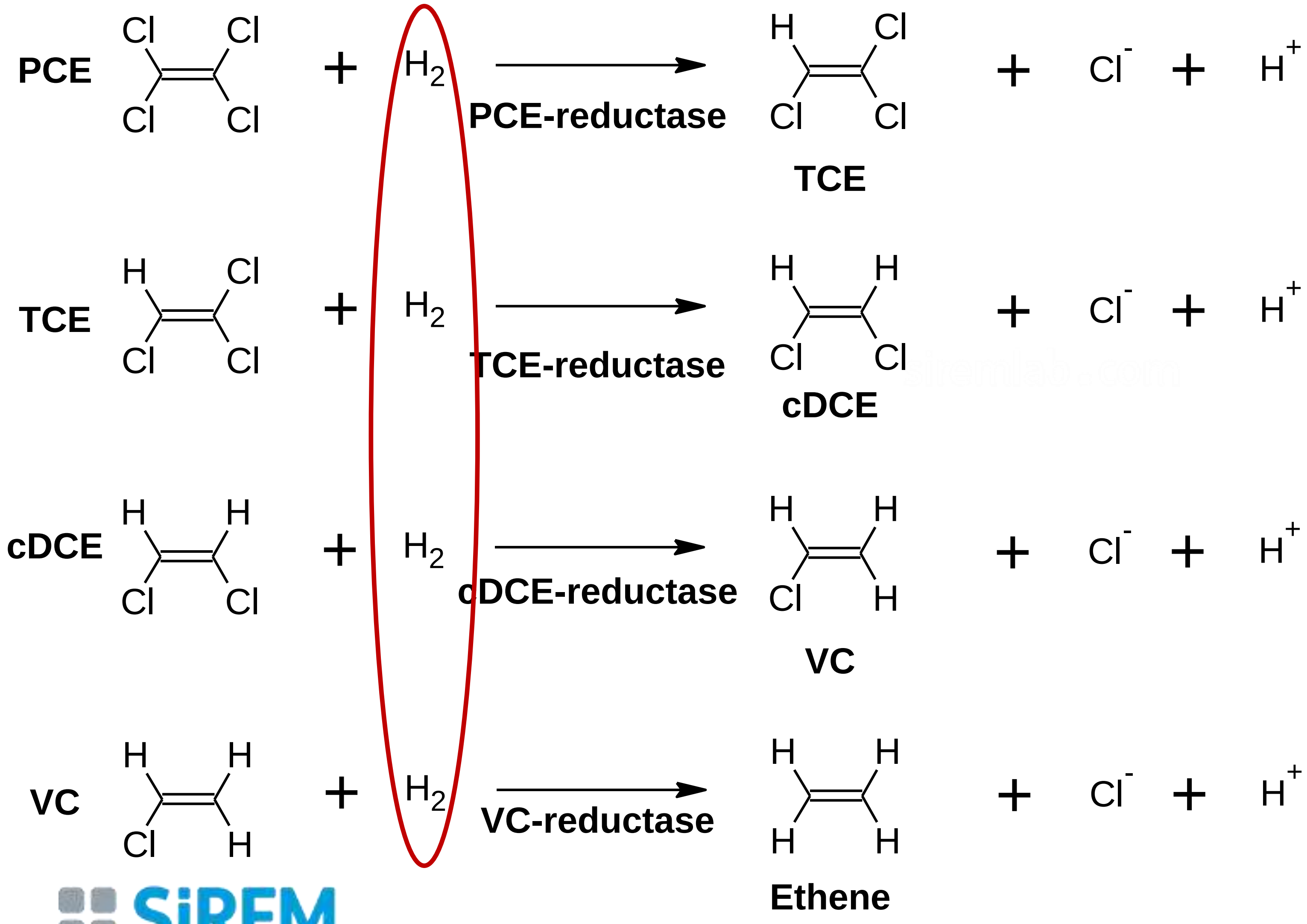
Volatile Fatty Acids (VFAs)

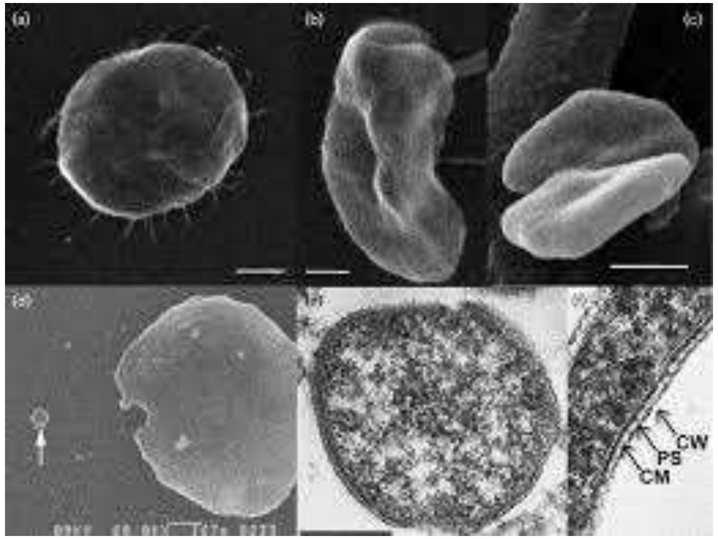
- Quantification used to assess electron donor status in bioremediation systems and fermentation
- Simple sampling procedures and laboratory analysis
- Typically done with a standard IC Method





Reductive Dechlorination by *Dhc*

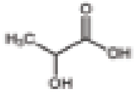
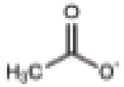
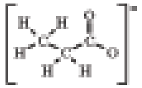
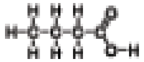
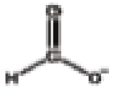
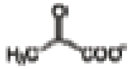




H_2 as Direct Electron Donor

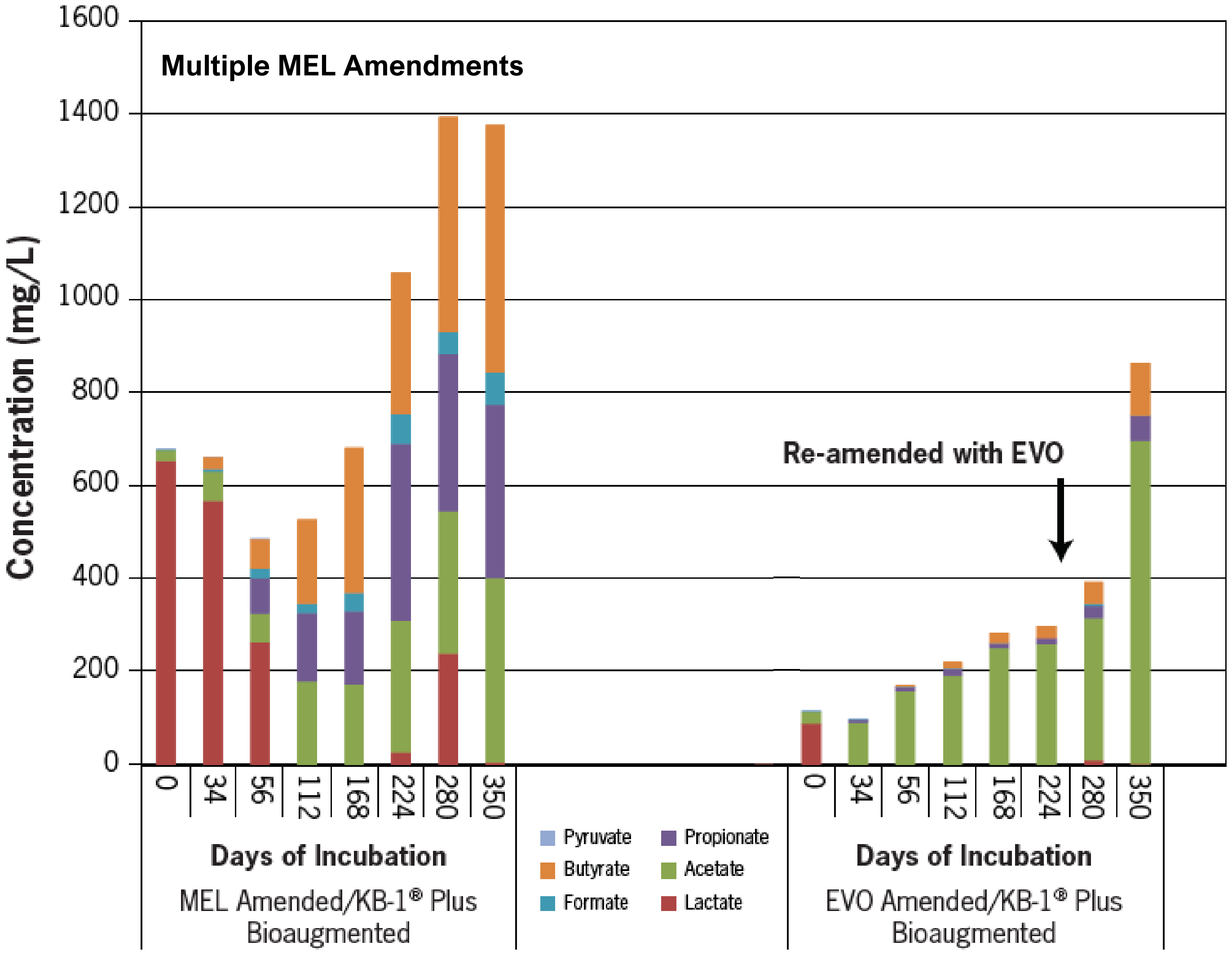
- Produced by fermentation organic substances
  - Carbohydrates
  - Alcohols
  - **Fatty Acids (VFAs)**
- Consumed quickly

Sources and Roles of Specific VFAs

VFA	Structure	Formula (Ion)	Source	Role
Lactate		$C_3H_6O_3^-$	Common primary amendment/component of EVO mixtures	Rapidly fermented to propionate and acetate producing hydrogen for dechlorination (Aulenta et al., 2007)
Acetate		$C_2H_2O_2^-$	From fermentation of lactate/EVO/sugars	Electron donor for some (incom-plete) dechlorination reactions (e.g., Krumholtz et al., 1996) Carbon source for *Dhc* (Cupples et al., 1993)
Propionate		$CH_3CH_2COO^-$	From fermentation of lactate/EVO/alcohols	Fermented to produce hydrogen and formate
Butyrate		$CH_3CH_2CH_2COO^-$	From fermentation of EVO/alcohols	Fermented to produce hydrogen and acetate
Formate		$CH_2O_2^-$	From fermentation of propionate	Fermented to produce hydrogen and bicarbonate
Pyruvate		$C_3H_4O_3^-$	From fermentation of sugars	Fermented to propionate and acetate with hydrogen production (Cope and Hughes, 2001)

SiREM

VFAs as an Electron Donor Status Indicator



During Active Fermentation

- Acetate generally increases over time
- Stabilization of acetate over time in absence of other VFAs may indicate exhaustion of electron donor supply
  - Longer lasting when compared to other VFAs with low energy yield
  - Mobile: will migrate downgradient
  - Tends to encourage acetoclastic methanogenesis
  - Will not stimulate cDCE → VC → Ethene

Case Study: Biotreatability East Coast Site

Mixed chlorinated ethenes, chlorinated ethanes, chlorinated methanes, CFC-113, BTEX, DCB's and MIBK

Contaminant	Concentration (mg/L)
PCE	43
TCE	30
cDCE	39
1,1,2,2-TECA	1.0
1,1,1-TCA	**100**
1,2-DCA	18
DCM	**190**
CFC-113	**40**
Total BTEX	25
CB	11
1,2-DCB	1.4
MIBK	11

Treatments

- Sterile and Active Controls
- Soluble Donor Amended
- EVO Donor Amended
- Soluble Donor Amended & KB-1® Plus Bioaugmented
- EVO Donor Amended & KB-1® Plus Bioaugmented

Site Groundwater

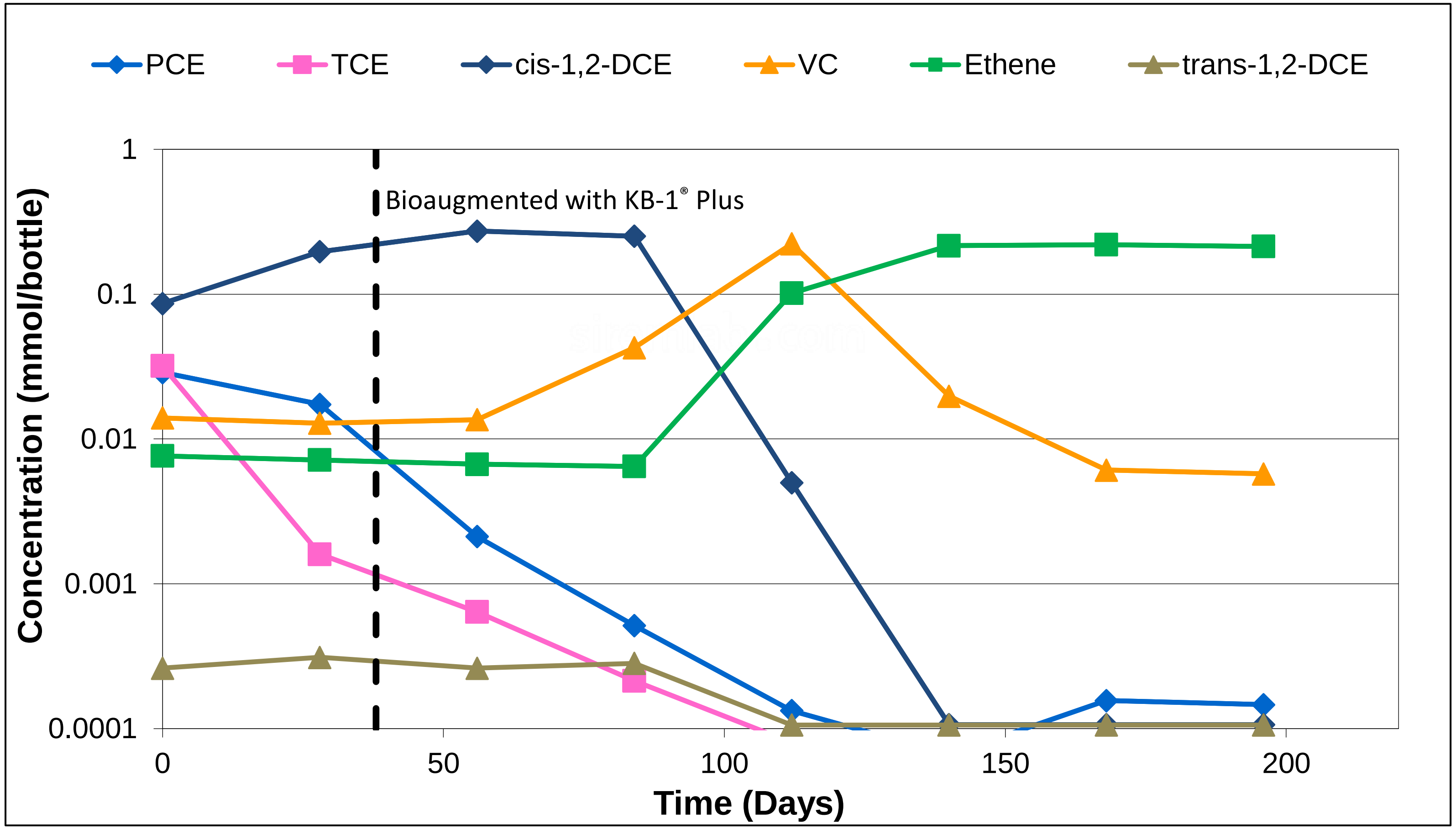
Dhc	1×10^7/liter
vcrA	5×10^6/liter
Dhb	2×10^7/liter

SiREM

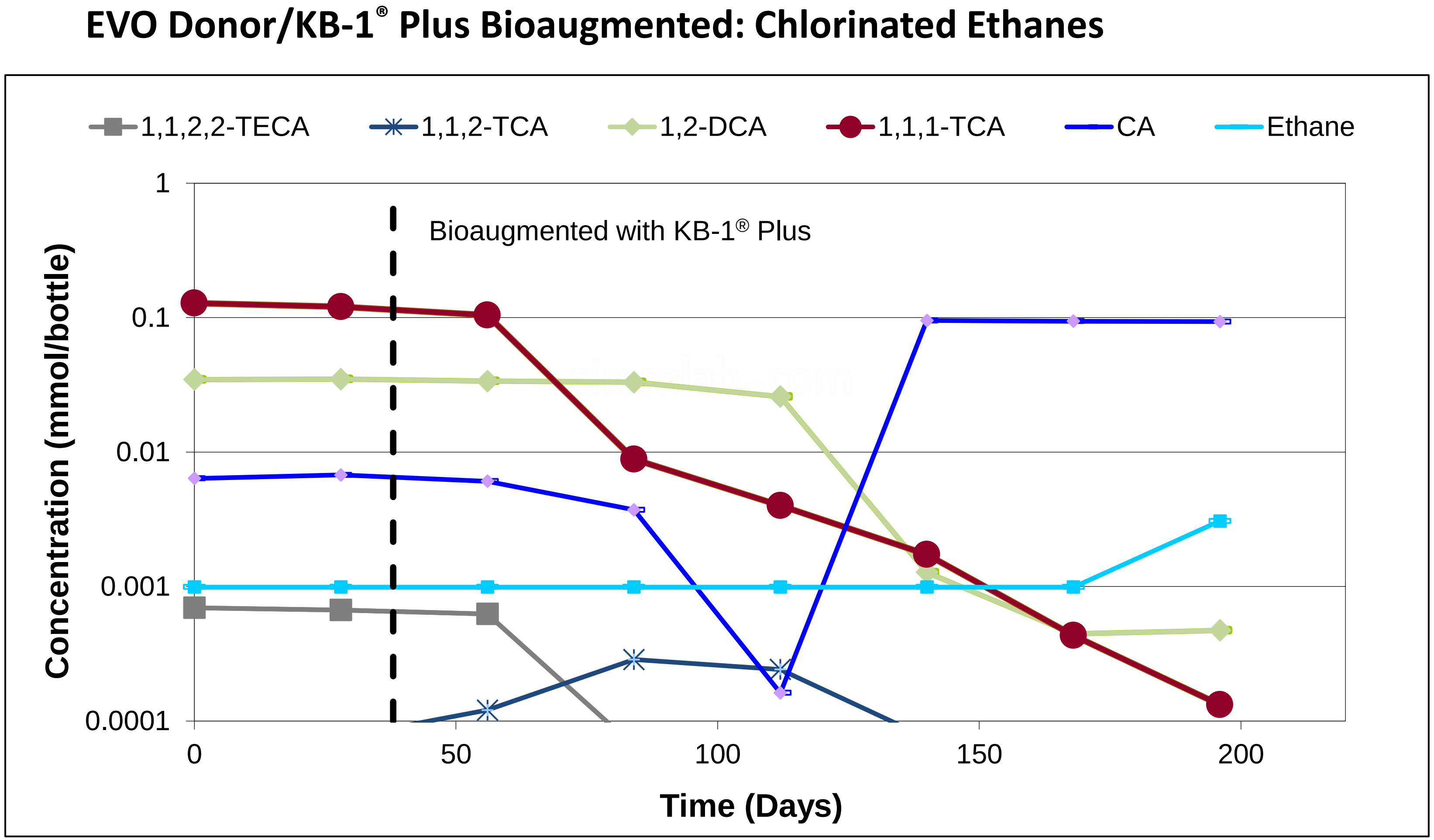
treatability studies

Case Study: Biotreatability East Coast Site

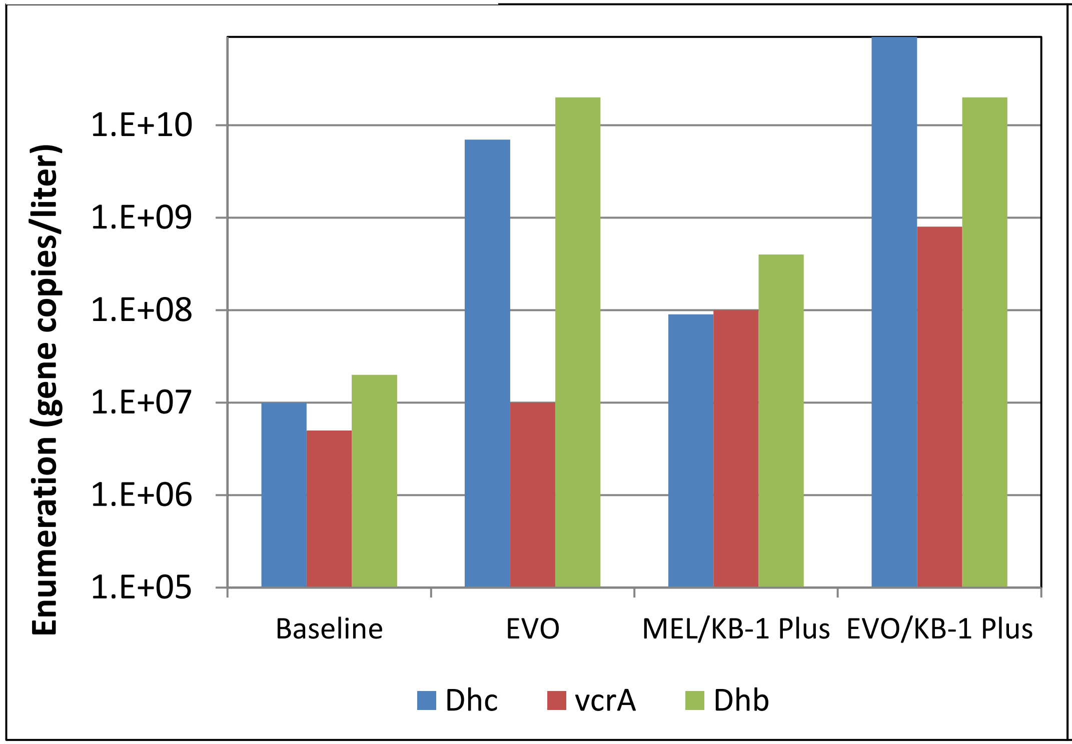
EVO Donor/KB-1® Plus Bioaugmented: Chlorinated Ethenes

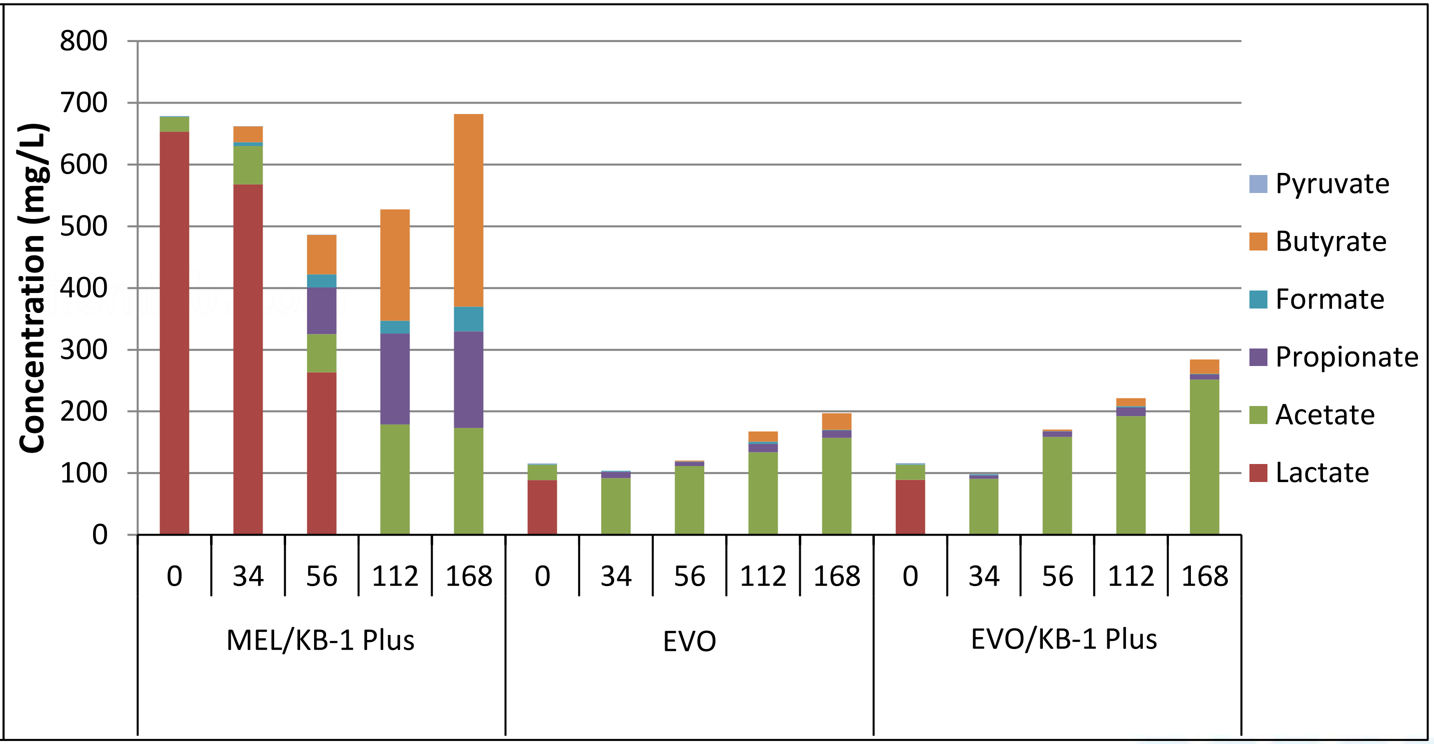


Case Study: Biotreatability East Coast Site



Case Study: Biotreatability East Coast Site





SiREM

Case Study: Bioaugmentation, California Site

EVO (EDS-ER™) & soluble donor

Chlorinated ethenes

- TCE
- PCE
- DCE
- VC

SiREM

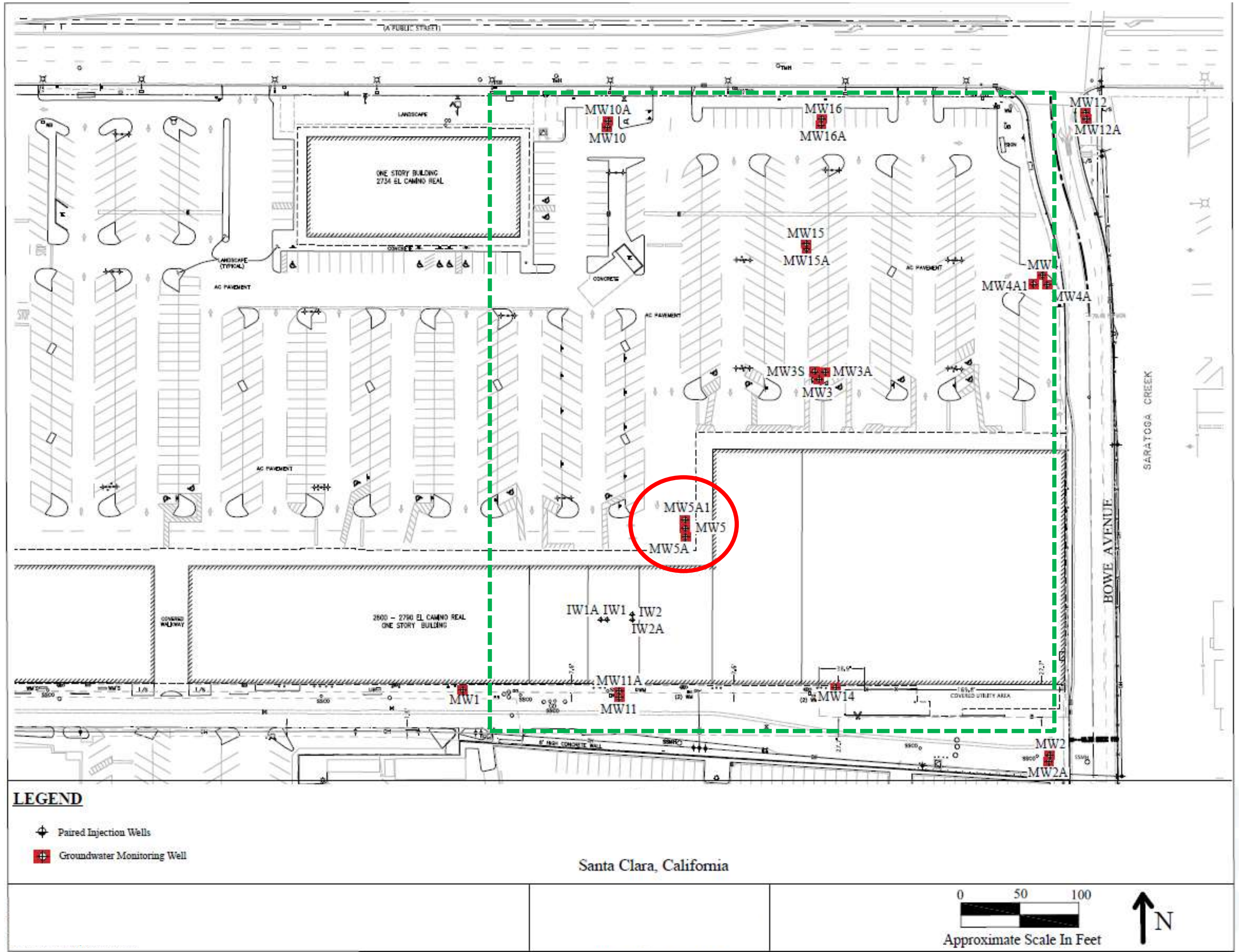
KB-1®

KB-1®
PRIMER

Case Study: Bioaugmentation, California Site

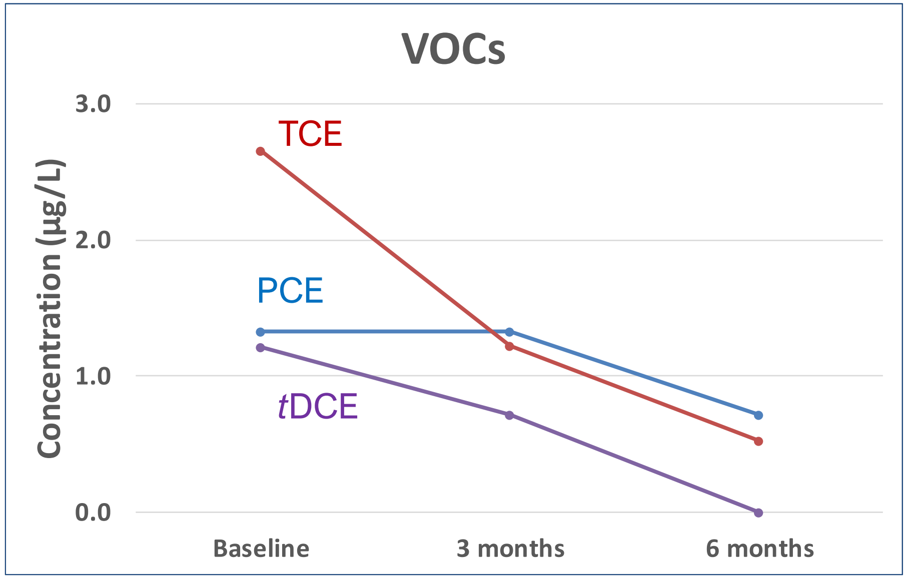
140 Injection Points Total

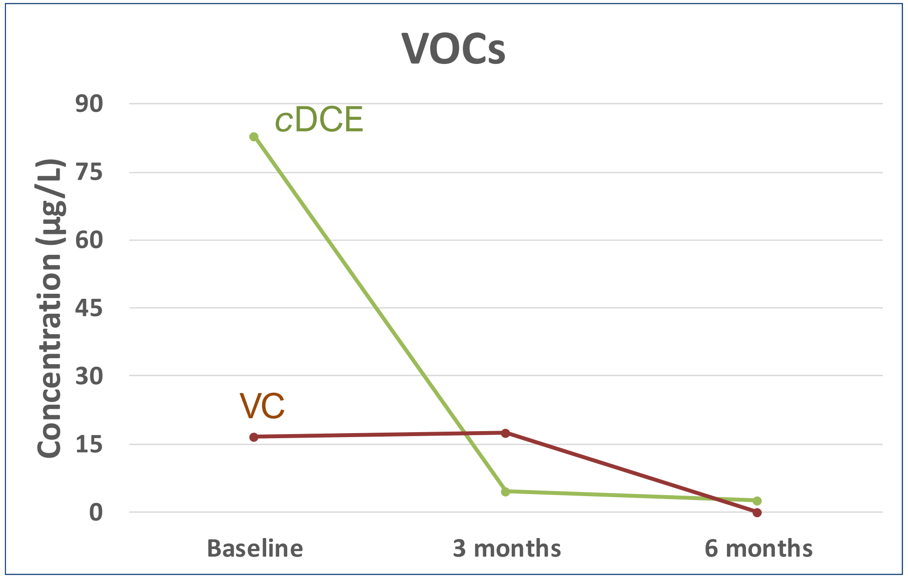
- Quarterly Monitoring

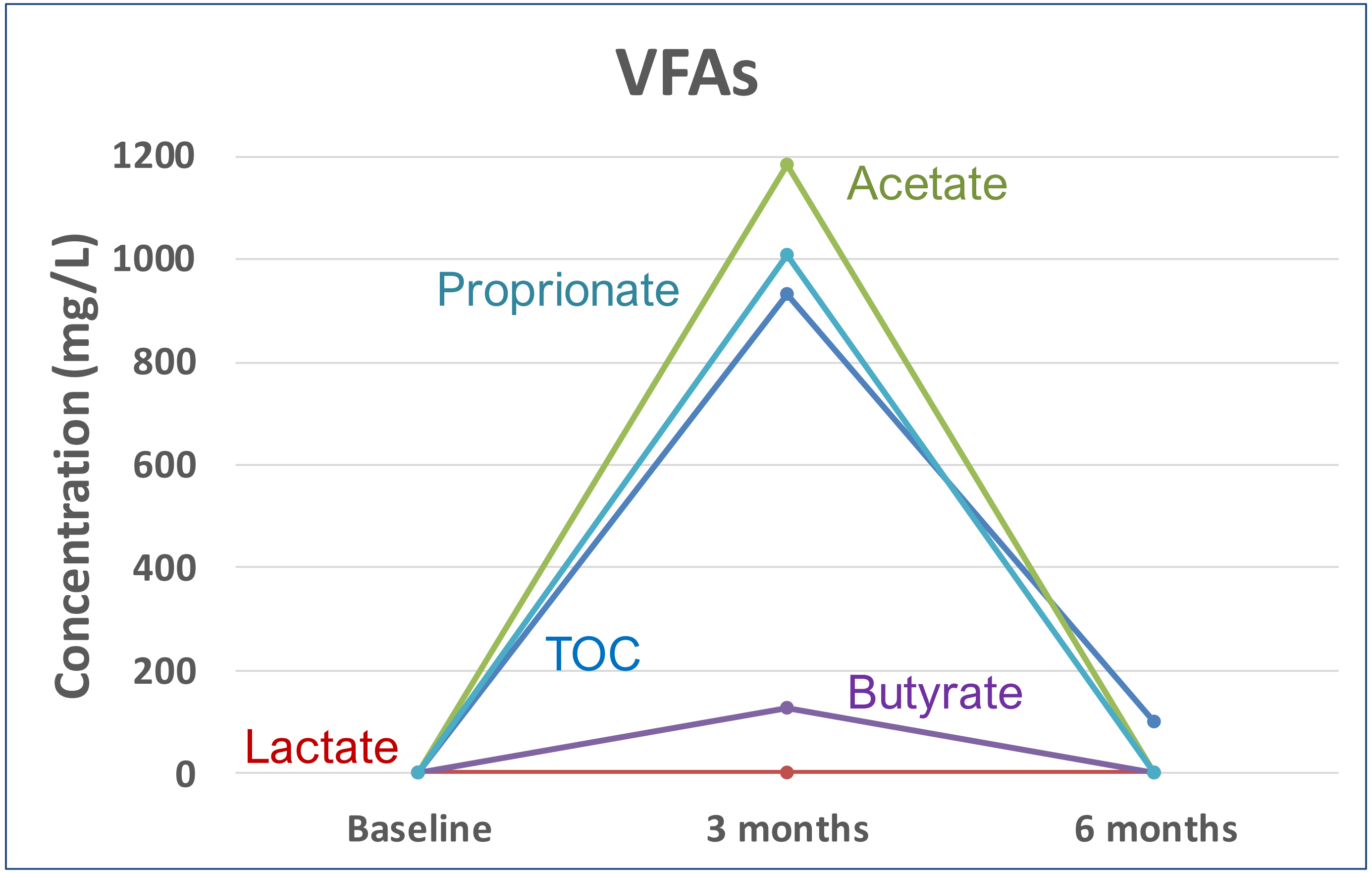


SiREM

Case Study: Bioaugmentation, California Site







Formate & Pyruvate N.D

Summary

Performance Monitoring

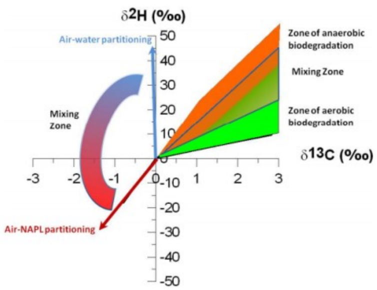
- Treatment Optimization
- Understanding redox conditions
- Monitor progress (microbial polulation growth, electron donor utilization, contaminate conversion).
- Data Driven Decisions

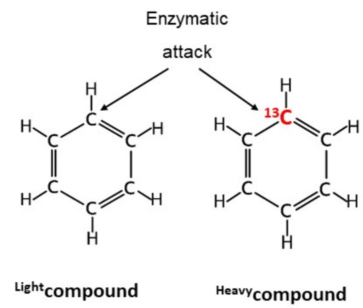
Affordable analyses provide valuable data for monitoring, managing and optimizing bioremediation systems

analytical testing

SiREM

Remediation Performance Monitoring Using CSIA for Chlorinated Solvents

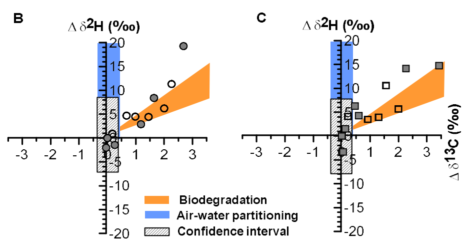


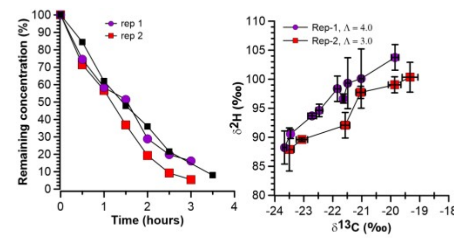


Daniel Bouchard, PhD

Project Scientist

Contamisotopes





Performance Monitoring to Assess Remediation Effectiveness

March 18th,2021

SiREM Leading Science · Lasting Solutions

tersus environmental

Context

Common *in situ* remediation approaches for chlorinated solvent contaminated sites:

i. Bioremediation (enhanced reductive dechlorination or EDR)

ii. ISCO

iii. ISCR (ZVI)

How do we know if treatment is proceeding as intended ?

i. Are the compounds degraded or diluted ?

Contamisotopes

Context

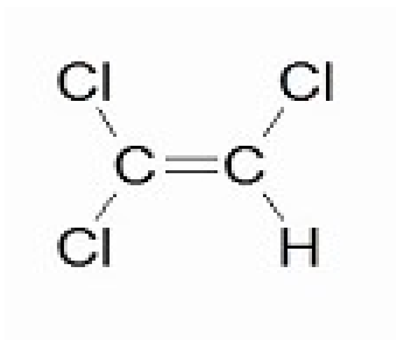
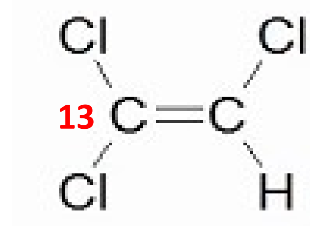
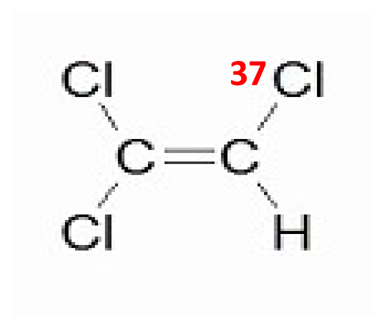
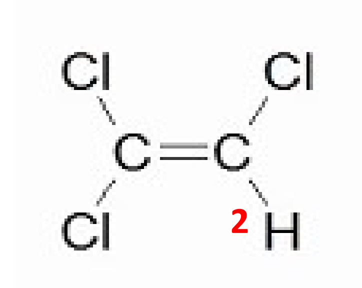
What is your monitoring program?

i. Concentration
   a. cVOC
   b. Ethene/ethane/methane
ii. Hydrogeochemical parameters:
   a. DO, ORP, pH
   b. NO_3, Iron, SO_4, H_2S
iii. Microbial population
   a. Change over time
   b. Right population present
iv. Are the compounds of concern degraded ?
   a. Compound-specific isotope analysis (CSIA)

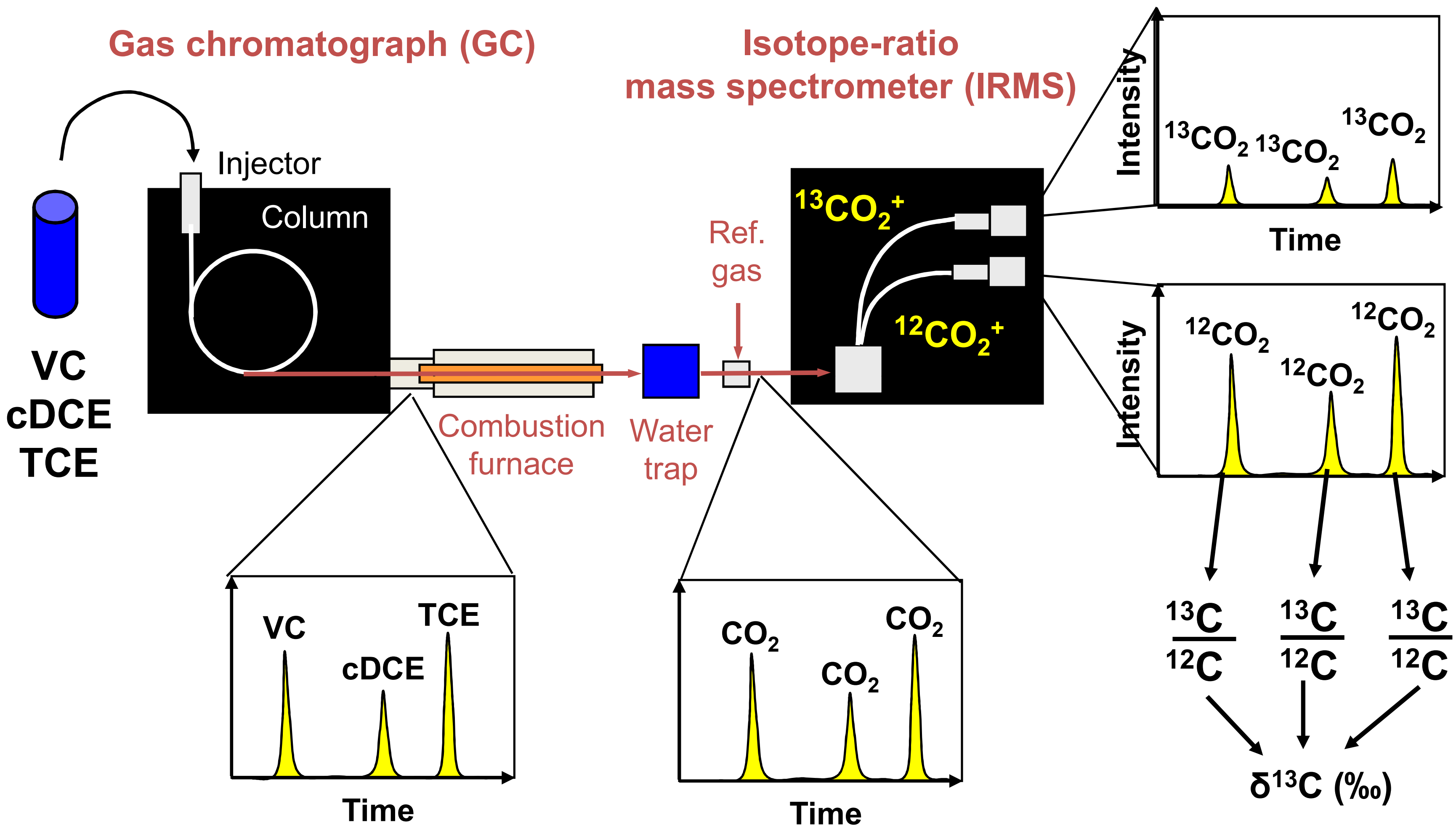
ContamIsotopes

CSIA: principles

TCE

Only light atoms (^{12}C, ^{35}Cl, ^{1}H)		Include 1 heavy atoms (^{13}C, ^{37}Cl, ^{2}H)
	≠	  

CSIA principles

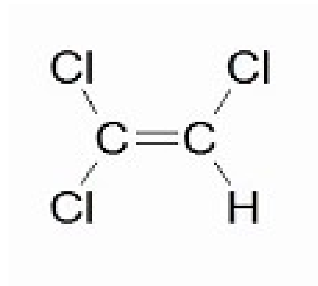


$$\delta^{13}C\ (‰) = \frac{{}^{13}C/{}^{12}C_{sample} - {}^{13}C/{}^{12}C_{standard}}{{}^{13}C/{}^{12}C_{standard}} \times 1000$$

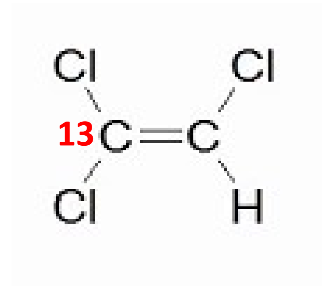
CSIA: principles

Implication of heavy isotopes

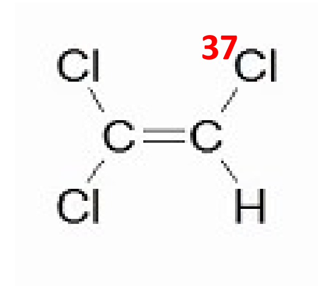
^{light}TCE



^{heavy}TCE



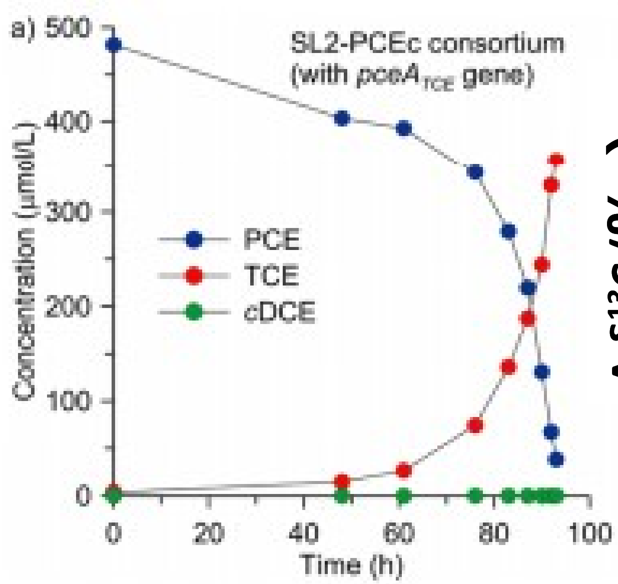
^{heavy}TCE

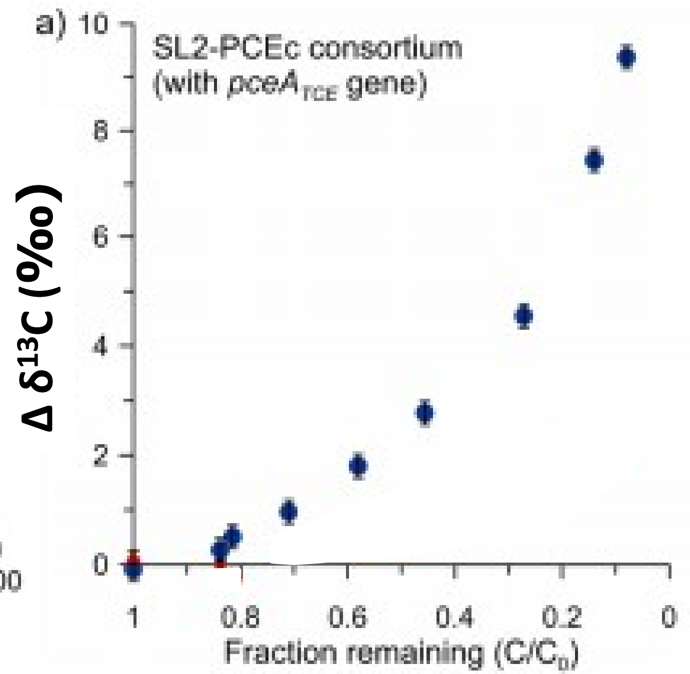


Biodegradation rate	normal	slower	slower
Chemical oxidation rate	normal	slower	slower

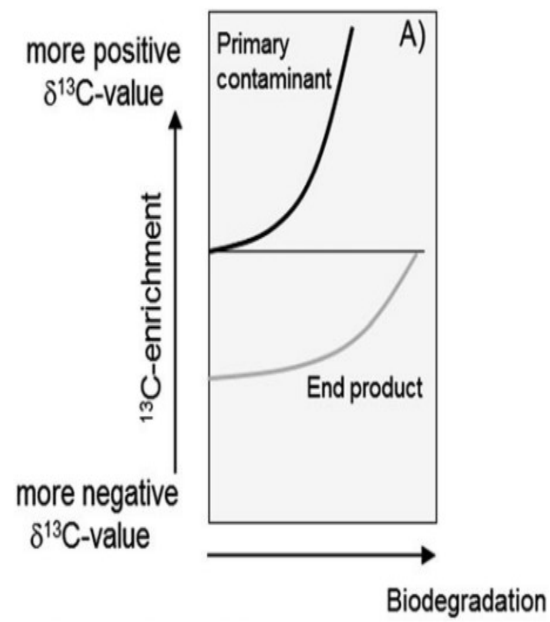
CSIA: principles

Implication of heavy isotopes





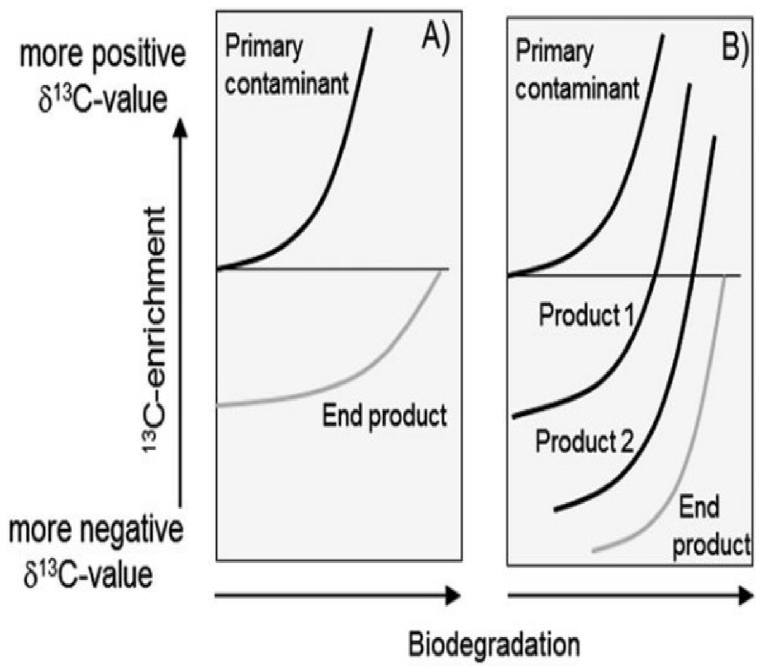
*Badin, et al, ES&T, 48, 9179-9186 ,**2014***



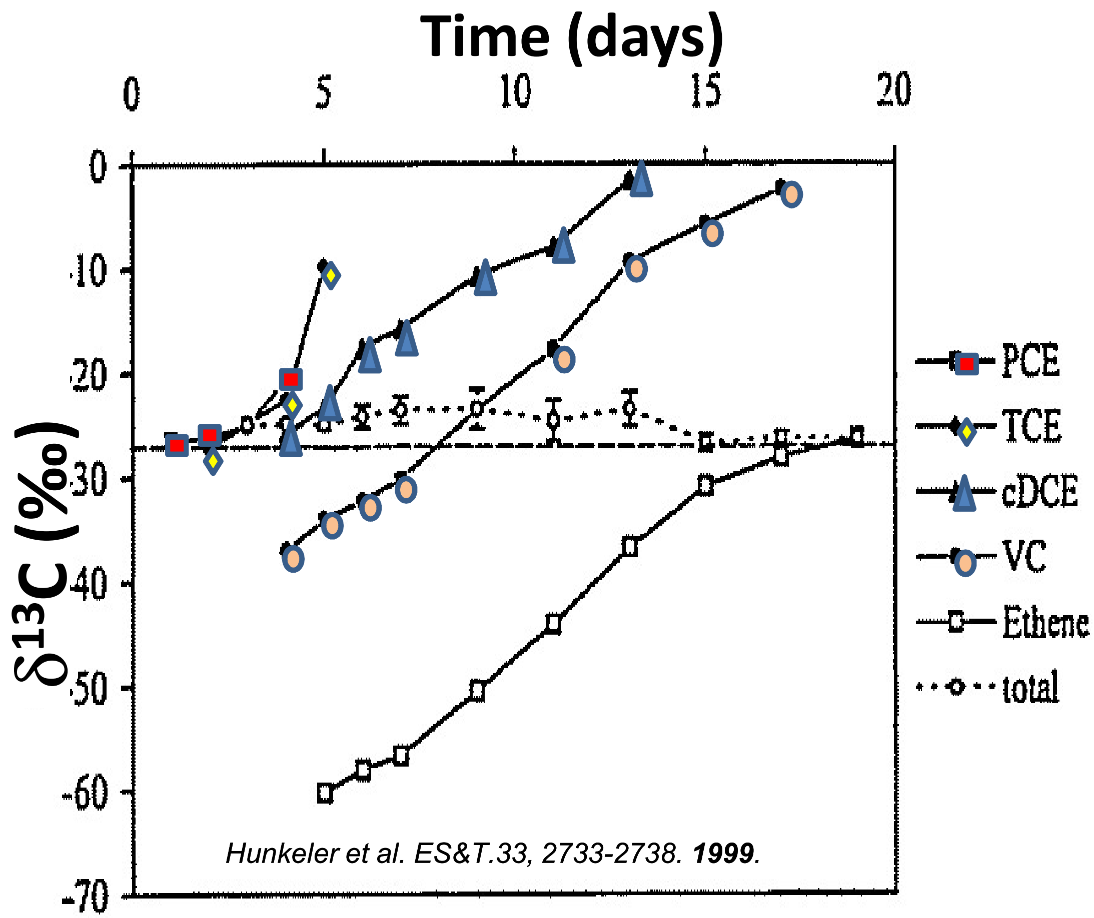
*Kuntze, et al, Handbook of Hydrocarbon and Lipid Microbiology. Springer. **2019***

CSIA: principles and applications

Isotopic mass balance



Kuntze, et al, Handbook of Hydrocarbon and Lipid Microbiology. Springer. ***2019***



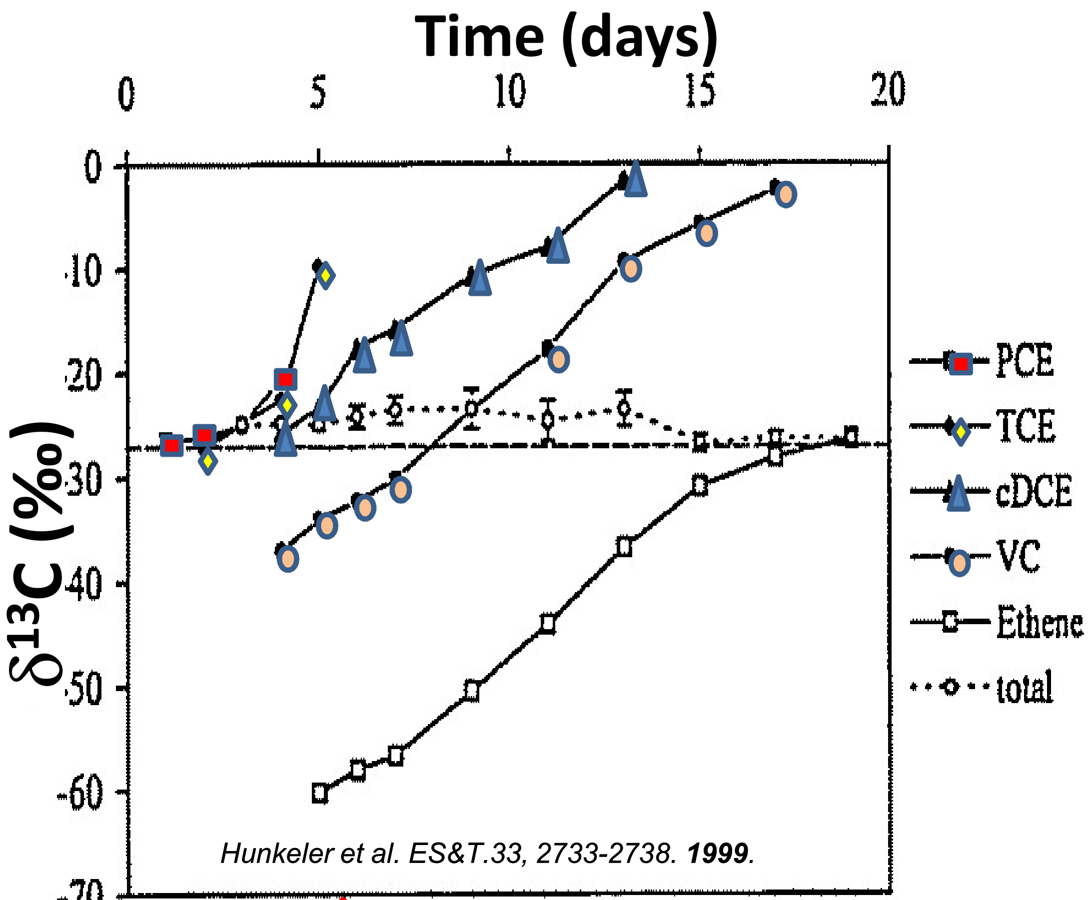
Hunkeler et al. ES&T.33, 2733-2738. ***1999****.*

CSIA: principles and applications

Isotopic mass balance

Initial :
PCE = -28 ‰

Final:
ethene = -28 ‰

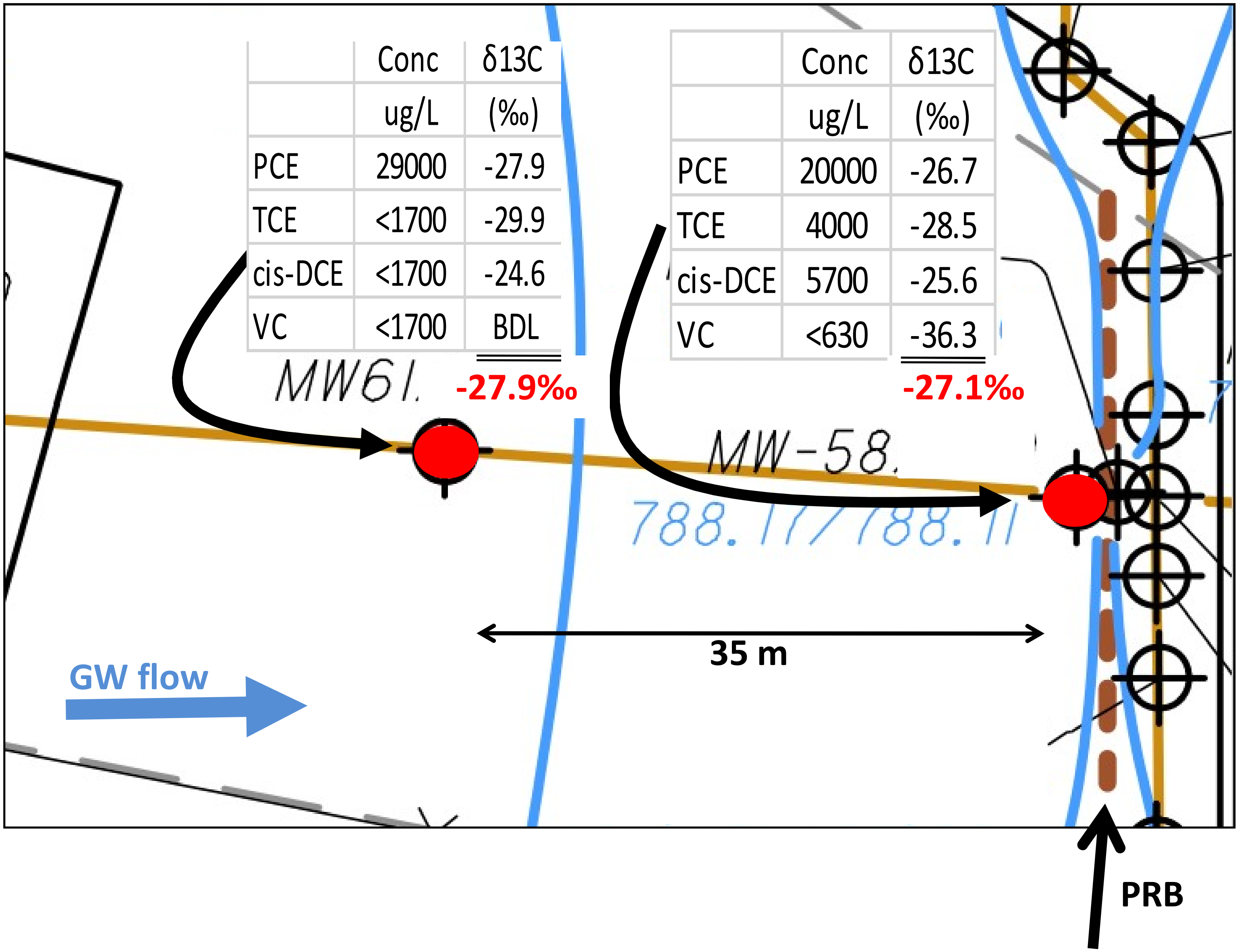


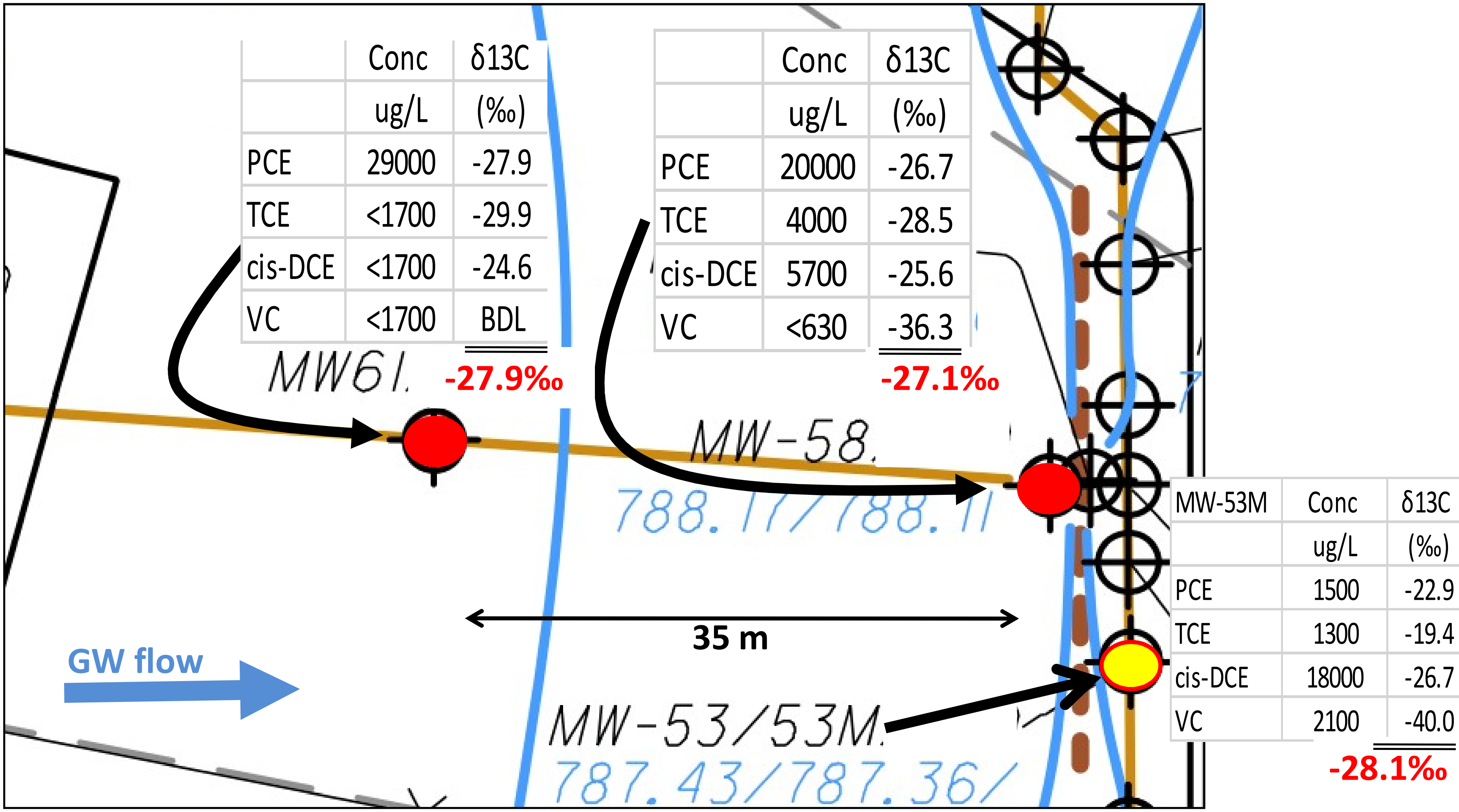
$$\delta^{13}C_{sum} = x_{PCE} \cdot \delta^{13}C_{PCE} + x_{TCE} \cdot \delta^{13}C_{TCE} + x_{DCE} \cdot \delta^{13}C_{DCE} + x_{VC} \cdot \delta^{13}C_{VC}$$

CSIA: principles and applications

Field application -

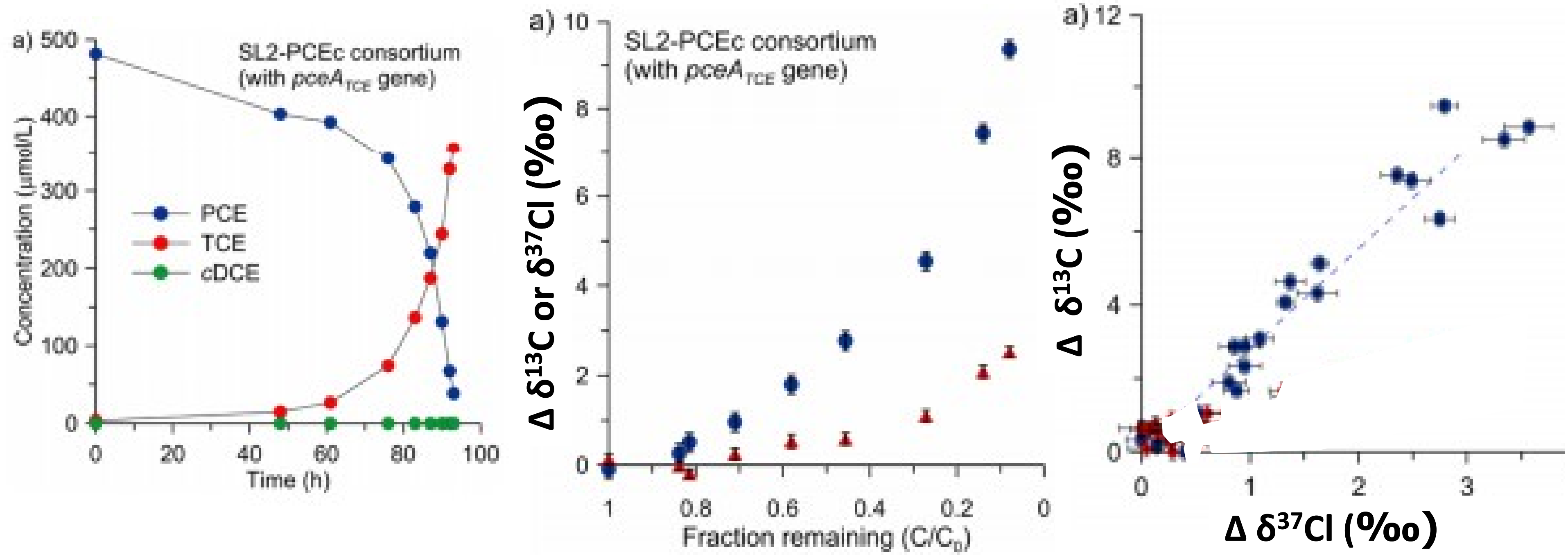
1. Bioremediation (source)
   i. Enhanced reductive dechlorination
2. Permeable reactive barrier (downgradient)
   i. ZVI


Conc ug/L | δ13C (‰)
PCE 29000 -27.9
TCE <1700 -29.9
cis-DCE <1700 -24.6
VC <1700 BDL
-27.9‰
MW61.
Conc ug/L | δ13C (‰)
PCE 20000 -26.7
TCE 4000 -28.5
cis-DCE 5700 -25.6
VC <630 -36.3
-27.1‰
MW-58.
788.17/788.11
35 m
GW flow
PRB


Conc ug/L | δ13C (‰)
PCE 29000 -27.9
TCE <1700 -29.9
cis-DCE <1700 -24.6
VC <1700 BDL
MW61
-27.9‰
Conc ug/L | δ13C (‰)
PCE 20000 -26.7
TCE 4000 -28.5
cis-DCE 5700 -25.6
VC <630 -36.3
-27.1‰
MW-58
788.17/788.11
MW-53M Conc ug/L | δ13C (‰)
PCE 1500 -22.9
TCE 1300 -19.4
cis-DCE 18000 -26.7
VC 2100 -40.0
-28.1‰
35 m
GW flow
MW-53/53M
787.43/787.36/

CSIA: principles and applications

Dual isotope plot ($\delta^{13}C$ vs $\delta^{37}Cl$)



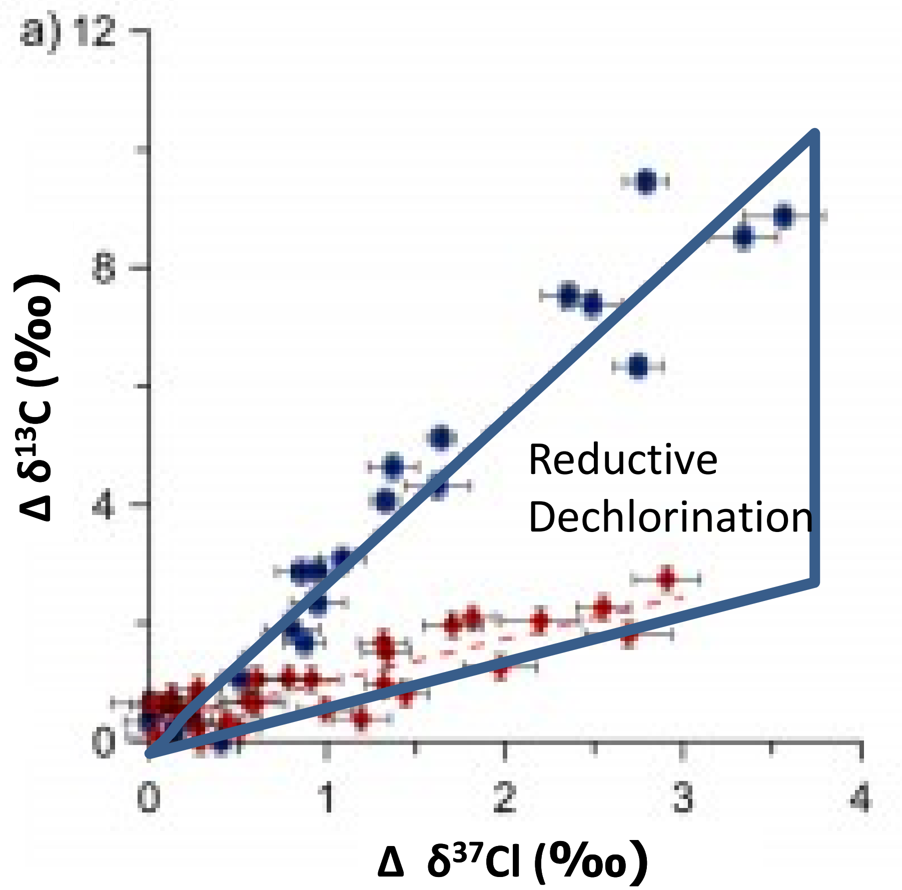
*Badin, et al, ES&T, 48, 9179-9186 ,**2014***

CSIA: principles and applications

Dual isotope plot ($\delta^{13}C$ vs $\delta^{37}Cl$)

- Pathway specific (graph)
- Process specific
- Distinguish 2 co-occurring processes
- For PCE
  - -Missing values for **$\delta^{37}Cl$** (ZVI, ISCO)

- PCE

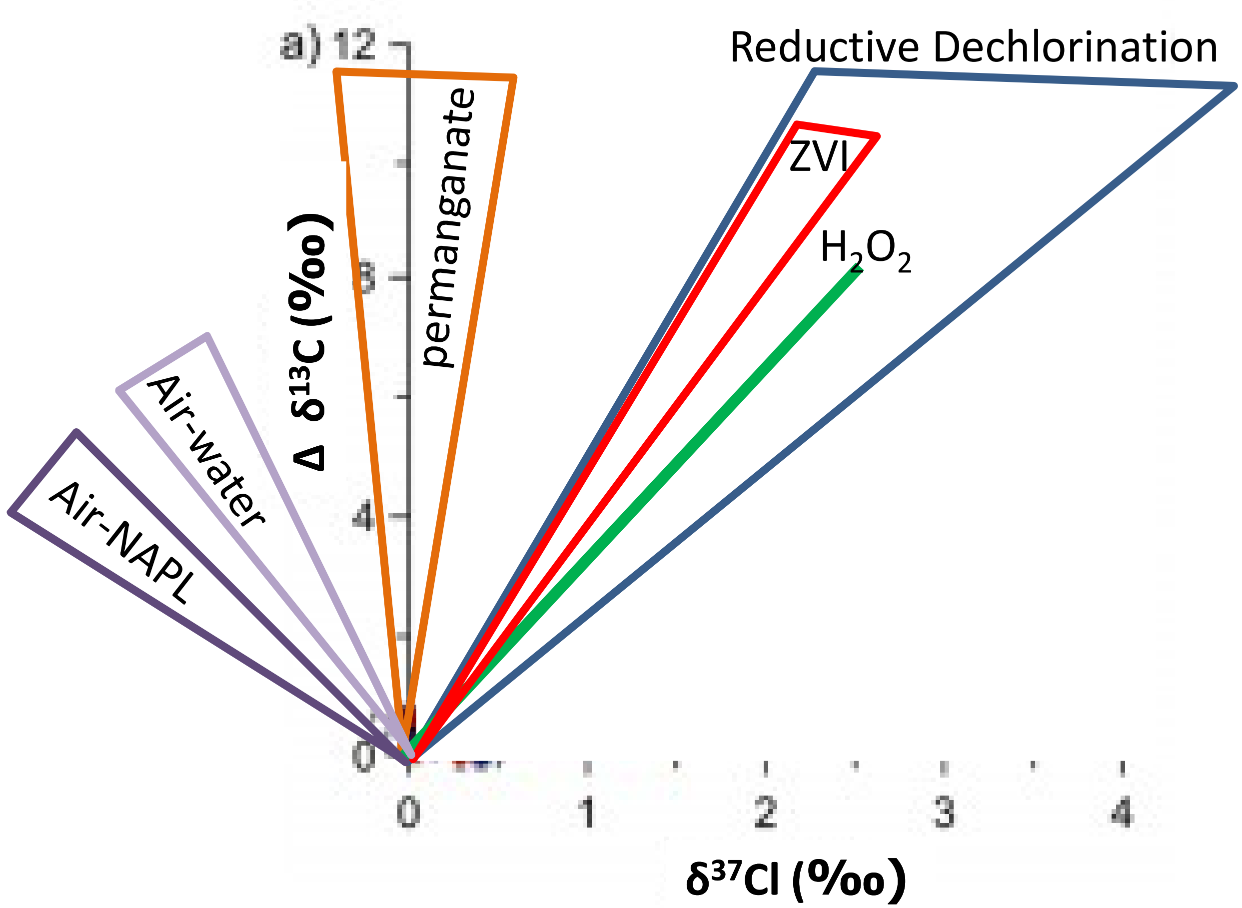


CSIA: principles and applications

Dual isotope plot ($\delta^{13}C$ vs $\delta^{37}Cl$)

- Process specific
- Distinguish 2 co-occurring processes
- For TCE
  - more complete
  - Overlapping $\delta^{13}C$ / $\delta^{37}Cl$ patterns

- TCE



Field deployment

Sampling procedures

i. Groundwater Sampling
   - Similar field procedure as for VOC concentrations
   - Additional 40 ml vials
   - Preservative, shipping and storage conditions
   - Detection limits (PCE-TCE-DCE-VC)
     - For $\delta^{13}C$: 5-15 ug/L
     - For $\delta^{37}Cl$: 5-15 ug/L

Summary & conclusion

CSIA application possibilities

i. Using **1** isotope :
  - destruction versus dilution (ERD, ISCO, ZVI)
  - DCE or VC stall
  - PCE-TCE-DCE-VC → validate VC destruction (by isotopic balance)

ii. Using **2** isotopes :
  i. to target a specific mass removal process among co-occurring mass removal processes
  - Limited data set (especially for PCE and DCE)
  - Overlapping isotope enrichment patterns (TCE)
  - Degradation (bio or ZVI) vs Chemical oxidation (permanganate)
  - Degradation Vs physical removal (SVE in vadoze, thermal remediation)

To be included in a multi-line of evidence approach

Contamisotopes

Summary & conclusion

To document treatment efficiency

i. Pilot scale
   i. Proof of concept
   ii. Identify potential treatment limitations

ii. Full scale
   i. Monitor the progress
   ii. Support decision to pursuit, to optimize the treatment
   iii. Provide evidences of treatment success / limitations

Thank you !

Daniel Bouchard, PhD
Contam-i-sotopes@outlook.com
Contam i sotopes

Performance Monitoring to Assess Remediation Effectiveness
March 18th,2021

tersus environmental

Contam i sotopes