

Design Considerations for Enhanced Reductive Dechlorination

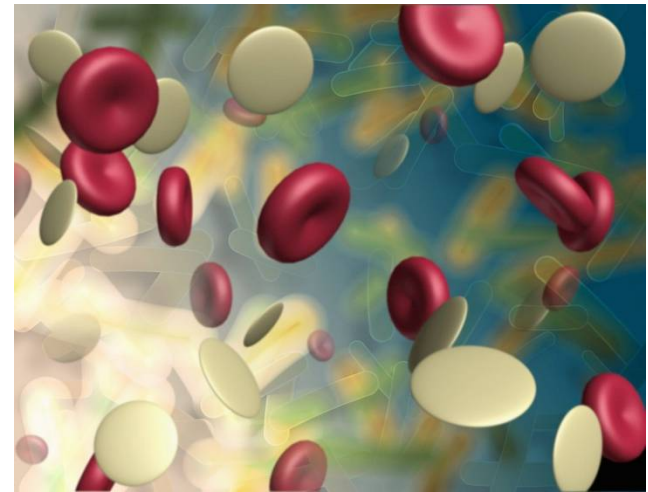
Dan Leigh PG, CHg

Webinar May 13, 2015

Presentation Outline

Introduction Dan Leigh P.G., C. Hg. – Peroxychem Environmental Solutions

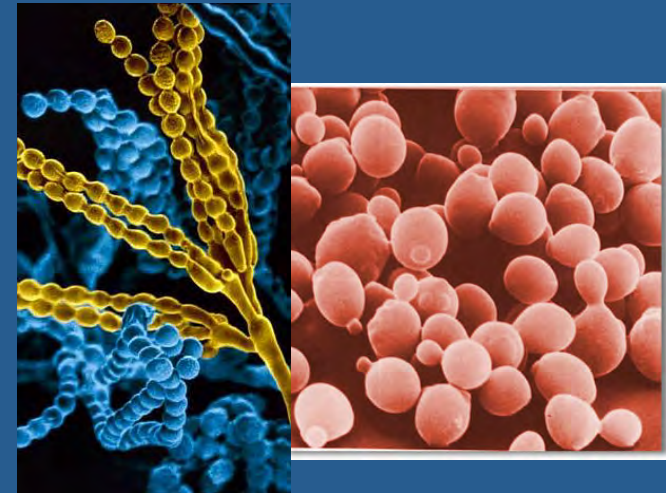
- **Basic concepts of biological and geochemical processes**
 - Respiration, fermentation, co metabolism
 - Electron acceptors and donors
 - Biotic and abiotic anaerobic degradation pathways of chlorinated ethenes
 - Enhancing aerobic and anaerobic bioremediation
 - Calculating substrate requirements
- **Site conditions considered not conducive to anaerobic bioremediation**
 - Inappropriate or insufficient bacteria
 - High dissolved oxygen
 - Low/High pH
 - High sulfate concentrations
- **Biogeochemical degradation**
 - Using high sulfate groundwater
- **In Situ Chemical Reduction (ISCR)**
 - ISCR-ERD Field Comparison



Bioremediation

Bioremediation can be defined as any process that uses microorganisms, fungi, green plants or their enzymes to return the natural environment altered by contaminants to its original condition.

- Natural, sustainable process
- Accomplished by naturally occurring organisms
- Uses organisms life process to degrade contaminants.
- Modifies environment to create conditions conducive to degradation of contaminants
- Can occur automatically (intrinsic bioremediation) or can be stimulated (enhanced bioremediation)



Basic concepts of biological, biogeochemical and chemical reduction processes

- Several biological processes occur during anaerobic bioremediation including:
 - Respiration: Aerobic and Anaerobic
 - Fermentation
 - Co-metabolism
- Respiration, the primary process applied for anaerobic bioremediation, requires the presence of inorganic electron donors and acceptors.
- Chemical reduction does not require biological processes (abiotic)
- Biotic and abiotic reductive degradation processes occur in distinct identifiable pathways.

Biologically Mediated Oxidation - Reduction

Negative

Positive

Biologically Mediated Oxidation - Reduction

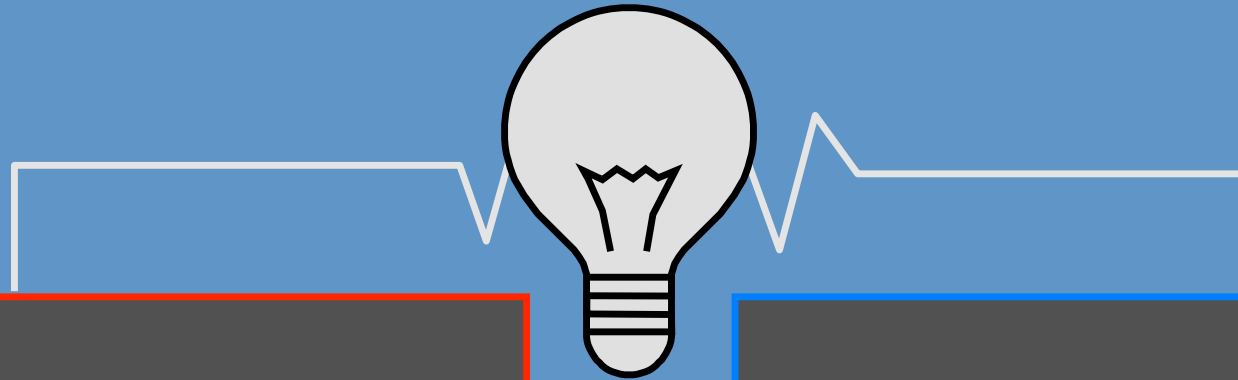


Negative

Positive

Resistor

Biologically Mediated Oxidation - Reduction



Negative

Positive

Biologically Mediated Oxidation - Reduction



Negative

Positive

e^-

e^-

e^-

e^-

e^-

e^-

e^-

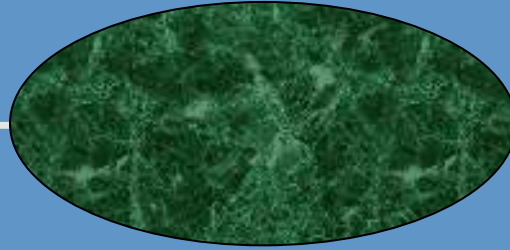
Biologically Mediated Oxidation - Reduction



Negative

Positive

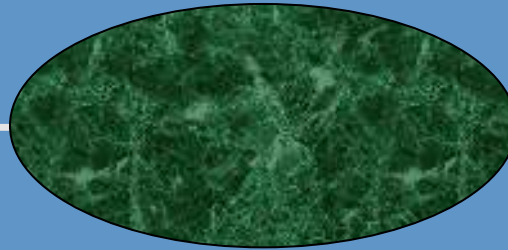
Biologically Mediated Oxidation - Reduction



Negative

Positive

Biologically Mediated Oxidation - Reduction



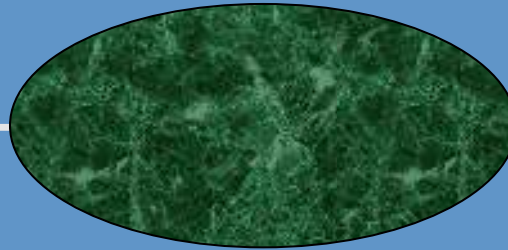
Electron Donor

Reduced



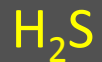
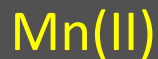
Electron Acceptor

Biologically Mediated Oxidation - Reduction



Electron Donor

Reduced

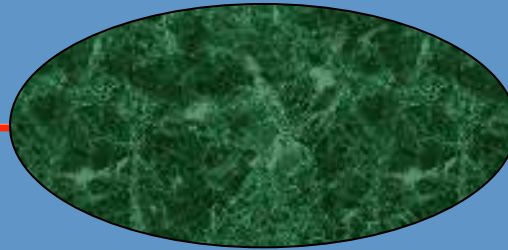


Electron Acceptor

Oxidized



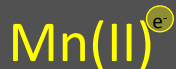
Biologically Mediated Oxidation - Reduction



Electron Donor

Reduced

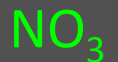
Oxidized



Electron Acceptor

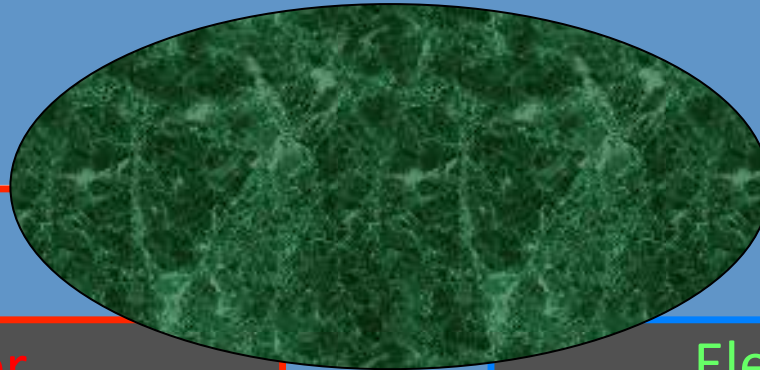
Reduced

Oxidized



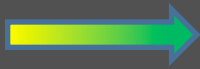
Biologically Mediated Oxidation - Reduction

Growth
Protein Synthesis
Reproduction

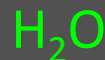
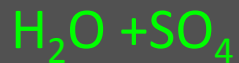
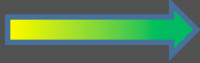
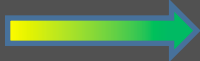
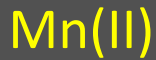
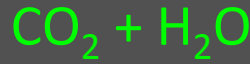


Electron Donor

Reduced



Oxidized

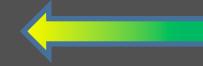
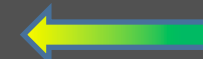
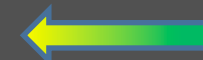
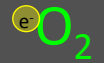


Electron Acceptor

Reduced



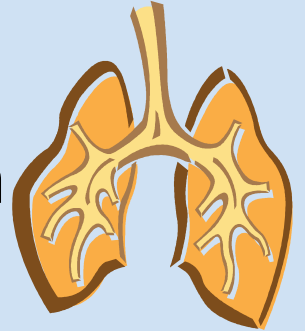
Oxidized



Aerobic and Anaerobic Respiration

- Aerobic respiration

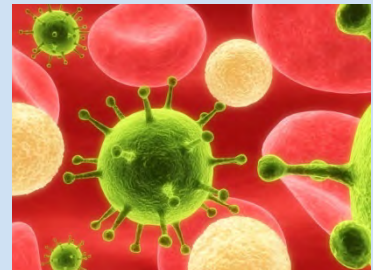
- Molecular oxygen (O_2) is the only electron acceptor used in the process



- Anaerobic respiration

- Any inorganic electron acceptor (other than oxygen) is used in the respiration process

- NO_3 , $Mn(IV)$, $As(V)$, $Fe(III)$, SO_4 , CO_2
- $Cr(VI)$, ClO_4



Many organisms generate energy by fermentation rather than respiration

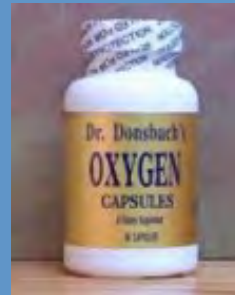
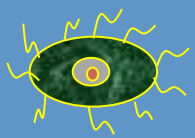
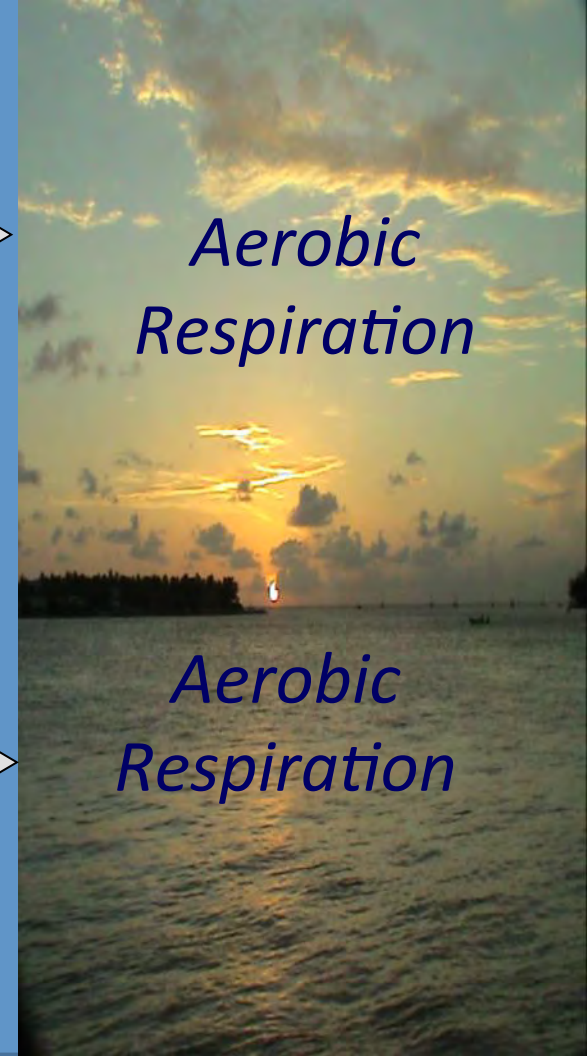
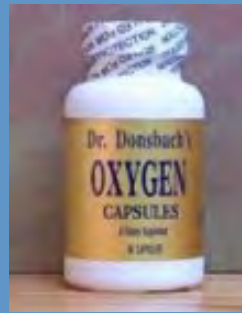
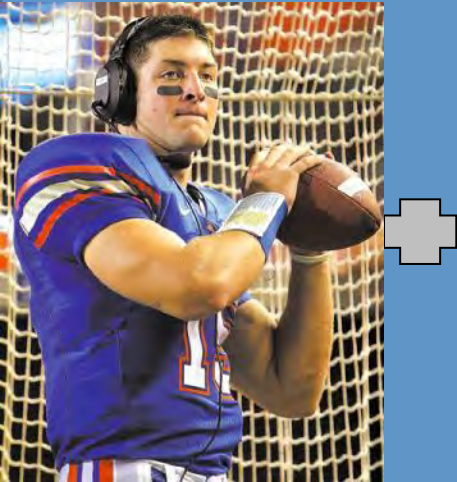
- Fermentation refers to the conversion of sugar to acids, gases and/or alcohol using yeast or bacteria.
- Fermentation does not use an inorganic electron transport chain (e.g. O_2 , NO_3 , $Mn(IV)$, SO_4 , CO_2) as does respiration.
- Fermentation uses a reduced carbon source (e.g. cellulose, lecithin, lactose, sugars).
 - to generate volatile fatty acids (VFAs e.g. lactic, acetic, propionic, valeric, butyric acids)
 - and gases (e.g. H_2 , CO_2 , CH_4)
- H_2 is used by dechlorinating bacteria to degrade chlorinated organics by chlororespiration.



Aerobic Respiration Process

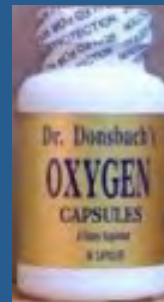
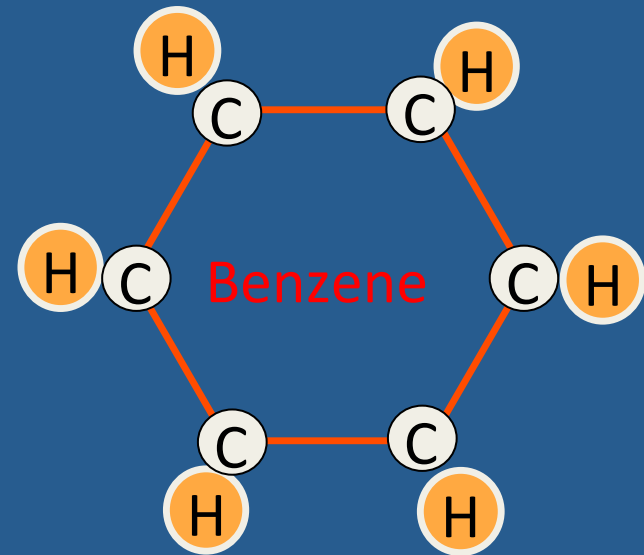
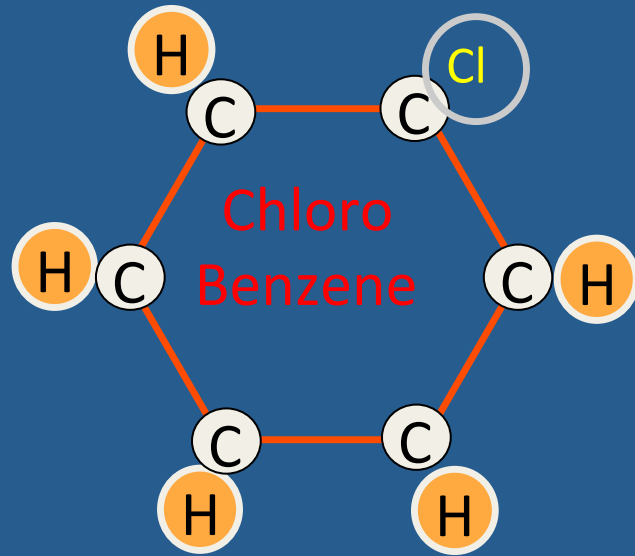


Eat & Breathe



Aerobic Respiration

Direct Oxidation – Aerobic Biodegradation of Benzene and Chlorobenzene

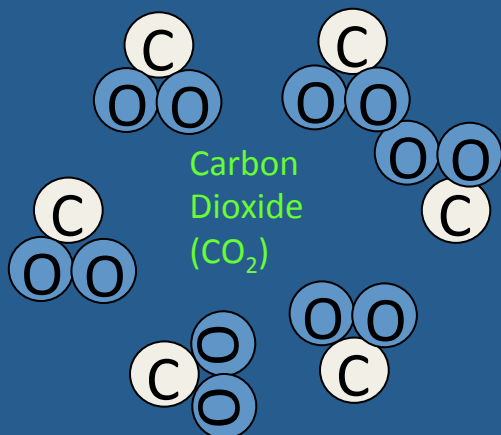


Direct Oxidation – Aerobic Biodegradation of Benzene and Chlorobenzene

HCl



Water (H₂O)

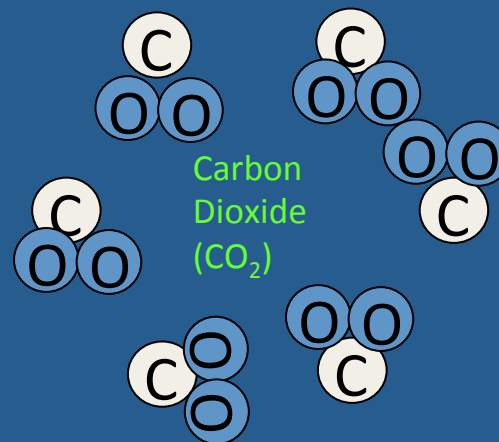


Carbon
Dioxide
(CO₂)

Water (H₂O)



Water (H₂O)



Carbon
Dioxide
(CO₂)

Water (H₂O)



Water (H₂O)

Anaerobic and aerobic respiration are similar

Biota



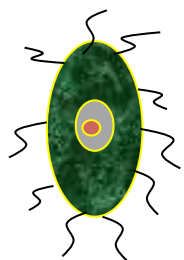
Electron Donor



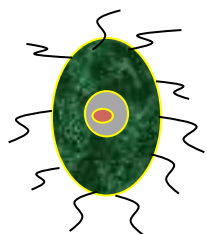
Electron Acceptor



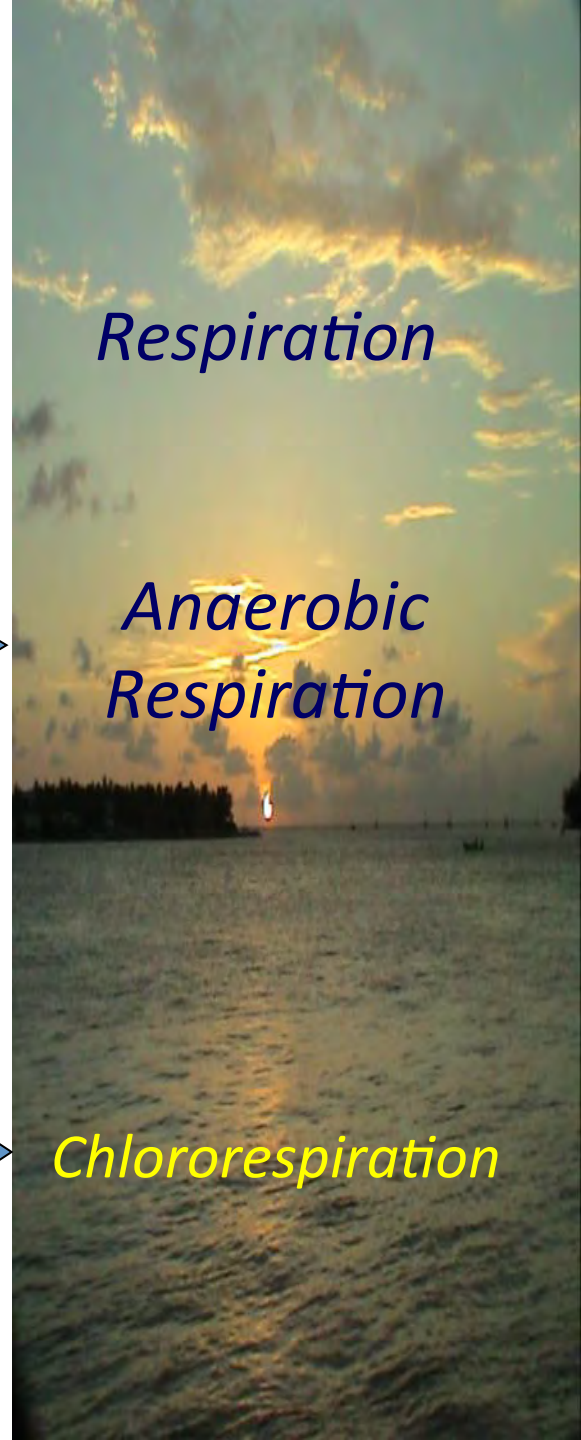
Respiration



Anaerobic Respiration



Chlororespiration



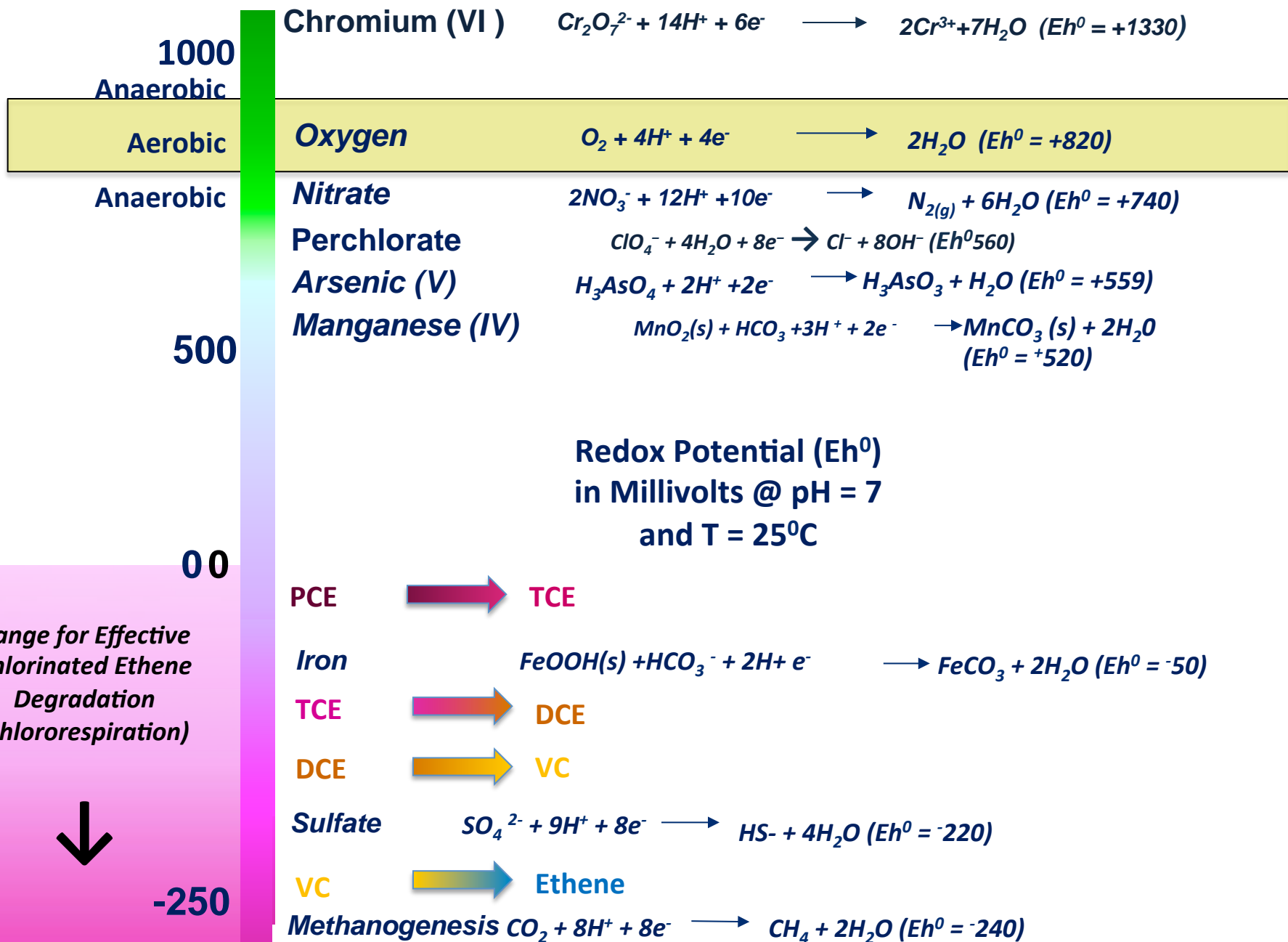
Contaminants that can be degraded by anaerobic processes

- **Chlorinated solvents** such as PCE, TCE, TCA, DCA, CCl_4 , chloroform and methylene chloride
- **Chlorobenzenes** including di- and tri-chlorobenzene
- **Energetic compounds** such as TNT, DNT, HMX, RDX, nitroglycerine and perchlorate.
- Most **pesticides** including DDT, DDE, dieldrin, 2,4-D and 2,4,5-T
- **Nitrate** compounds
- Petroleum hydrocarbons

This presentation focuses on biological and geochemical processes that occur during the anaerobic degradation of chlorinated ethenes (CEs).

Eh range for Chlorinated Ethene Degradation

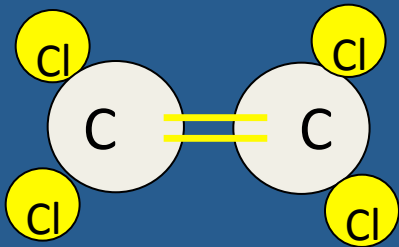
Decreasing Amount of Energy Released During Electron Transfer



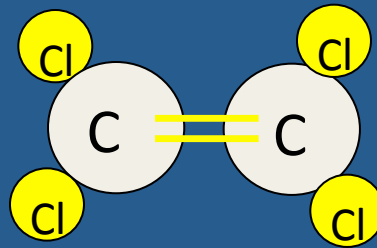
Biological Reductive Dechlorination of Chlorinated Ethenes

ORP

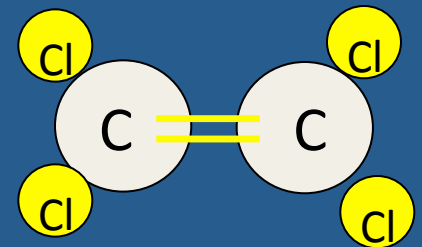
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PCE



PCE



PCE

Biological Reductive Dechlorination of Chlorinated Ethenes

ORP

0

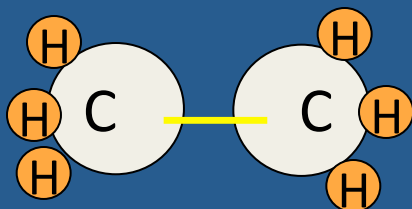
-50

-150

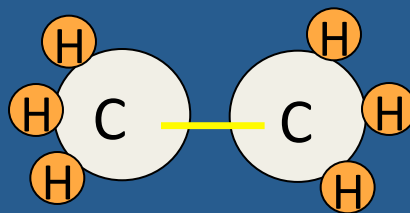
-200

-250

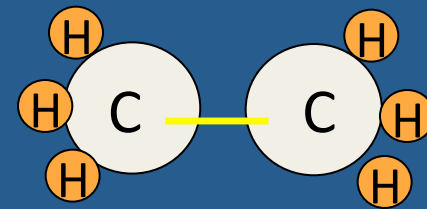
-300



Ethane



Ethane

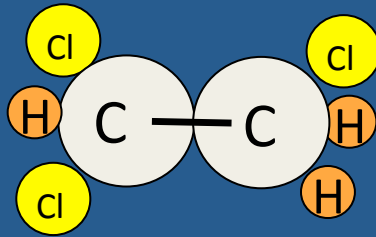


Ethane

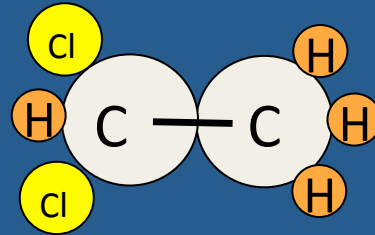
Dichloroelimination of Chlorinated Ethanes

ORP

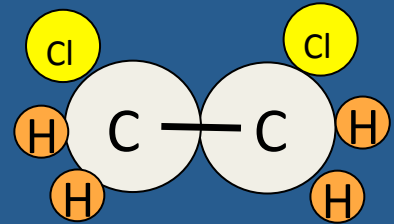
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1,1,2-TCA

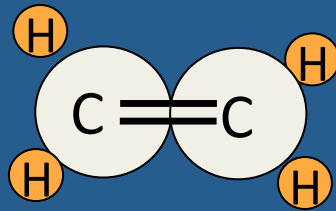
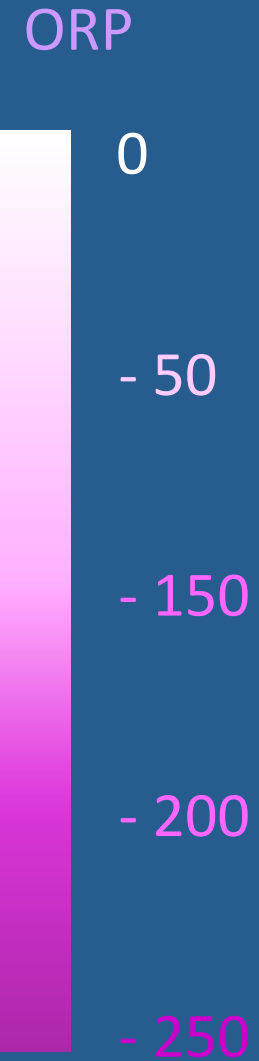


1,1-DCA

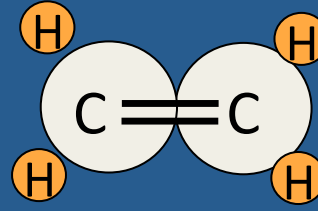


1,2-DCA

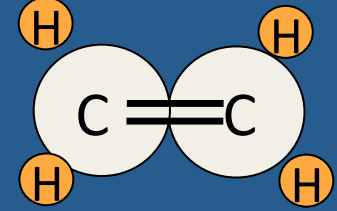
Dichloroelimination of Chlorinated Ethanes



Ethene

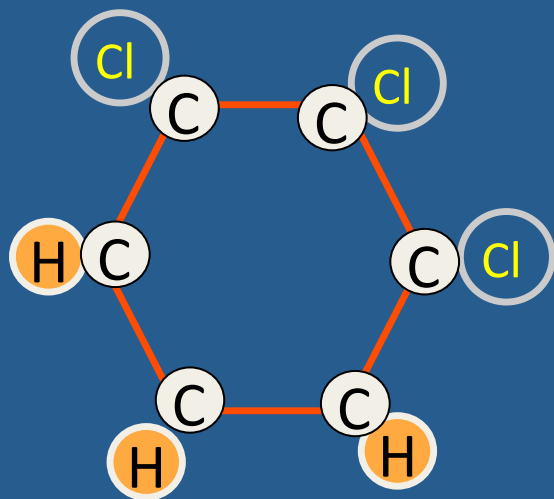


Ethene

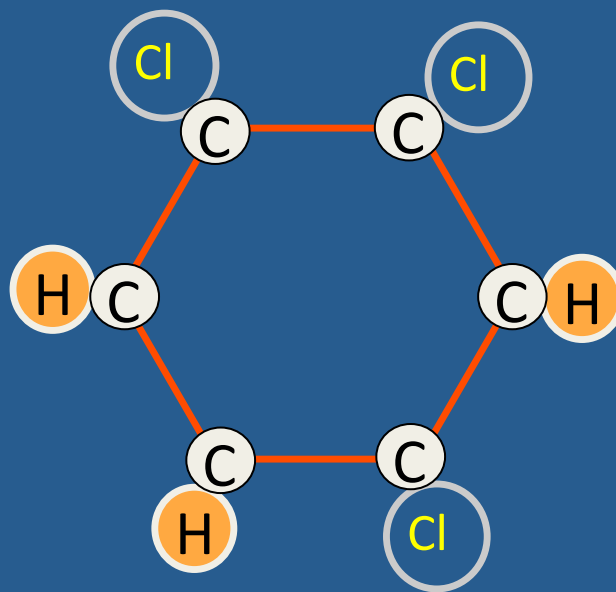


Ethene

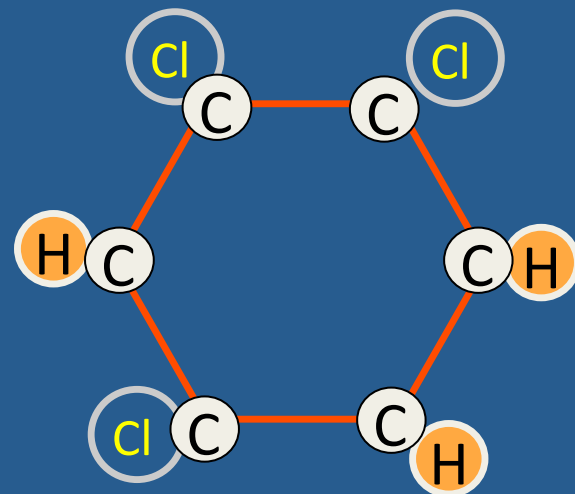
Reductive Dechlorination of Chlorinated Benzenes



1,2,3-TCB

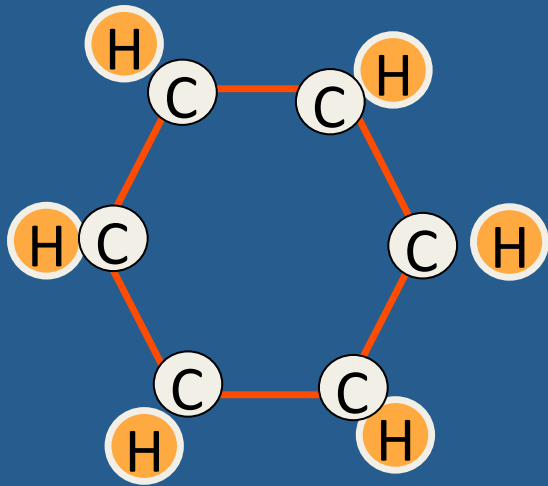


1,2,4-TCB

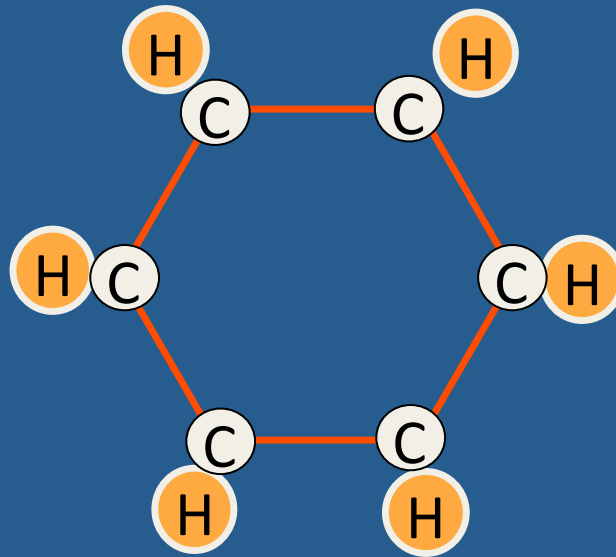


1,2,5-TCB

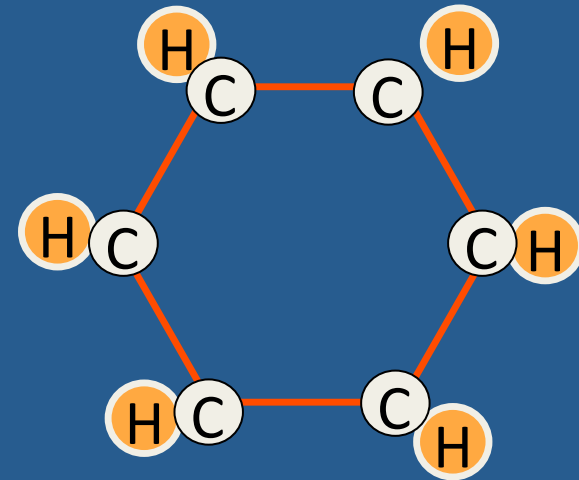
Reductive Dechlorination of Chlorinated Benzenes



Benzene



Benzene



Benzene

Co-metabolic oxidation

The microbial breakdown of a contaminant in which the contaminant is oxidized incidentally by an enzyme or cofactor that is produced during microbial metabolism of another compound is called aerobic/anaerobic co-metabolism.

- Co-metabolic degradation applies respiration processes:
 - Electron donor: (e.g., methane, ethane, ethene, propane, butane, toluene, phenol, ammonia)
PLUS: electron acceptor (e.g., O_2 , SO_4)
- Enzymes generated to degrade food source also degrades CEs and other contaminants.
- The degrading organism does not gain energy during the process.
- The presence of electron donor may inhibit contaminant degradation.

Co-metabolism can be a challenge to apply.

- Often requires substantial engineering effort
- It is difficult to identify co-metabolic degradation in the aquifer
- May not be an efficient use of substrate

Enhancing Bioremediation Processes

Bioremediation process is conducted by providing what is limiting the complete degradation process.

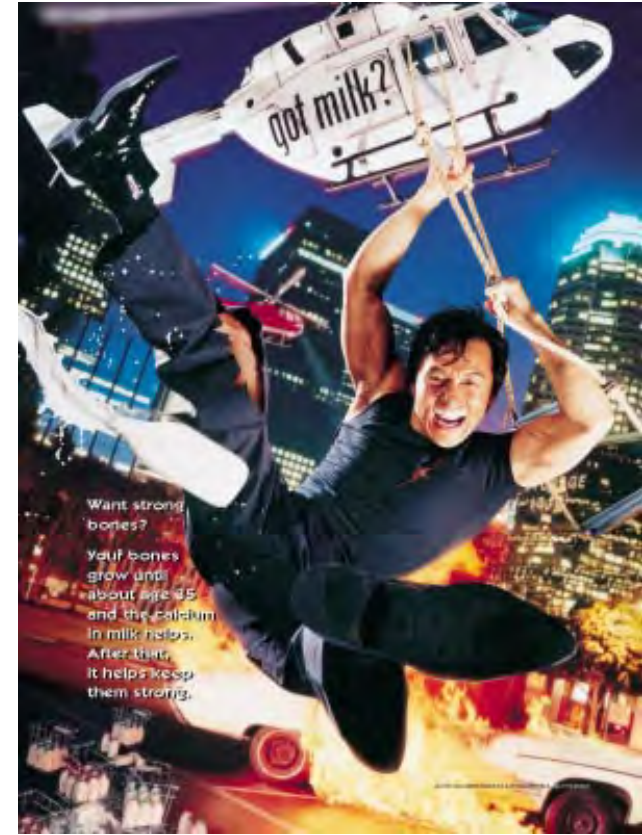
- Electron acceptor (e.g., oxygen, nitrate, ferric, sulfate) or
- Electron donor (e.g., molecular hydrogen (H₂), organics)
- Bacteria

Additional supplements can be made to enhance synergistic effects.

- Sulfate
- Iron

Other supplements can be made to further enhance the anaerobic process.

- Chemical reductants (e.g., ZVI, ferrous iron)
- Nutrients (N, P, K, Micronutrients, buffers)



Electron donors for H₂ production

Molasses	Acetic acid and its salts
Starch	Lactic acid and its salts
Cheese whey	Propionic acid and its salts
Emulsified vegetable oil	Citric acid and its salts
Corn syrup	Various Bean Oils (soy, guar)
Lactose	Benzoic acid and its salts
Glucose	Oleic acid and its salts
Ethanol	Polylactate esters of fatty acids (e.g., Glycerol tripolylactate)
Methanol	Food process byproducts including milk whey or yeast extract
Propanol	Complex organic material such as wood chips
Lecithin	Complex sugars
Glycerol, xylitol, sorbitol	
Molecular H ₂	

Only H₂ has been shown to be an electron donor for cis 1,2-DCE and vinyl chloride conversion to ethene

Theoretical H₂ Production by Donor Substrate

Electron Donor	Electron equivalent per mole
acetate	4
propionate	3
lactate	2
fructose/glucose	12
sucrose/lactose	24
linoleic acid	50
glycerol	7
lecithin	122

H₂ demand for select electron acceptors

Electron Acceptor	Electron equivalents per mole
Oxygen	4
Nitrate	4
Sulfate	8
Carbon dioxide	8
Manganese (IV)	2
Ferric iron (III)	1
PCE - tetrachloroethene	8
TCE – trichloroethene	6
DCE – dichloroethene	4
VC – vinyl chloride	2

Electron acceptors can be in solid form

- **Solid electron acceptors occur as:**
 - **oxides**
 - **salts**
 - **minerals**
- **Solid electron acceptors are not accounted for by dissolved phase analysis.**
- **Reduction of sulfate causes disequilibrium resulting in increased metals concentration.**

Some mineral electron acceptors

- **Barite – BaSO_4**
- **Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$**
- **Anhydrite – CaSO_4**
- **Hannebachite – $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$**
- **Anglesite (PbSO_4)**
- **Magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ or Fe_3O_4)**
- **Hematite (Fe_2O_3)**

Reducing/reductive degradation enhancement compounds

Ferrous Chloride

Sodium Dithionite

Ferrous Carbonate

Calcium Polysulfide

Ferrous Gluconate

Zero-Valent Iron

Sorbitol Cysteinate

Granular
Emulsified
Micro-scale

Sodium Sulfide

Nano-scale

How Much Electron Donor Do I Need?

ESTCP ER200627 (20101) Bruce Henry, Parsons

Site Name: **Joint Base Andrews - Site SS26** RETURN TO COVER PAGE

1. Treatment Zone Physical Dimensions

Width (Perpendicular to predominant groundwater flow direction)
 Length (Parallel to predominant groundwater flow)
 Saturated Thickness
 Treatment Zone Cross Sectional Area
 Treatment Zone Volume
 Treatment Zone Total Pore Volume (total volume x total porosity)
 Design Period of Performance

NOTE: Open cells are user input.

Values	Range	Units
175	1-10,000	feet
900	1-1,000	feet
24	1-100	feet
4200	--	ft ²
3,780,000	--	ft ³
8,484,588	--	gallons
4.0	.5 to 5	year

2. Treatment Zone Hydrogeologic Properties

Total Porosity
 Effective Porosity
 Average Aquifer Hydraulic Conductivity
 Average Hydraulic Gradient
 Average Groundwater Seepage Velocity through the Treatment Zone
 Average Groundwater Seepage Velocity through the Treatment Zone
 Average Groundwater Flux through the Treatment Zone
 Soil Bulk Density
 Soil Fraction Organic Carbon (foc)

0.3	.05-50	
0.3	.05-50	
5.08	.01-1000	ft/day
0.006939	0.1-0.0001	ft/ft
0.12	--	ft/day
42.9	--	ft/yr
404,316	--	gallons/year
1.7	1.4-2.0	gm/cm ³
0.0005	0.0001-0.1	

3. Initial Treatment Cell Electron-Acceptor Demand (one total pore volume)

A. Aqueous-Phase Native Electron Acceptors

Oxygen
 Nitrate (denitrification)
 Sulfate
 Carbon Dioxide (estimated as the amount of methane produced)

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
5.0	354.00	7.94	44.58	4
2.0	141.60	12.30	11.51	5
10	708.00	11.91	59.45	8
10.0	708.00	1.99	355.78	8

Soluble Competing Electron Acceptor Demand (lb.) 471.32

B. Solid-Phase Native Electron Acceptors

(Based on manganese and iron produced)
 Manganese (IV) (estimated as the amount of Mn (II) produced)
 Iron (III) (estimated as the amount of Fe (II) produced)

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
1.0	84.30	27.25	3.09	2
1.0	84.30	55.41	1.52	1

Solid-Phase Competing Electron Acceptor Demand (lb.) 4.61

C. Soluble Contaminant Electron Acceptors

Tetrachloroethene (PCE)
 Trichloroethene (TCE)
 Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)
 Vinyl Chloride (VC)
 Carbon Tetrachloride (CT)
 Trichloromethane (or chloroform) (CF)
 Dichloromethane (or methylene chloride) (MC)
 Chloromethane
 Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)
 Trichloroethane (1,1,1-TCA and 1,1,2-TCA)
 Dichloroethane (1,1-DCA and 1,2-DCA)
 Chloroethane
 Perchlorate

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
0.018	1.27	20.57	0.06	8
0.638	45.17	21.73	2.08	6
0.546	38.66	24.05	1.61	4
0.073	5.17	31.00	0.17	2
0.000	0.00	19.08	0.00	8
0.000	0.00	19.74	0.00	6
0.000	0.00	21.06	0.00	4
0.000	0.00	25.04	0.00	2
0.000	0.00	20.82	0.00	8
0.020	1.38	22.06	0.06	6
0.007	0.52	24.55	0.02	4
0.019	1.35	32.00	0.04	2
0.000	0.00	12.33	0.00	6

Total Soluble Contaminant Electron Acceptor Demand (lb.) 4.04

Stoichiometric Hydrogen Electron

D. Sorbed Contaminant Electron Acceptors

(Soil Concentration = Koc x foc x Cgw)

Tetrachloroethene (PCE)
 Trichloroethene (TCE)
 Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)
 Vinyl Chloride (VC)
 Carbon Tetrachloride (CT)
 Trichloromethane (or chloroform) (CF)
 Dichloromethane (or methylene chloride) (MC)
 Chloromethane
 Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)
 Trichloroethane (1,1,1-TCA and 1,1,2-TCA)
 Dichloroethane (1,1-DCA and 1,2-DCA)
 Chloroethane
 Perchlorate

Koc (mL/g)	Soil Conc. (mg/kg)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
263	0.00	0.95	20.57	0.05	8
107	0.03	13.70	21.73	0.63	6
45	0.01	4.93	24.05	0.20	4
3.0	0.00	0.04	31.00	0.00	2
224	0.00	0.00	19.08	0.00	8
63	0.00	0.00	19.74	0.00	6
28	0.00	0.00	21.06	0.00	4
25	0.00	0.00	25.04	0.00	2
117	0.00	0.00	20.82	0.00	8
105	0.00	0.41	22.06	0.02	6
30	0.00	0.04	24.55	0.00	4
3	0.00	0.01	32.00	0.00	2
0.00	0.00	0.00	12.33	0.00	6

Total Sorbed Contaminant Electron Acceptor Demand (lb.) 0.90

(continued)

4. Treatment Cell Electron-Acceptor Flux (per year)

A. Soluble Native Electron Acceptors

Oxygen
 Nitrate (denitrification)
 Sulfate
 Carbon Dioxide (estimated as the amount of Methane produced)

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
5.0	16.87	7.94	2.12	4
2.0	6.75	10.25	0.66	5
10	33.74	11.91	2.83	8
10	33.74	1.99	16.95	8

Total Competing Electron Acceptor Demand Flux (lb/yr) 22.6

B. Soluble Contaminant Electron Acceptors

Tetrachloroethene (PCE)
 Trichloroethene (TCE)
 Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)
 Vinyl Chloride (VC)
 Carbon Tetrachloride (CT)
 Trichloromethane (or chloroform) (CF)
 Dichloromethane (or methylene chloride) (MC)
 Chloromethane
 Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)
 Trichloroethane (1,1,1-TCA and 1,1,2-TCA)
 Dichloroethane (1,1-DCA and 1,2-DCA)
 Chloroethane
 Perchlorate

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
0.018	0.06	20.57	0.00	8
0.638	2.15	21.73	0.10	6
0.546	1.84	24.05	0.08	4
0.073	0.25	31.00	0.01	2
0.000	0.00	19.08	0.00	8
0.000	0.00	19.74	0.00	6
0.000	0.00	21.06	0.00	4
0.000	0.00	25.04	0.00	2
0.000	0.00	20.82	0.00	8
0.020	0.07	22.06	0.00	6
0.007	0.02	24.55	0.00	4
0.019	0.06	32.00	0.00	2
0.000	0.00	12.33	0.00	6

Total Soluble Contaminant Electron Acceptor Demand Flux (lb/yr) 0.19

Initial Hydrogen Requirement First Year (lb) 503.6

Total Life-Cycle Hydrogen Requirement (lb) 571.9

5. Design Factors

Microbial Efficiency Uncertainty Factor
 Methane and Solid-Phase Electron Acceptor Uncertainty
 Remedial Design Factor (e.g., Substrate Leaving Reaction Zone)

2X - 4X
 2X - 4X
 1X - 3X

Design Factor 10.0

Total Life-Cycle Hydrogen Requirement with Design Factor (lb) 5,719.3

6. Acronyms and Abbreviations

°C = degrees celsius
 µs/cm = microsiemens per centimeter
 cm/day = centimeters per day
 cm²/sec = centimeters per second
 ft² = square feet
 ft/day = feet per day
 ft/ft = foot per foot
 ft/yr = feet per year
 gm/cm³ = grams per cubic centimeter
 kg of CaCO₃ per mg = kilograms of calcium carbonate per milligram
 lb = pounds
 mg/100 g = milliequivalents per 100 grams
 mg/kg = milligrams per kilogram
 mg/L = milligrams per liter
 mV = millivolts
 m/yr = meters per year
 su = standard pH units
 wt/wt H₂ = concentration molecular hydrogen, weight per weight

How Much Electron Donor Do I Need?

ESTCP ER200627 (20101) Bruce Henry, Parsons

Site Name:

Joint Base Andrews - Site SS26

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NOTE: Open cells are user input.

1. Treatment Zone Physical Dimensions

- Width (Perpendicular to predominant groundwater flow direction)
- Length (Parallel to predominant groundwater flow)
- Saturated Thickness
- Treatment Zone Cross Sectional Area
- Treatment Zone Volume
- Treatment Zone Total Pore Volume (total volume x total porosity)
- Design Period of Performance

Values	Range	Units
175	1-10,000	feet
900	1-1,000	feet
24	1-100	feet
4200	--	ft ²
3,780,000	--	ft ³
8,484,588	--	gallons
4.0	.5 to 5	year

2. Treatment Zone Hydrogeologic Properties

- Total Porosity
- Effective Porosity
- Average Aquifer Hydraulic Conductivity
- Average Hydraulic Gradient
- Average Groundwater Seepage Velocity through the Treatment Zone
- Average Groundwater Seepage Velocity through the Treatment Zone
- Average Groundwater Flux through the Treatment Zone 0
- Soil Bulk Density
- Soil Fraction Organic Carbon (foc)

0.3	.05-50	
0.3	.05-50	
5.08	.01-1000	ft/day
0.006939	0.1-0.0001	ft/ft
0.12	--	ft/day
42.9	--	ft/yr
404,316	--	gallons/year
1.7	1.4-2.0	gm/cm ³
0.0005	0.0001-0.1	

3. Initial Treatment Cell Electron-Acceptor Demand (one total pore volume)

Tetrachloroethene (PCE)	0.018	1.27	20.57	0.06	8
Trichloroethene (TCE)	0.638	45.17	21.73	2.08	6
Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)	0.546	38.66	24.05	1.61	4
Vinyl Chloride (VC)	0.073	5.17	31.00	0.17	2
Carbon Tetrachloride (CT)	0.000	0.00	19.08	0.00	8
Trichloromethane (or chloroform) (CF)	0.000	0.00	19.74	0.00	6
Dichloromethane (or methylene chloride) (MC)	0.000	0.00	21.06	0.00	4
Chloromethane	0.000	0.00	25.04	0.00	2
Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)	0.000	0.00	20.82	0.00	8
Trichloroethane (1,1,1-TCA and 1,1,2-TCA)	0.020	1.38	22.06	0.06	6
Dichloroethane (1,1-DCA and 1,2-DCA)	0.007	0.52	24.55	0.02	4
Chloroethane	0.019	1.35	32.00	0.04	2
Perchlorate	0.000	0.00	12.33	0.00	6
Total Soluble Contaminant Electron Acceptor Demand (lb.)	4.04				

Stoichiometric Hydrogen Electron

Remedial Design Factor (e.g., Substrate Leaving Reaction Zone)

Design Factor 10.0
1X - 3X

Total Life-Cycle Hydrogen Requirement with Design Factor (lb) 5,719.3

6. Acronyms and Abbreviations

°C = degrees celsius
 µs/cm = microsiemens per centimeter
 cm/day = centimeters per day
 cm³/sec = centimeters per second
 ft² = square feet
 ft/day = feet per day
 ft/ft = foot per foot
 ft/yr = feet per year
 gm/cm³ = grams per cubic centimeter
 kg of CaCO₃ per mg = kilograms of calcium carbonate per milligram
 lb = pounds
 meq/100 g = milliequivalents per 100 grams
 mg/kg = milligrams per kilogram
 mg/L = milligrams per liter
 m/min = meters per meters
 mV = millivolts
 m/yr = meters per year
 su = standard pH units
 w/wt H₂ = concentration molecular hydrogen, weight per weight

How Much Electron Donor Do I Need?

ESTCP ER200627 (20101) Bruce Henry, Parsons

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A. Aqueous-Phase Native Electron Acceptors

Oxygen
 Nitrate (denitrification)
 Sulfate
 Carbon Dioxide (estimated as the amount of methane produced)

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
5.0	354.00	7.94	44.58	4
2.0	141.60	12.30	11.51	5
10	708.00	11.91	59.45	8
10.0	708.00	1.99	355.78	8
Soluble Competing Electron Acceptor Demand (lb.)			471.32	

B. Solid-Phase Native Electron Acceptors

(Based on manganese and iron produced)
 Manganese (IV) (estimated as the amount of Mn (II) produced)
 Iron (III) (estimated as the amount of Fe (II) produced)

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
1.0	84.30	27.25	3.09	2
1.0	84.30	55.41	1.52	1
Solid-Phase Competing Electron Acceptor Demand (lb.)			4.61	

C. Soluble Contaminant Electron Acceptors

Tetrachloroethene (PCE)
 Trichloroethene (TCE)
 Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)
 Vinyl Chloride (VC)
 Carbon Tetrachloride (CT)
 Trichloromethane (or chloroform) (CF)
 Dichloromethane (or methylene chloride) (MC)
 Chloromethane
 Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)
 Trichloroethane (1,1,1-TCA and 1,1,2-TCA)
 Dichloroethane (1,1-DCA and 1,2-DCA)
 Chloroethane
 Perchlorate

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
0.018	1.27	20.57	0.06	8
0.638	45.17	21.73	2.08	6
0.546	38.66	24.05	1.61	4
0.073	5.17	31.00	0.17	2
0.000	0.00	19.08	0.00	8
0.000	0.00	19.74	0.00	6
0.000	0.00	21.06	0.00	4
0.000	0.00	25.04	0.00	2
0.000	0.00	20.82	0.00	8
0.020	1.38	22.06	0.06	6
0.007	0.52	24.55	0.02	4
0.019	1.35	32.00	0.04	2
0.000	0.00	12.33	0.00	6
Total Soluble Contaminant Electron Acceptor Demand (lb.)			4.04	

How Much Electron Donor Do I Need?

ESTCP ER200627 (20101) Bruce Henry, Parsons

Total Soluble Contaminant Electron Acceptor Demand (lb.) **4.04**

D. Sorbed Contaminant Electron Acceptors

(Soil Concentration = Koc x foc x Cgw)

Contaminant	Koc (mL/g)	Soil Conc. (mg/kg)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Tetrachloroethene (PCE)	263	0.00	0.95	20.57	0.05	8
Trichloroethene (TCE)	107	0.03	13.70	21.73	0.63	6
Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)	45	0.01	4.93	24.05	0.20	4
Vinyl Chloride (VC)	3.0	0.00	0.04	31.00	0.00	2
Carbon Tetrachloride (CT)	224	0.00	0.00	19.08	0.00	8
Trichloromethane (or chloroform) (CF)	63	0.00	0.00	19.74	0.00	6
Dichloromethane (or methylene chloride) (MC)	28	0.00	0.00	21.06	0.00	4
Chloromethane	25	0.00	0.00	25.04	0.00	2
Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)	117	0.00	0.00	20.82	0.00	8
Trichloroethane (1,1,1-TCA and 1,1,2-TCA)	105	0.00	0.41	22.06	0.02	6
Dichloroethane (1,1-DCA and 1,2-DCA)	30	0.00	0.04	24.55	0.00	4
Chloroethane	3	0.00	0.01	32.00	0.00	2
Perchlorate	0.0	0.00	0.00	12.33	0.00	6

Total Sorbed Contaminant Electron Acceptor Demand (lb.) **0.90**

(continued)

4. Treatment Cell Electron-Acceptor Flux (per year)

A. Soluble Native Electron Acceptors

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole	
Oxygen	5.0	16.87	7.94	2.12	4
Nitrate (denitrification)	2.0	6.75	10.25	0.66	5
Sulfate	10	33.74	11.91	2.83	8
Carbon Dioxide (estimated as the amount of Methane produced)	10	33.74	1.99	16.95	8

Total Competing Electron Acceptor Demand Flux (lb/yr) **22.6**

Trichloroethane (1,1,1-TCA and 1,1,2-TCA)	0.020	1.00	22.06	0.02	6
Dichloroethane (1,1-DCA and 1,2-DCA)	0.007	0.52	24.55	0.02	4
Chloroethane	0.019	1.35	32.00	0.04	2
Perchlorate	0.000	0.00	12.33	0.00	6

Total Soluble Contaminant Electron Acceptor Demand (lb.) **4.04**

B. Soluble Contaminant Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt H ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Tetrachloroethene (PCE)	0.018	0.06	20.57	0.00	8
Trichloroethene (TCE)	0.638	2.15	21.73	0.10	6
Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)	0.546	1.84	24.05	0.08	4
Vinyl Chloride (VC)	0.073	0.25	31.00	0.01	2
Carbon Tetrachloride (CT)	0.000	0.00	19.08	0.00	8
Trichloromethane (or chloroform) (CF)	0.000	0.00	19.74	0.00	6
Dichloromethane (or methylene chloride) (MC)	0.000	0.00	21.06	0.00	4
Chloromethane	0.000	0.00	25.04	0.00	2
Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)	0.000	0.00	20.82	0.00	8
Trichloroethane (1,1,1-TCA and 1,1,2-TCA)	0.020	0.07	22.06	0.00	6
Dichloroethane (1,1-DCA and 1,2-DCA)	0.007	0.02	24.55	0.00	4
Chloroethane	0.019	0.06	32.00	0.00	2
Perchlorate	0.000	0.00	12.33	0.00	6
Total Soluble Contaminant Electron Acceptor Demand Flux (lb/yr)				0.19	

Initial Hydrogen Requirement First Year (lb) **503.6**

Total Life-Cycle Hydrogen Requirement (lb) **571.9**

5. Design Factors

Microbial Efficiency Uncertainty Factor

2X - 4X

Methane and Solid-Phase Electron Acceptor Uncertainty

2X - 4X

Remedial Design Factor (e.g., Substrate Leaving Reaction Zone)

1X - 3X

Design Factor **10.0**

Total Life-Cycle Hydrogen Requirement with Design Factor (lb) **5,719.3**

6. Acronyms and Abbreviations

°C =degrees celsius

meq/100 g = milliequivalents per 100 grams

µs/cm = microsiemens per centimeter

mg/kg = milligrams per kilogram

cm/day = centimeters per day

mg/L = milligrams per liter

cm/sec = centimeters per second

m/m = meters per meters

ft² = square feet

mV = millivolts

ft/day = feet per day

m/yr = meters per year

ft/ft = foot per foot

su = standard pH units

ft/yr = feet per year

wt/wt H₂ = concentration molecular hydrogen, weight per weight

gm/cm³ = grams per cubic centimeter

kg of CaCO₃ per mg = kilograms of calcium carbonate per milligram

lb = pounds

B. Soluble Contaminant Electron Acceptors

	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt H ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Tetrachloroethene (PCE)	0.018	0.06	20.57	0.00	8
Trichloroethene (TCE)	0.638	2.15	21.73	0.10	6
Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)	0.546	1.84	24.05	0.08	4
Vinyl Chloride (VC)	0.073	0.25	31.00	0.01	2
Carbon Tetrachloride (CT)	0.000	0.00	19.08	0.00	8
Trichloromethane (or chloroform) (CF)	0.000	0.00	19.74	0.00	6
Dichloromethane (or methylene chloride) (MC)	0.000	0.00	21.06	0.00	4
Chloromethane	0.000	0.00	25.04	0.00	2
Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)	0.000	0.00	20.82	0.00	8
Trichloroethane (1,1,1-TCA and 1,1,2-TCA)	0.020	0.07	22.06	0.00	6
Dichloroethane (1,1-DCA and 1,2-DCA)	0.007	0.02	24.55	0.00	4
Chloroethane	0.019	0.06	32.00	0.00	2
Perchlorate	0.000	0.00	12.33	0.00	6
Total Soluble Contaminant Electron Acceptor Demand Flux (lb/yr)				0.19	
Initial Hydrogen Requirement First Year (lb)				503.6	
Total Life-Cycle Hydrogen Requirement (lb)				571.9	

5. Design Factors

Microbial Efficiency Uncertainty Factor	2X - 4X
Methane and Solid-Phase Electron Acceptor Uncertainty	2X - 4X
Remedial Design Factor (e.g., Substrate Leaving Reaction Zone)	1X - 3X
Design Factor	10.0
Total Life-Cycle Hydrogen Requirement with Design Factor (lb)	5,719.3

6. Acronyms and Abbreviations

°C =degrees celsius	meq/100 g = milliequivalents per 100 grams
μs/cm = microsiemens per centimeter	mg/kg = milligrams per kilogram
cm/day = centimeters per day	mg/L = milligrams per liter
cm/sec = centimeters per second	m/m = meters per meters
ft ² = square feet	mV = millivolts
ft/day = feet per day	m/yr = meters per year
ft/ft = foot per foot	su = standard pH units
ft/yr = feet per year	wt/wt H ₂ = concentration molecular hydrogen, weight per weight
gm/cm ³ = grams per cubic centimeter	
kg of CaCO ₃ per mg = kilograms of calcium carbonate per milligram	
lb = pounds	

B. Soluble Contaminant Electron Acceptors

Tetrachloroethene (PCE)
 Trichloroethene (TCE)
 Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)
 Vinyl Chloride (VC)
 Carbon Tetrachloride (CT)
 Trichloromethane (or chloroform) (CF)
 Dichloromethane (or methylene chloride) (MC)
 Chloromethane
 Tetrachloroethane (1,1,1,2-PCA and 1,1,2,2-PCA)
 Trichloroethane (1,1,1-TCA and 1,1,2-TCA)
 Dichloroethane (1,1-DCA and 1,2-DCA)
 Chloroethane
 Perchlorate

Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h ₂)	Hydrogen Demand (lb)	Electron Equivalents per Mole
0.018	0.06	20.57	0.00	8
0.638	2.15	21.73	0.10	6
0.546	1.84	24.05	0.08	4
0.073	0.25	31.00	0.01	2
0.000	0.00	19.08	0.00	8
0.000	0.00	19.74	0.00	6
0.000	0.00	21.06	0.00	4
0.000	0.00	25.04	0.00	2
0.000	0.00	20.82	0.00	8
0.020	0.07	22.06	0.00	6
0.007	0.02	24.55	0.00	4
0.019	0.06	32.00	0.00	2
0.000	0.00	12.33	0.00	6

Total Soluble Contaminant Electron Acceptor Demand Flux (lb/yr)

0.19

Initial Hydrogen Requirement First Year (lb)

503.6

Total Life-Cycle Hydrogen Requirement (lb)

571.9

5. Design Factors

Microbial Efficiency Uncertainty Factor

2X - 4X

Methane and Solid-Phase Electron Acceptor Uncertainty

2X - 4X

Remedial Design Factor (e.g., Substrate Leaving Reaction Zone)

1X - 3X

Design Factor

10.0

Total Life-Cycle Hydrogen Requirement with Design Factor (lb)

5,719.3

6. Acronyms and Abbreviations

°C =degrees celsius

µs/cm = microsiemens per centimeter

cm/day = centimeters per day

cm/sec = centimeters per second

ft² = square feet

ft/day = feet per day

ft/ft = foot per foot

ft/yr = feet per year

gm/cm³ = grams per cubic centimeter

kg of CaCO₃ per mg = kilograms of calcium carbonate per milligram

lb = pounds

meq/100 g = milliequivalents per 100 grams

mg/kg = milligrams per kilogram

mg/L = milligrams per liter

m/m = meters per meter

mV = millivolts

m/yr = meters per year

su = standard units

wt/wt H₂ = concentration

Typically organic electron donor in situ target concentration is between 1 and 10 g/L TOC

Undesired or Unexpected Results

More daughter products than anticipated

- Adsorbed
- DNAPL

Incomplete degradation (e.g. cis DCE or VC stall)

- No, or insufficient Dhc population
- Insufficient /too much substrate
- Inefficient distribution of substrate and culture
- Geochemical issues (e.g., sulfide toxicity, nutrients)
- pH outside appropriate range



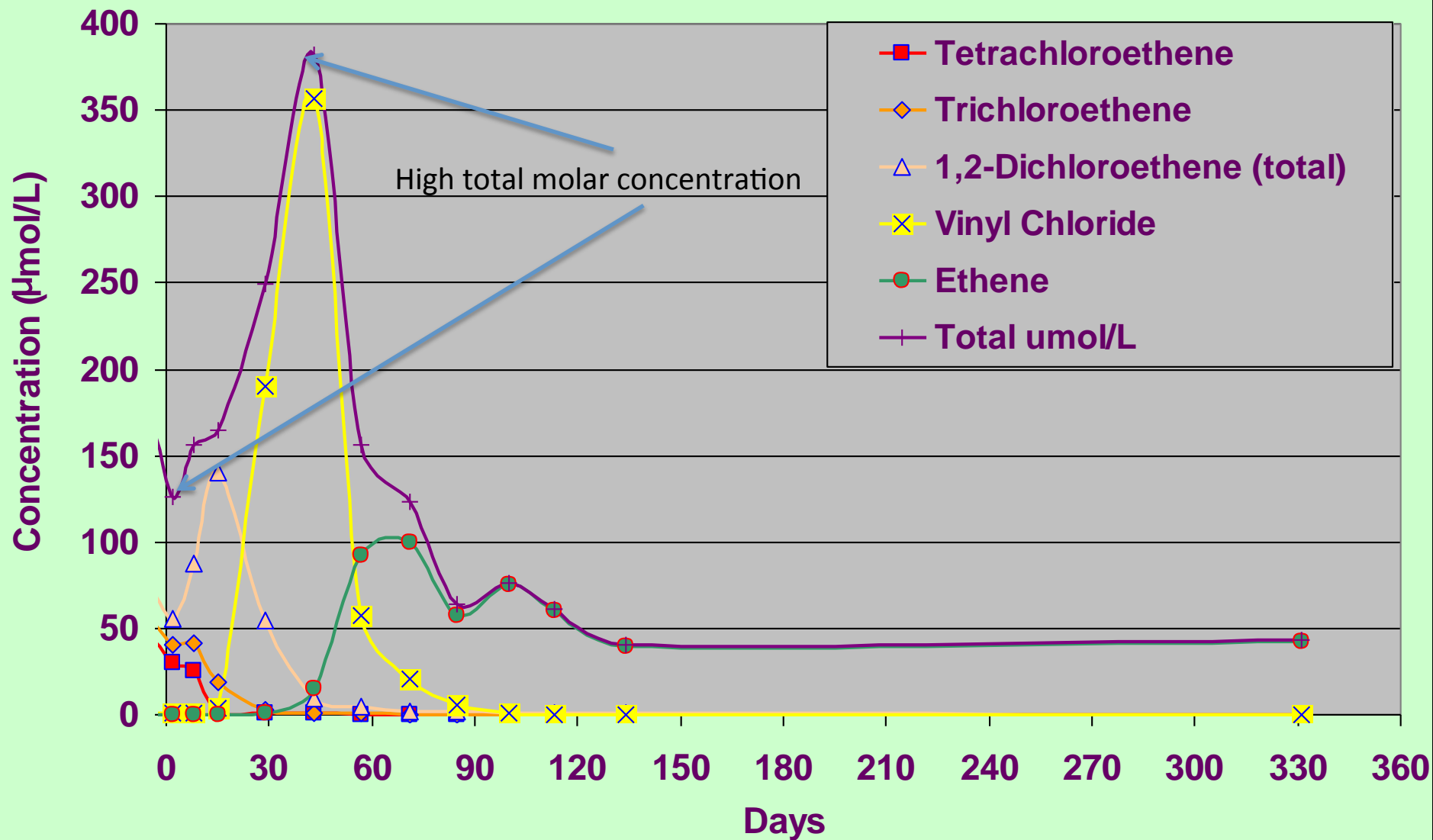
Contaminants disappear without generation of daughter products

- May be partitioning into substrate
- May be biogeochemical/abiotic degradation

Contaminants disappear but come back after substrate is gone.

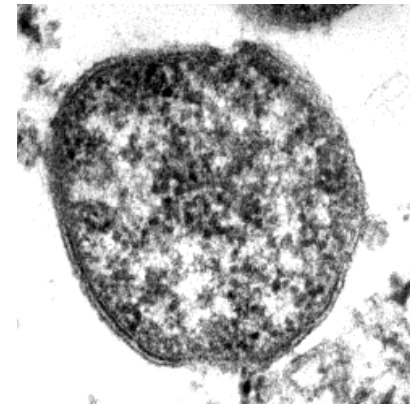
- Other source of contaminants
- DNAPL possible
- High adsorbed phase
- Matrix diffusion

Increased Dissolved Phase Chlorinated Ethenes During Bioremediation



Biostimulation vs. Bioaugmentation

- **Biostimulation** is the modification of the environment to stimulate existing bacteria capable of bioremediation
 - **Nutrients** – e.g. nitrogen, phosphorous, potassium
 - **Electron acceptors** – e.g.. oxygen, nitrate, manganese, ferric iron, sulfate, carbon dioxide
 - **Electron donors** – e.g.. lactate, EVO, lecithin, cellulose, lactose
- **Bioaugmentation** is the introduction of a group of natural microbial strains or genetically engineered variants to achieve bioremediation
 - **Indigenous** – Native to site
 - **Exogenous** - introduced



Various organisms approved for bioaugmentation

Dehalococcoides (Dhc) Geobacter

Dehalobacter

Corynebacterium

Dehalogenimonas

Nitrosomonas

Desulfuromonas

Nitrobacter

Desulfitobacterium

Rhodococcus

Desulfovibrio

Pseudomonas fluorescens

Sulfurospirillum

Methylobium petroleiphilum

Alcaligenes faecalis

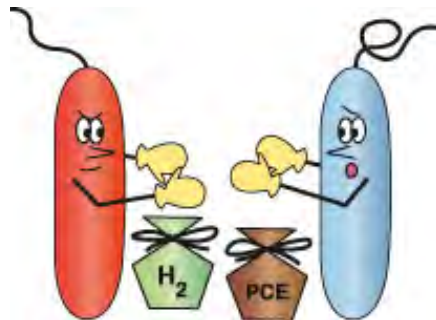
Methanotrophs

Arthrobacter

Methylosinus

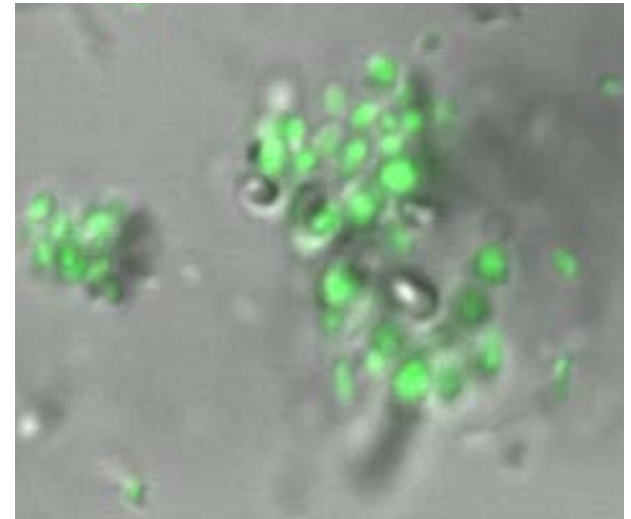
Is 'Bioaugmentation Necessary?

- Only one organism (*Dehalococcoides sp*) (*Dhc*) demonstrated to completely degrade PCE and TCE to ethene
- Dechlorinating organisms may not be present at sufficient concentrations at many sites.
 - $> 1 \times 10^7$ *Dhc* cells/L considered necessary for remediation
- The indigenous organism may not be efficient at dechlorination.
 - Final step may be co-metabolic, which is slow
- Indigenous organisms (e.g. methanogenic bacteria) may outcompete dechlorinators such as *Dhc* for H_2 .



Bioaugmentation in Aerobic Aquifers

- Dhc is an obligate anaerobe.
- Does not grow in presence of O_2
- Aerobic aquifers contain little, if any, Dhc.
- Aerobic aquifers often not considered appropriate for biological ERD.
- Substantial effort considered necessary to bioaugment in aerobic aquifers but not necessarily true.
- Bioaugmentation probably necessary treat CEs biologically in aerobic aquifers.



Considerations when Bioaugmenting

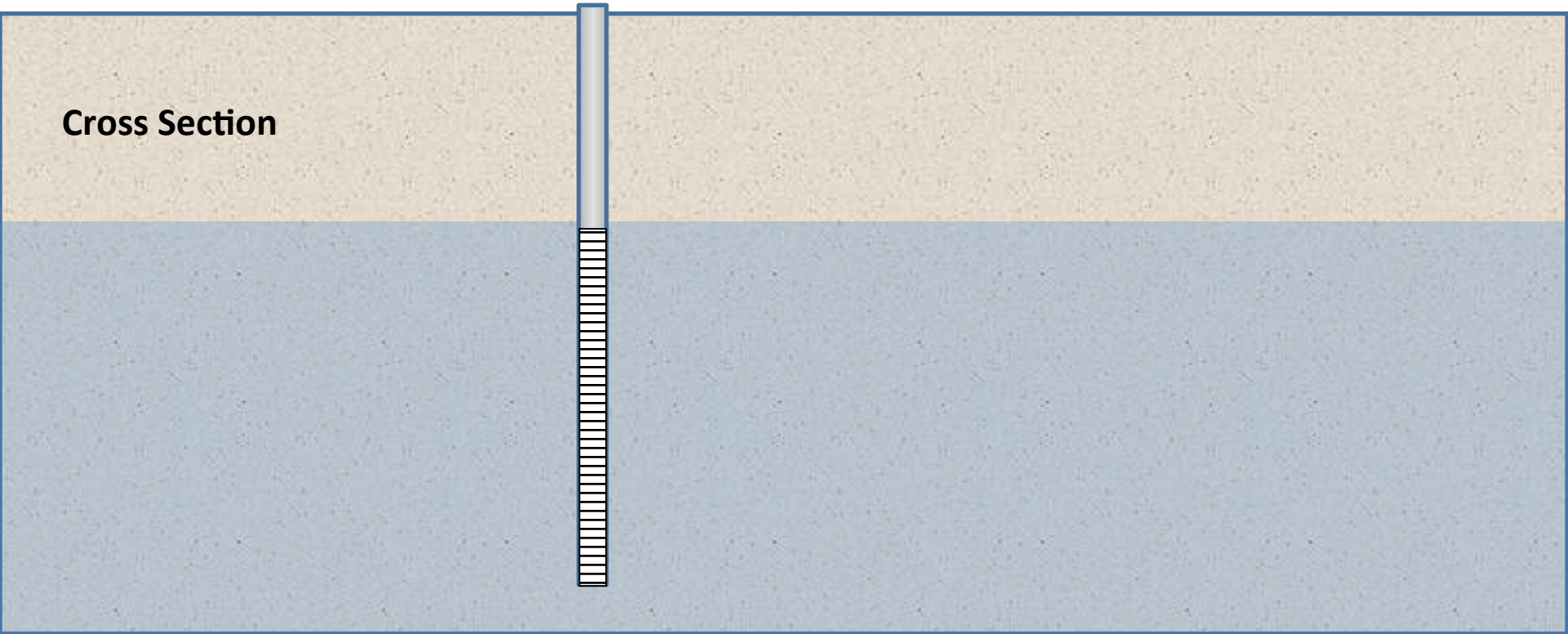
- Establishment of reducing conditioning of the aquifer prior to bioaugmentation, although helpful, is costly and may not be necessary
- The addition of organic substrate to aerobic water usually sufficient to protect culture from oxygen.
- Preferable to use site groundwater for injection.
- Potable (hydrant) water has chlorine in it to kill bacteria.
- Adding buffer to bioaugmentation water may raise pH too high

Bioaugmentation methods applied to overcome aerobic conditions

Plan View

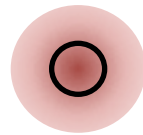


Cross Section



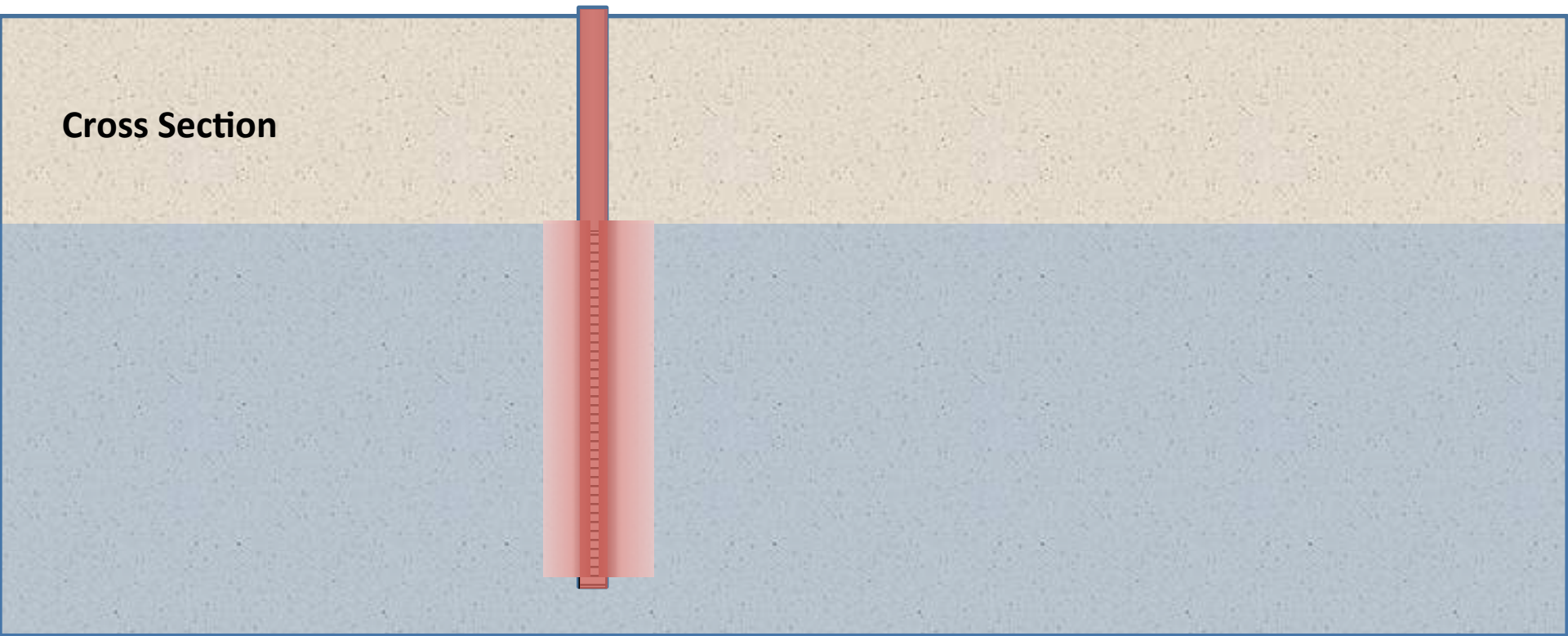
Bioaugmentation methods applied to overcome aerobic conditions

Plan View



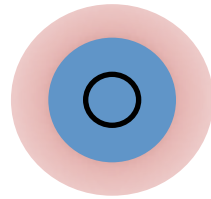
Inject 25% Substrate

Cross Section



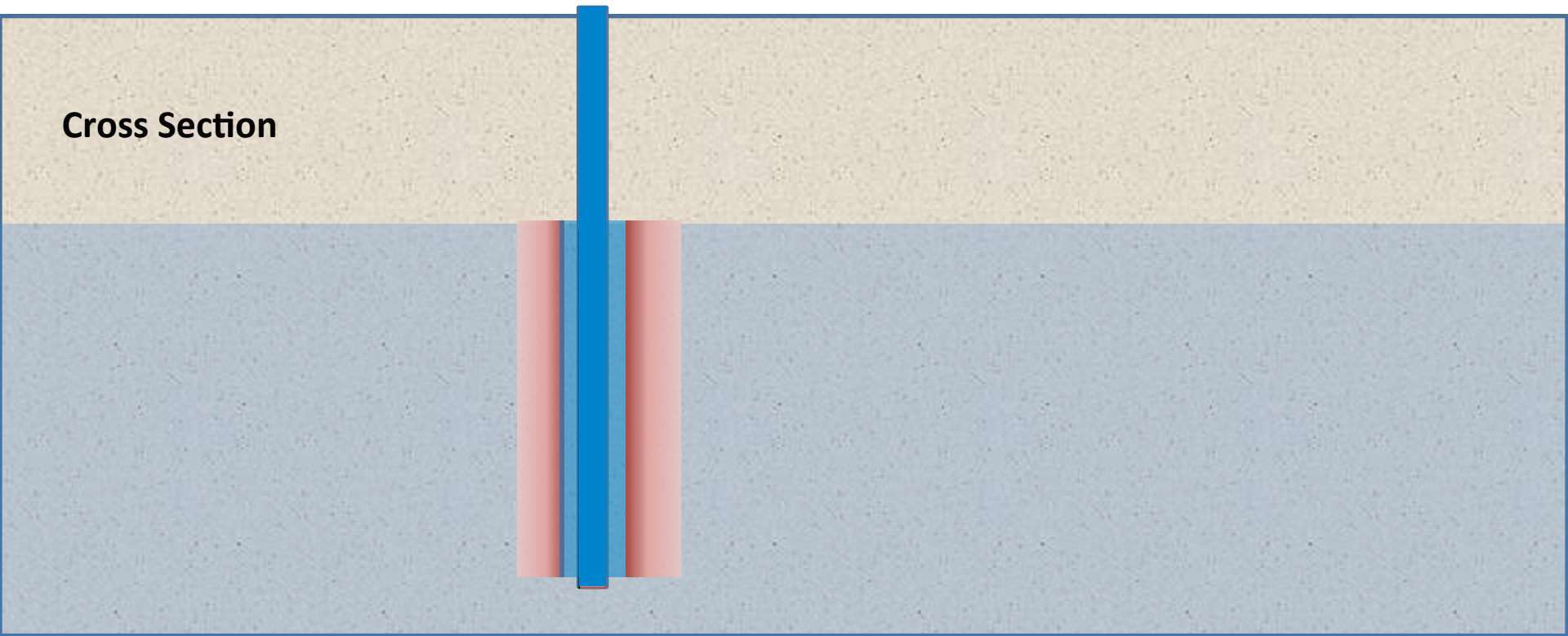
Bioaugmentation methods applied to overcome aerobic conditions

Plan View



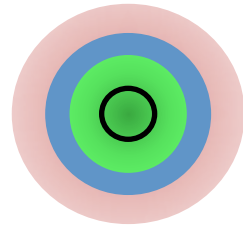
Inject Anaerobic Chase Water

Cross Section



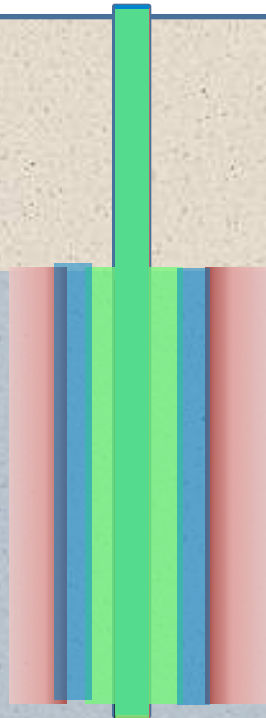
Bioaugmentation methods applied to overcome aerobic conditions

Plan View



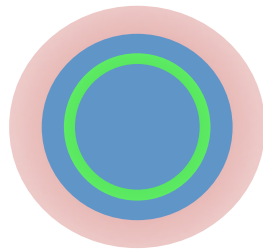
Inject Bioaugmentation Culture

Cross Section



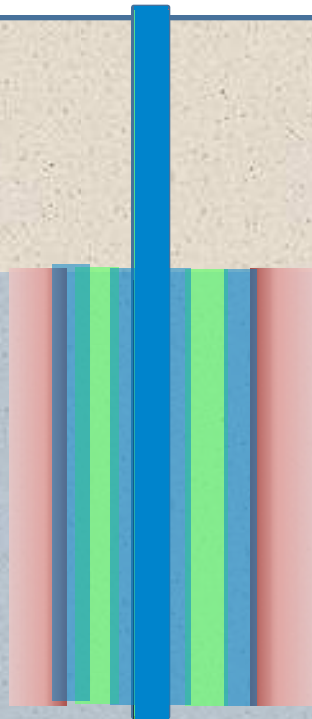
Bioaugmentation methods applied to overcome aerobic conditions

Plan View



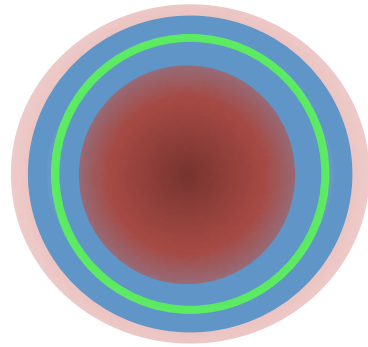
Inject Chase Water

Cross Section

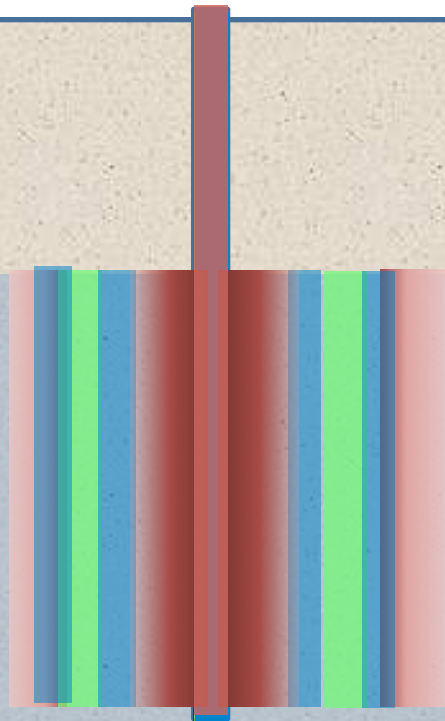


Bioaugmentation methods applied to overcome aerobic conditions

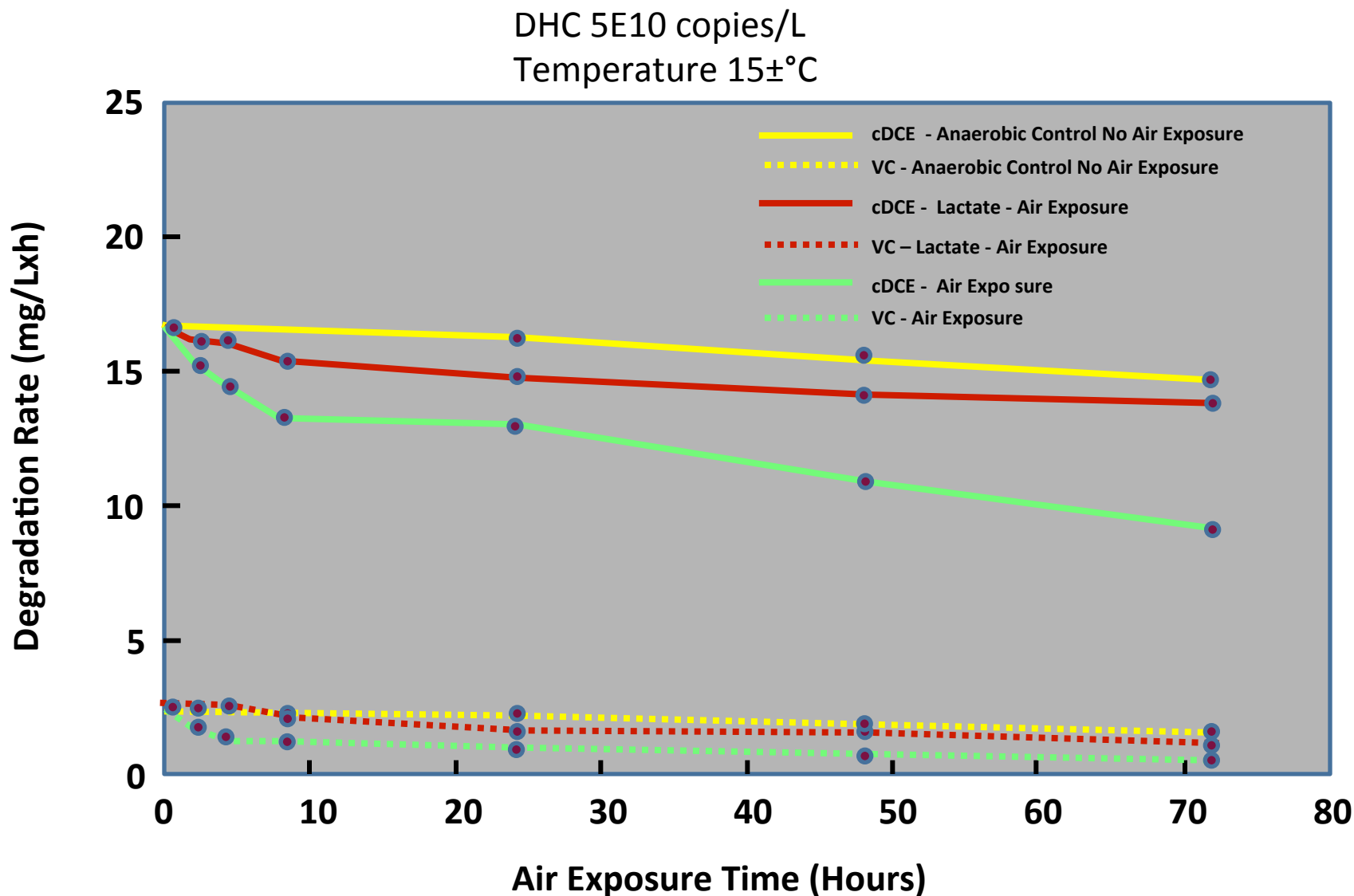
Plan View



Cross Section

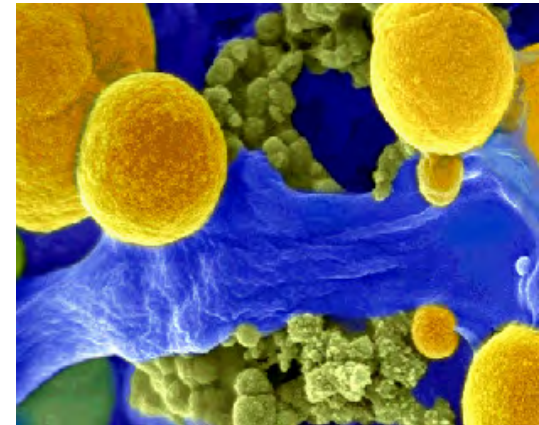


cDCE and VC Degradation Rates of SDC-9™ Exposed to Air (With and Without Organic Substrate)

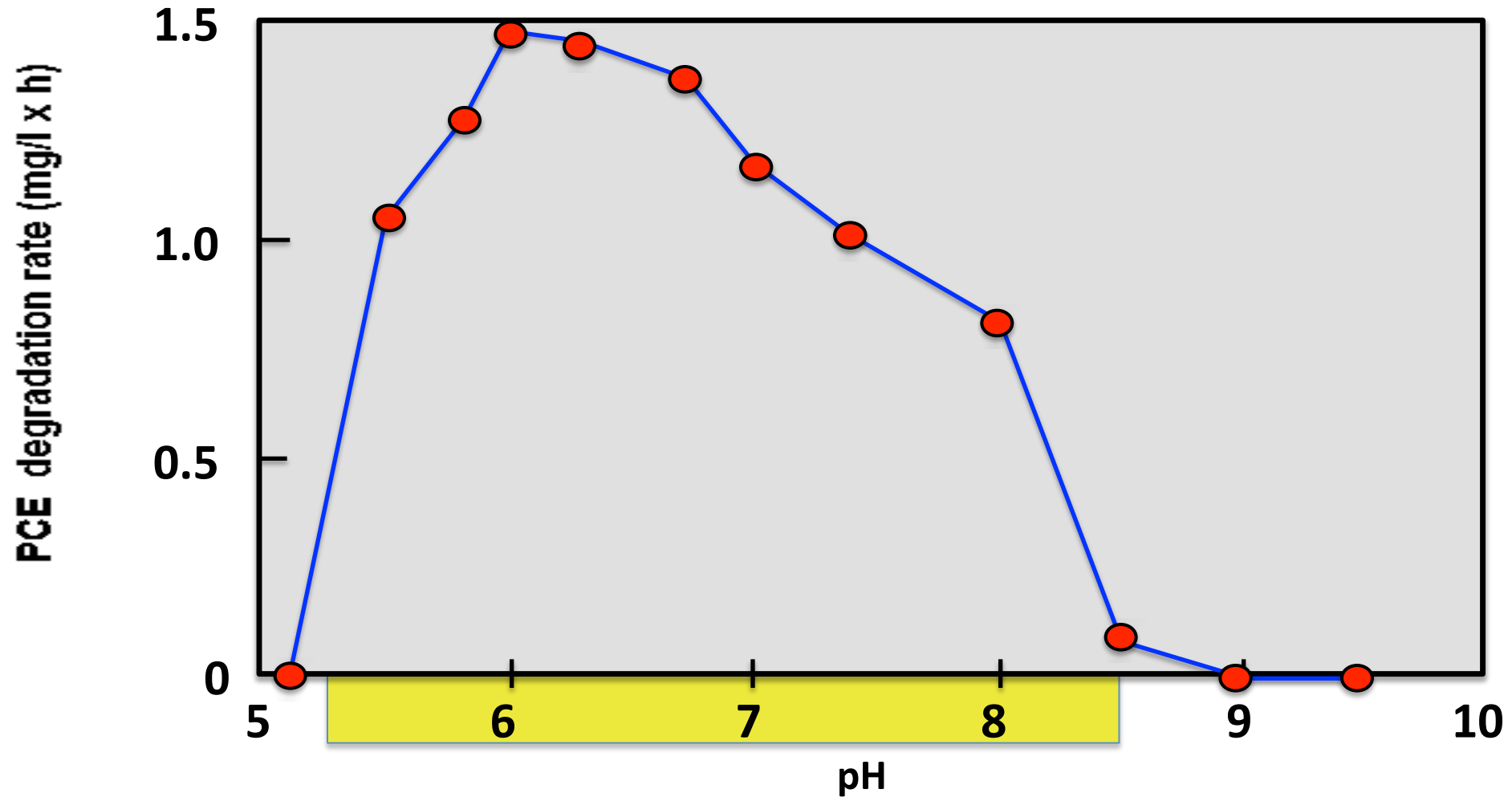


Anaerobic biodegradation can be conducted only in a defined range of pH

- Dhc are very sensitive to pH
- Addition of organic substrates causes pH drop
- Some other organisms (e.g., methanogens/SRBs) are not as sensitive to pH
- SRB's and methanogens outcompete dechlorinators for available H_2
- Dechlorinating bacteria can lose ability to dechlorinate



Dechlorination rates by Dhc are substantially affected by pH



Solution to Elevated pH

Buffers:

Sodium Bicarbonate

Potassium Bicarbonate

Sodium hydroxide

Calcium Carbonate



Remember Dhc sensitive to high pH as well

ZVI also buffers pH - ISCR

Sulfide Toxicity

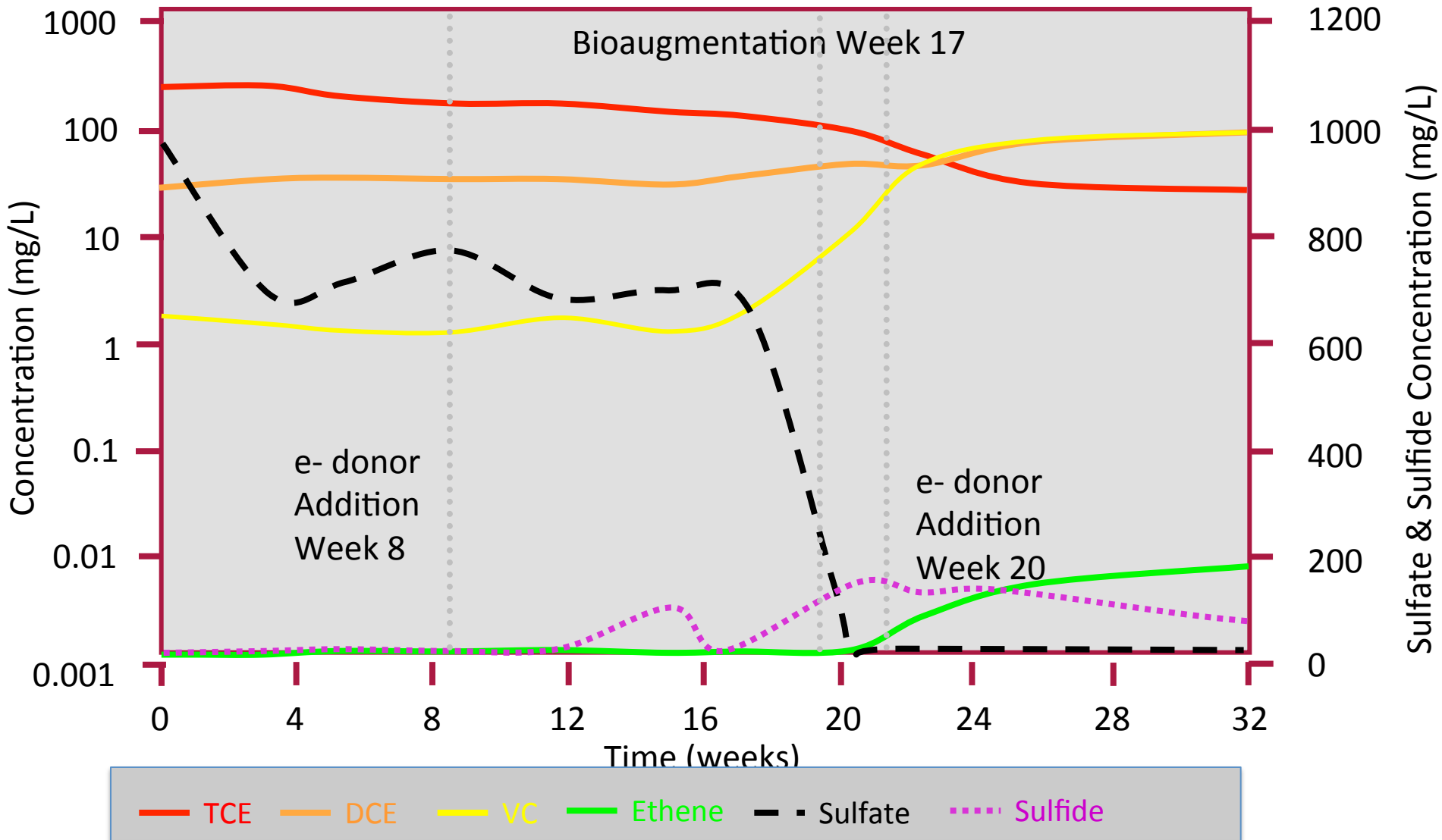
Elevated concentrations of sulfide can inhibit anaerobic biodegradation

- Sulfate reduction stimulated during anaerobic bioremediation
- Sulfate converted into HS^- which is toxic to bacteria
- If sufficient ferrous iron is present, sulfide will precipitate as ferrous sulfide species
- If iron *insufficient*, toxic levels of HS^- may accumulate.
 - Carbonate aquifers
 - Very high sulfate concentrations ($> 1,000 \text{ mg/L}$)
- Addition of iron can solve sulfide toxicity issues



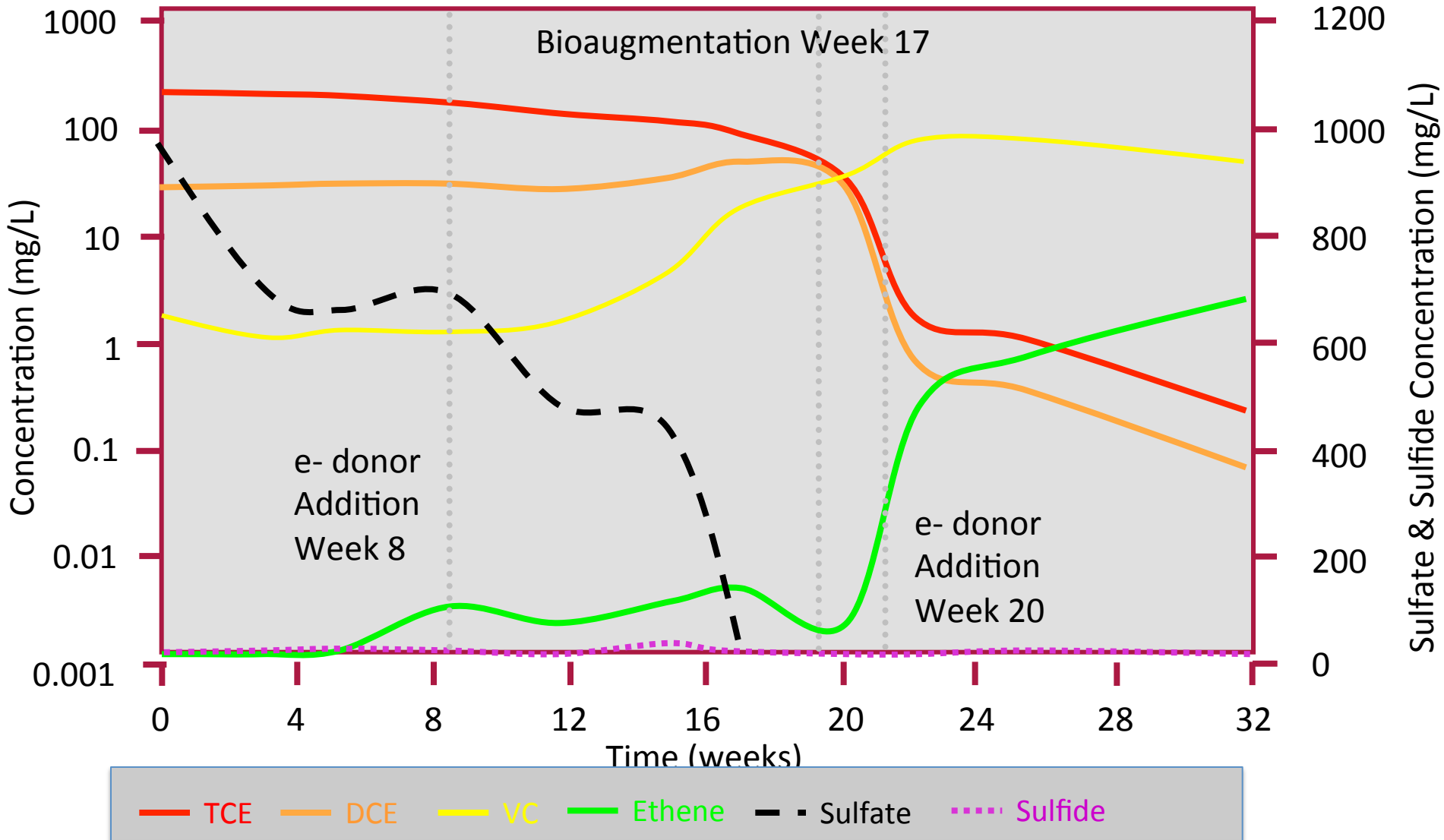
Example of sulfide toxicity

Bench tests – ambient conditions



Example of sulfide toxicity

Bench tests – Fe-sulfide precipitation



Biogeochemical Transformation

Processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.

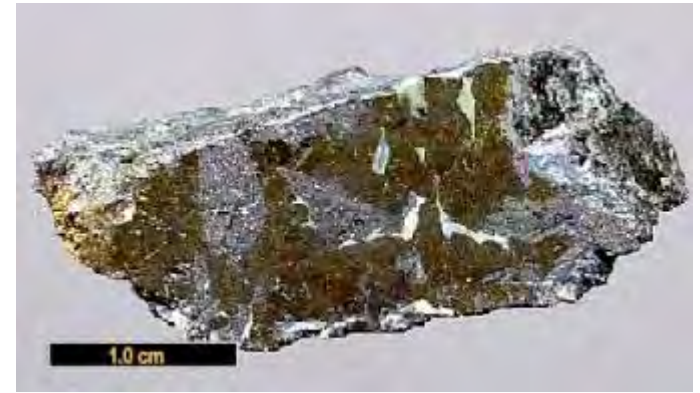
Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)



Pyrite (FeS_2)



Magnetite (Fe_3O_4)

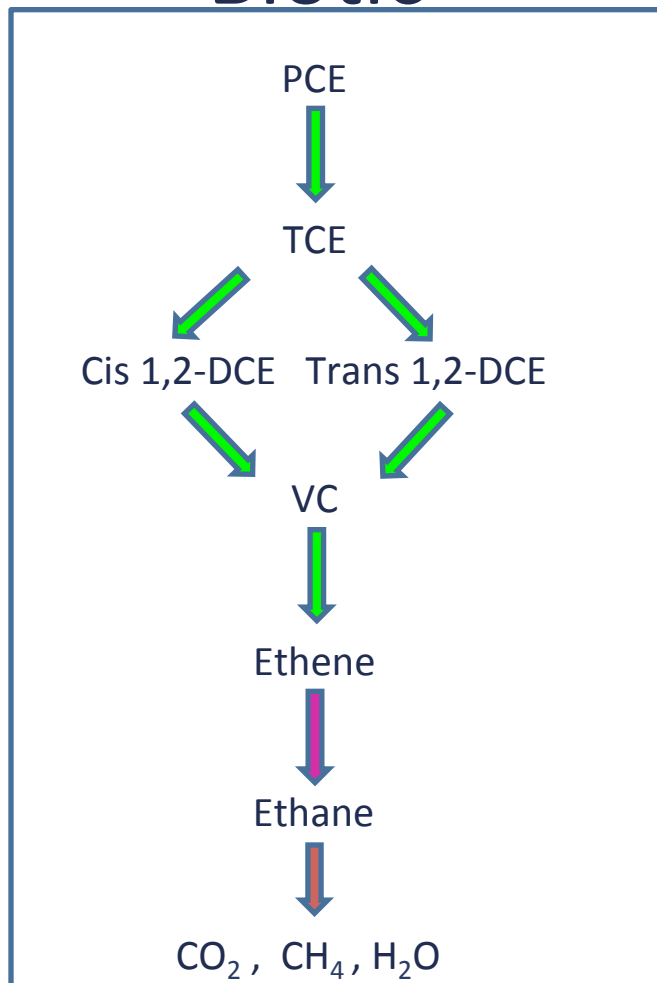




Mackinawite ($\text{Fe}_{(1+x)}\text{S}$)

β–Elimination does not generate stable toxic daughter products

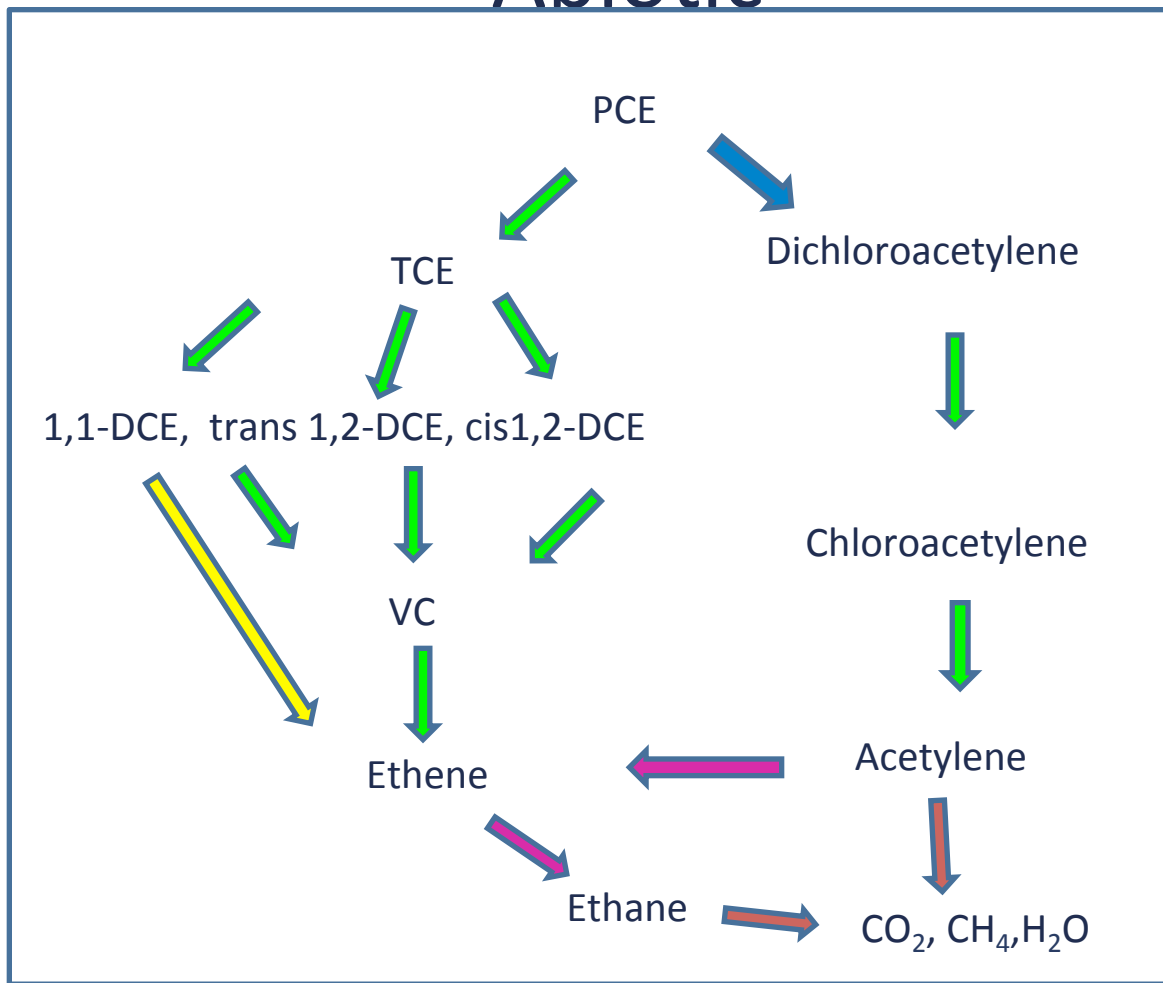
Biogeochemical Degradation Pathways



Biotic



 α-elimination
 β-elimination

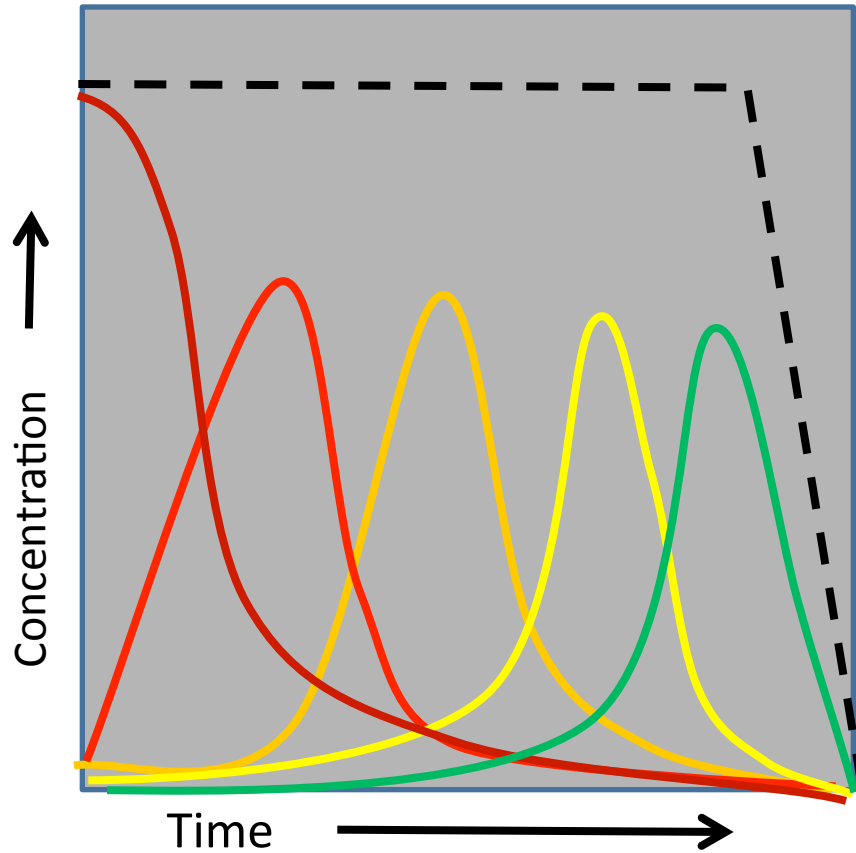
Abiotic



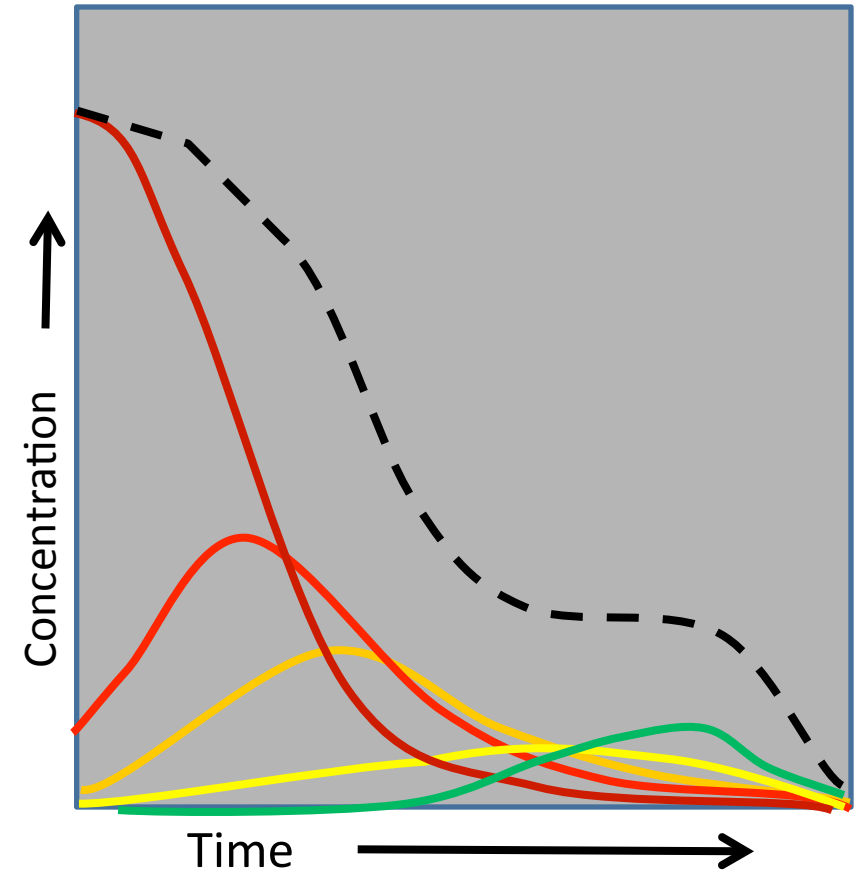
 Hydrogenolysis
 Hydrogenation

Anticipated Change in CE Molar Concentration

Biological Degradation (Chlororespiration)



Abiotic Degradation (β elimination)



— PCE — TCE — DCE — VC — Ethene — Total

Sulfide Precipitation

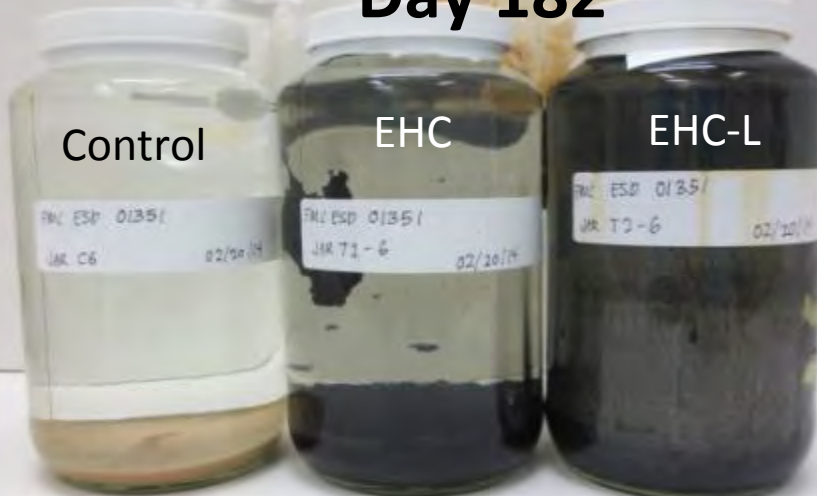
Day 60



Day 124



Day 182



EHC Precipitate

mg/Kg	Sulfide	31000
	Total Fe	210000
mMol/Kg	Sulfide	967
	Total Fe	3760

EHC-L + Iron Precipitate

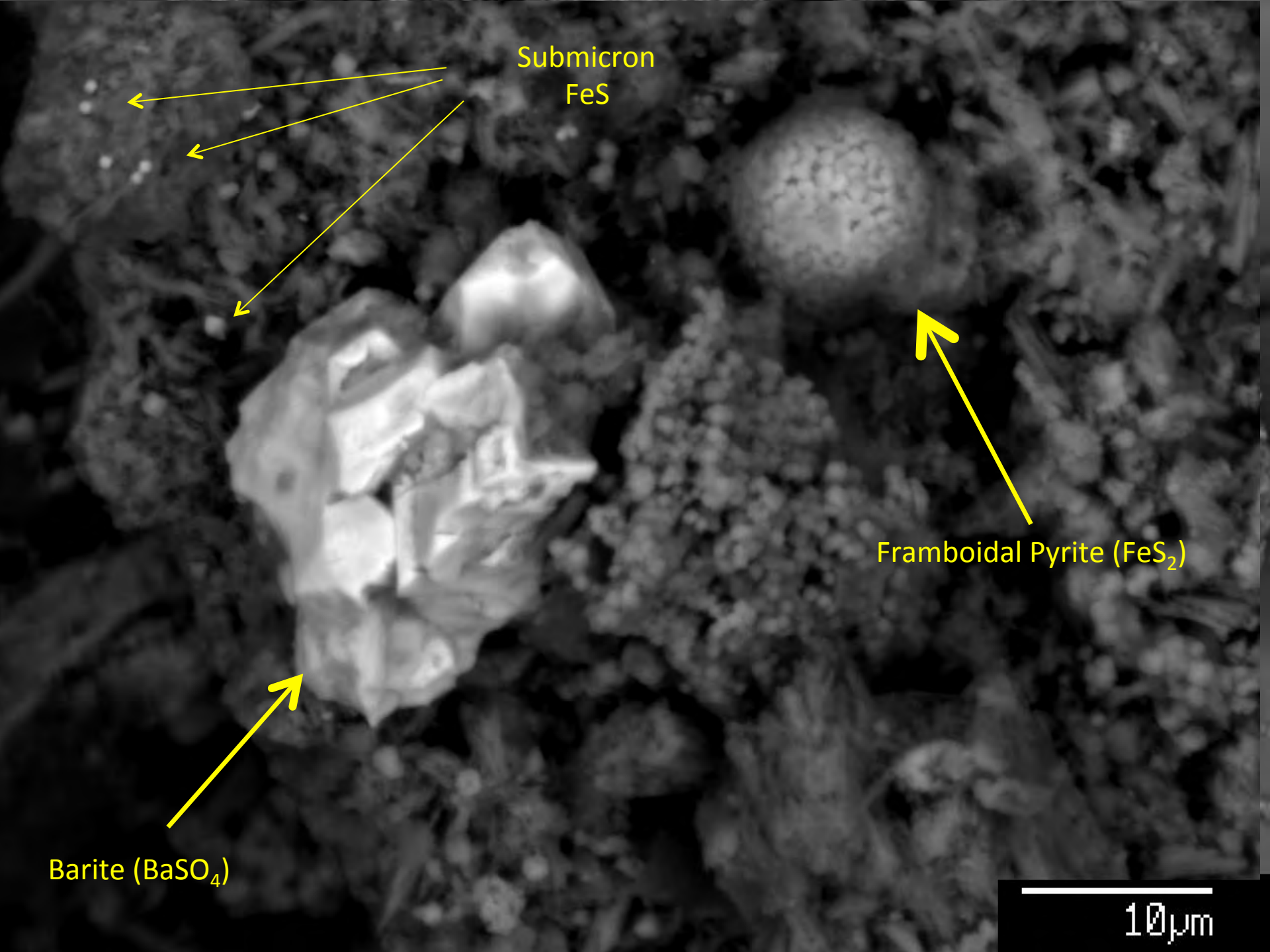
mg/Kg	Sulfide	42000
	Total Fe	130000
Mmol/Kg	Sulfide	1310
	Total Fe	2328

Quartz, Calcium Carbonate

Back Scatter Electron Image



10 μm



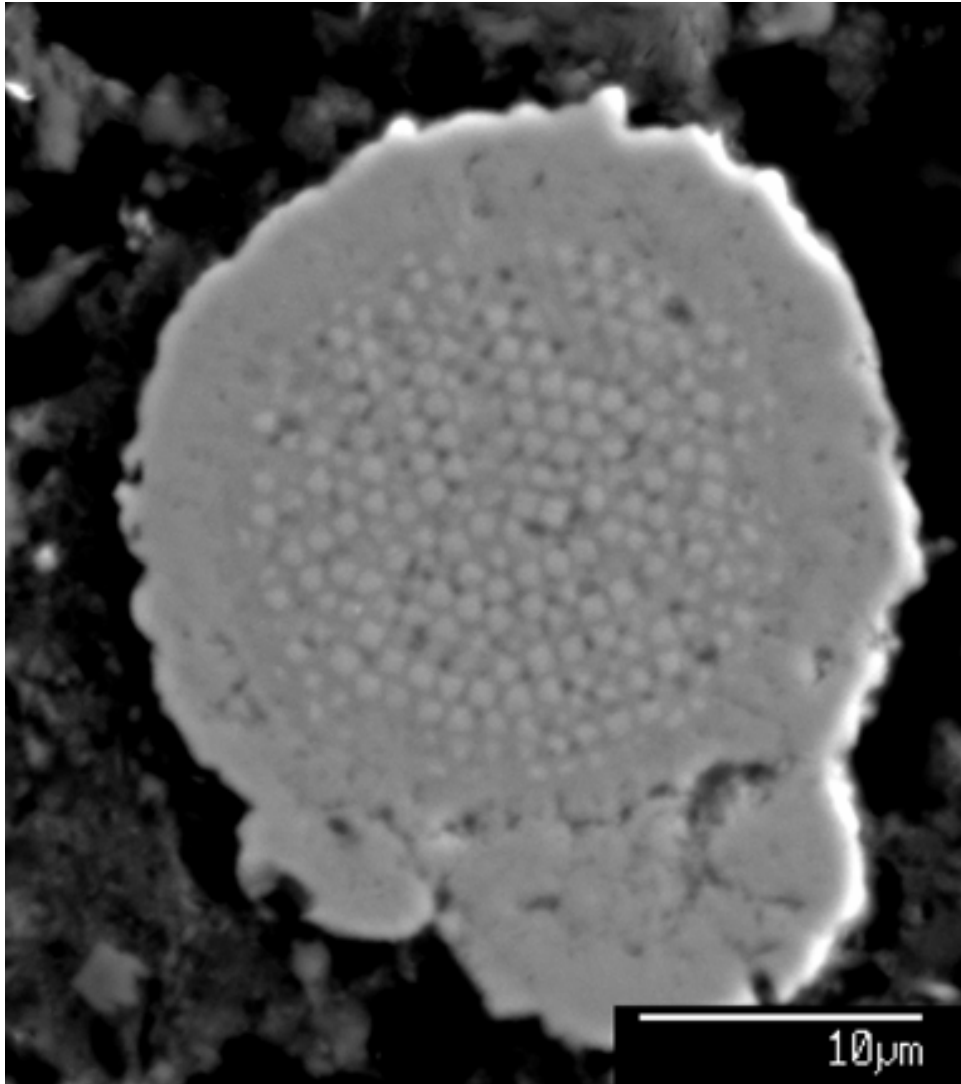
Submicron
FeS

Framboidal Pyrite (FeS_2)

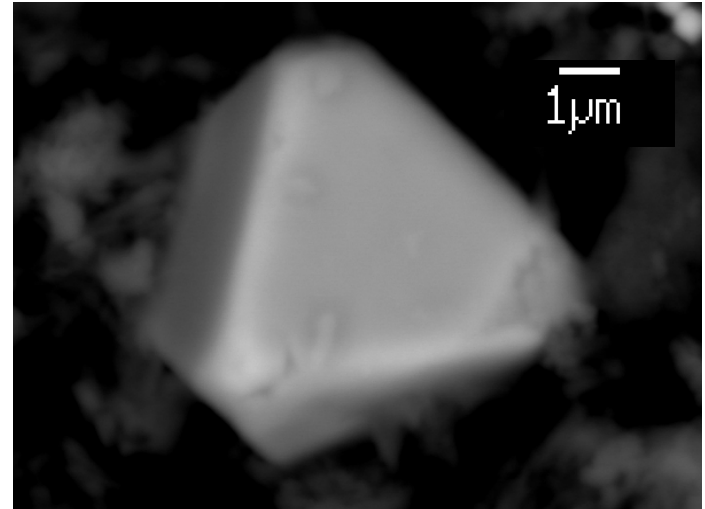
Barite (BaSO_4)

10 μm

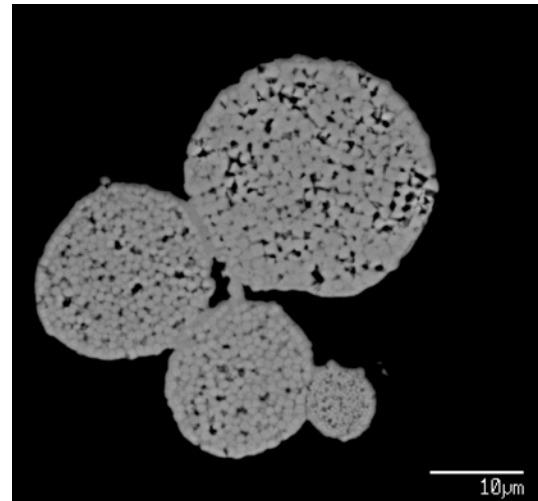
FeS₂ Occurs as Euhedral and Framboidal Pyrite



Framboidal FeS₂ and FeS

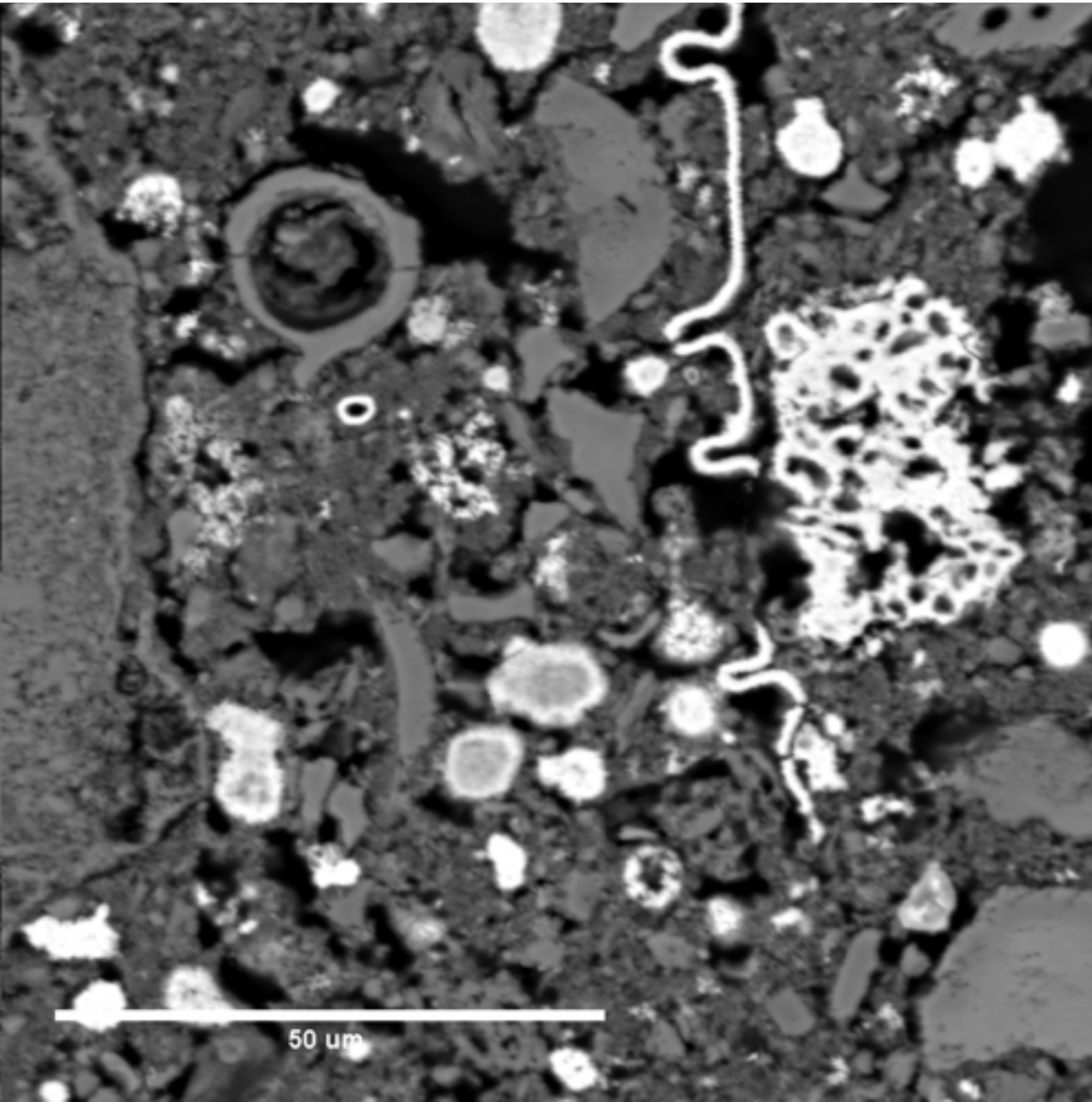


Euhedral Pyrite (FeS₂)

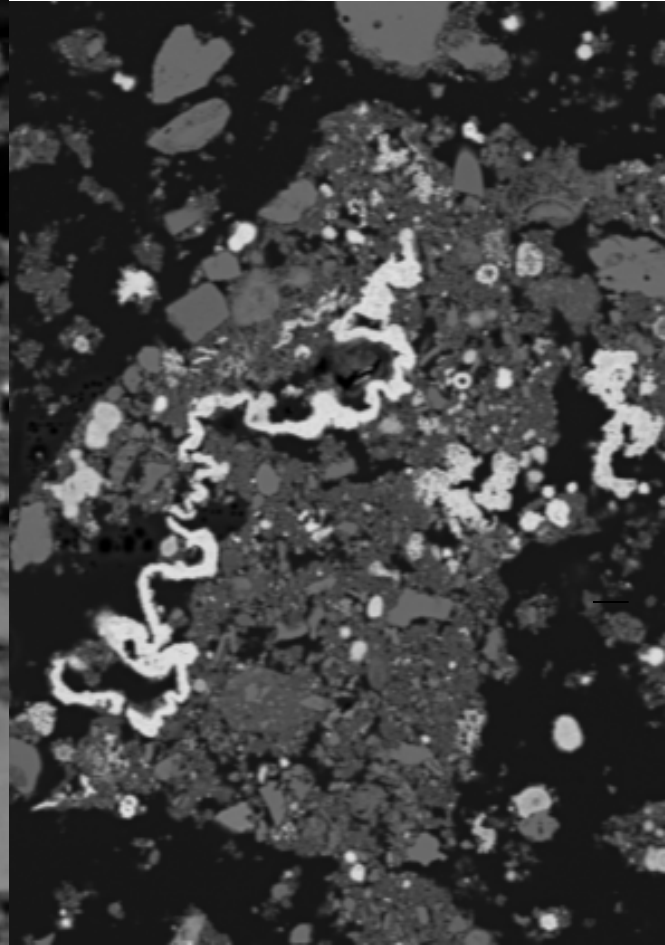


Framboidal Pyrite (FeS₂)

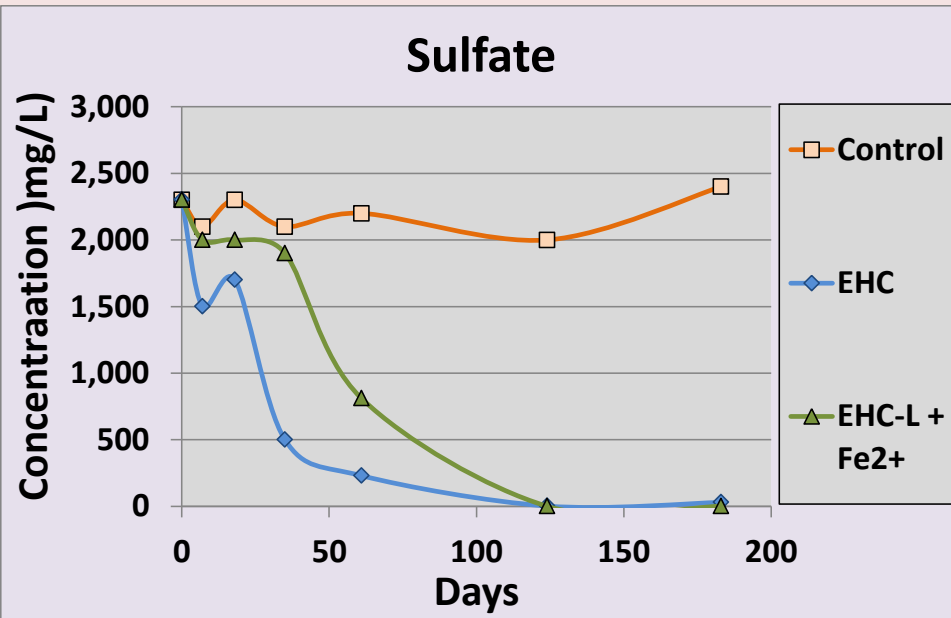
Electron Microprobe - Fe + S Spectra



FeS present as
fine ($\sim 3 - 5 \mu\text{m}$)
coating



Sulfide Precipitation Analytical Results



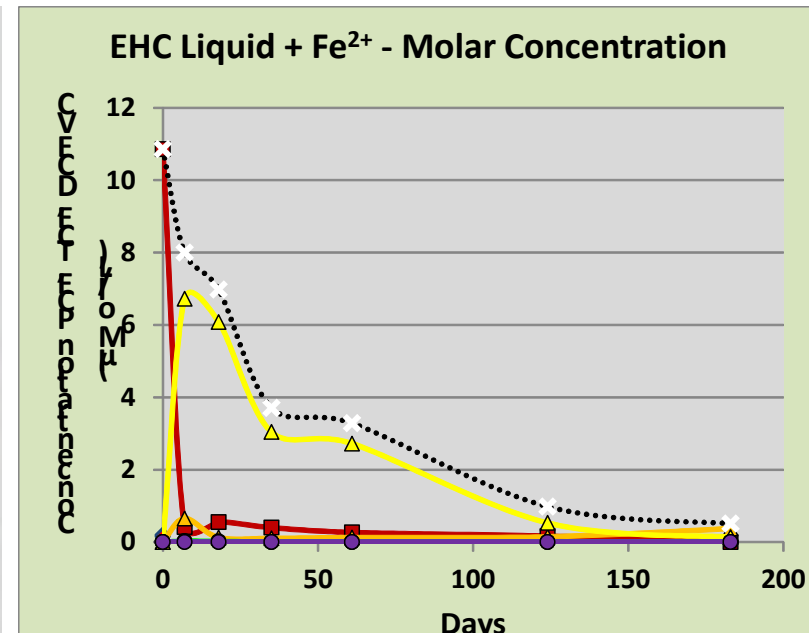
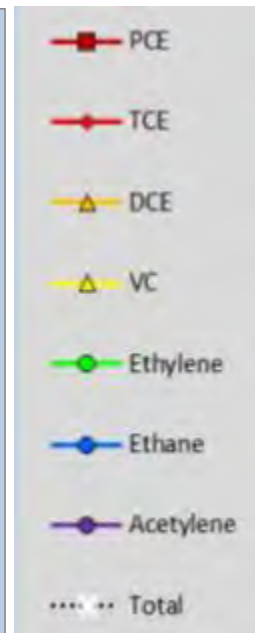
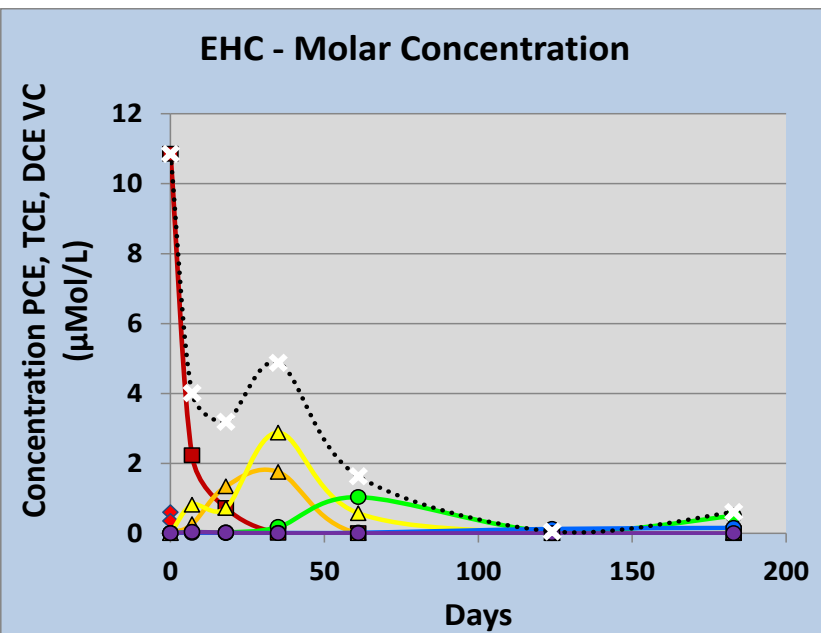
High sulfate concentrations can be reduced

Requires additional electron donor

May require Fe to precipitate sulfide

Electrons are not wasted but stored as FeS

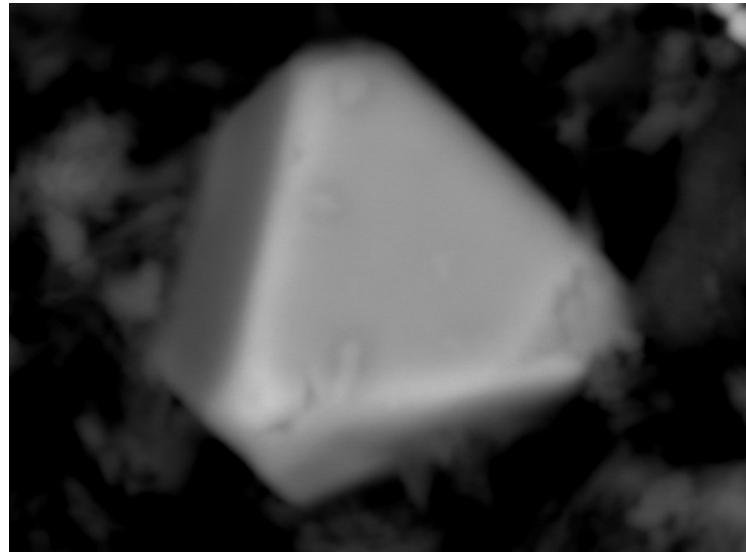
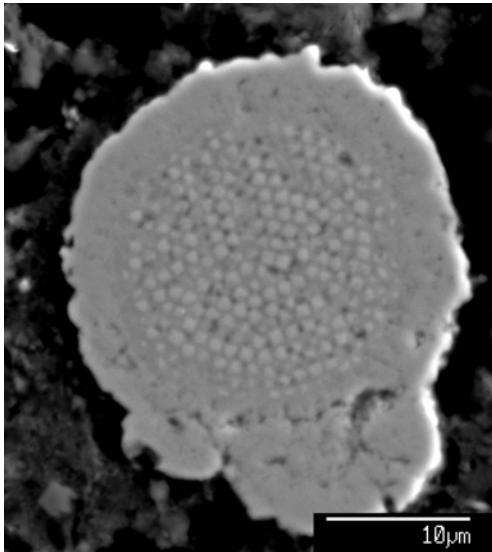
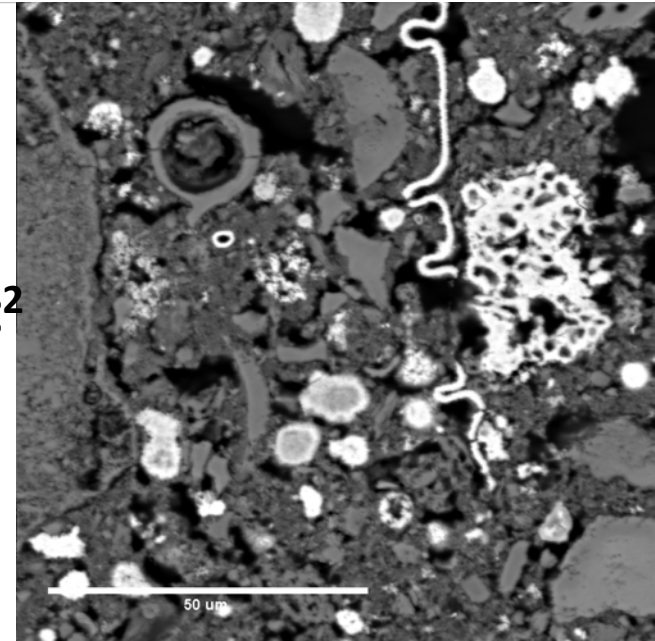
Iron sulfides establish an abiotic pathway



Process generates reactive FeS

3,000 mg/L sulfate + Fe²⁺:

- Produces framboidal and euhedral pyrite
- Produces a 1 to 5 μM thick FeS coating 1.2 ft²
- Large surface area increases rate of biogeochemical degradation



FeS Precipitation

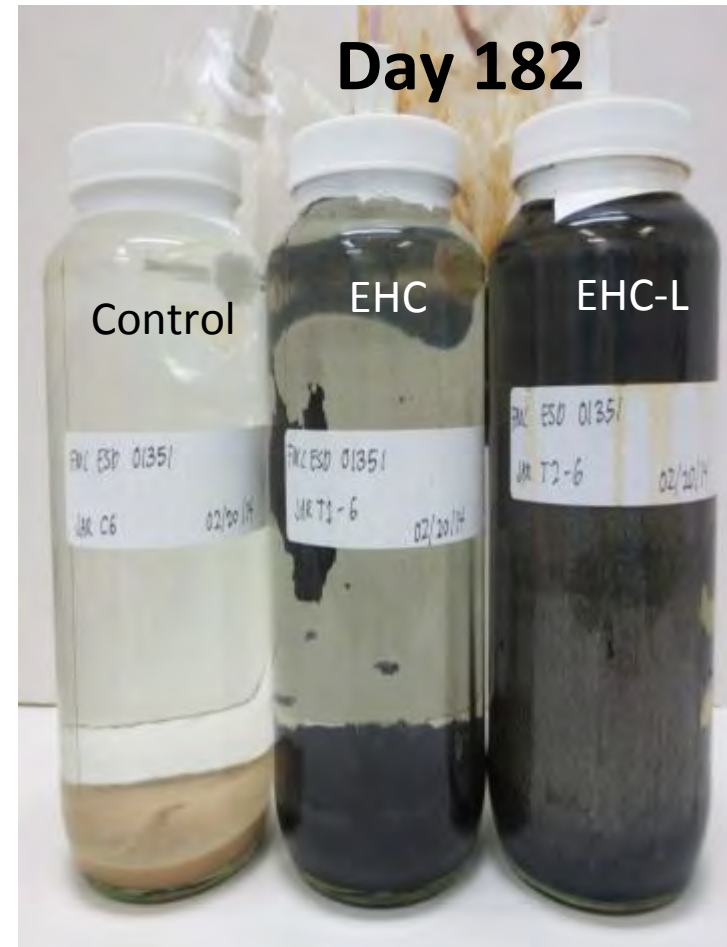
FeS does not fill pore space

Reduction of 1 Liter of 3,000 mg/L of sulfate and precipitation as ferrous sulfide produces:

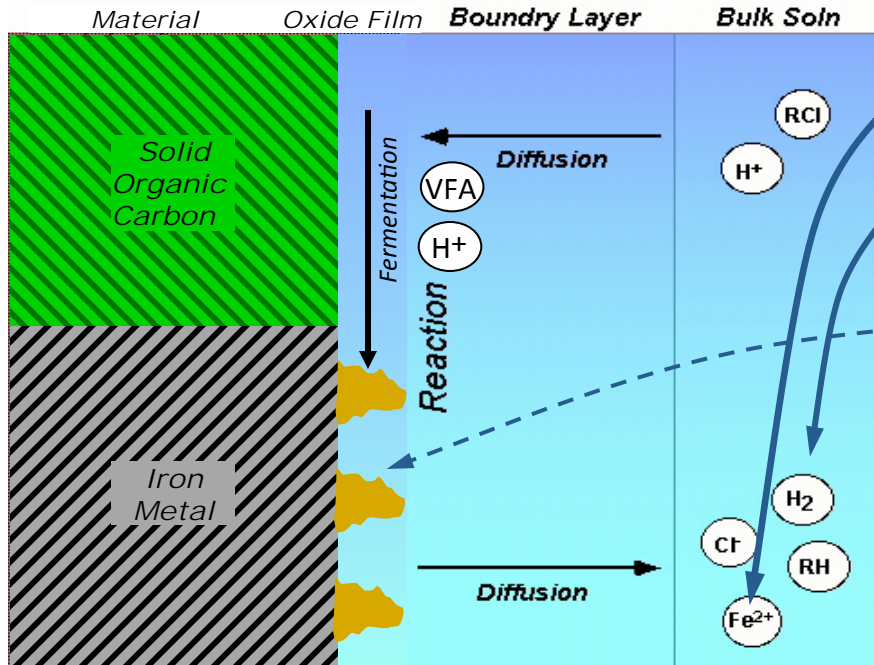
0.56 cm³ Mackinawite (FeS, 4.9 g/cm³)
~0.05% of volume of pore space

0.38 cm³ Pyrite (FeS₂, 4.8 to 5.0 g/cm³)
~ 0.04% of volume of pore space

Significant reductions in hydraulic conductivity would not be expected from FeS precipitation



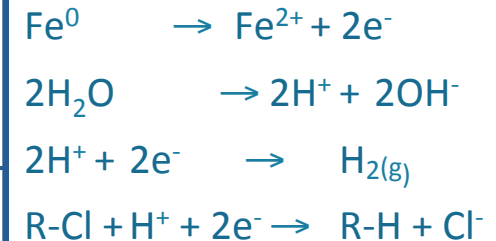
Combining Biotic and Abiotic Processes: Multiple Dechlorination Mechanisms



Fe+2 generation

H₂ generation

ZVI Reactions:



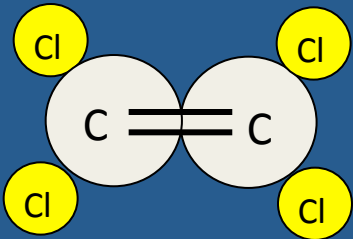
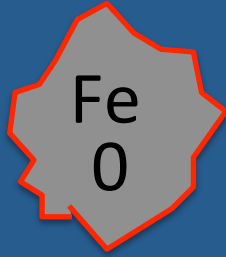
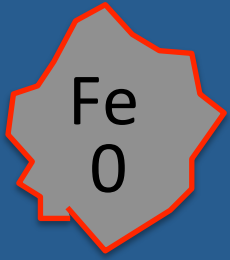
Production of organic acids (VFAs):

- Serves as electron donor for microbial reduction of CVOCs and other oxidized species such as O_2 , NO_3 , SO_4
- The release of acids keeps the pH down and thereby serve to reduce precipitate formation on ZVI surfaces to increase reactivity
- Increase rate of iron corrosion/ H_2 generation

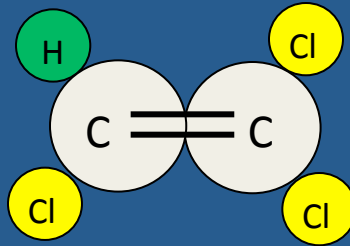
Favorable thermodynamic conditions for dechlorination:

- Combined oxygen consumption from carbon fermentation and iron oxidation \rightarrow Strongly reduced environment (-250 to -500 mV)
- High electron/ H^+ pressure

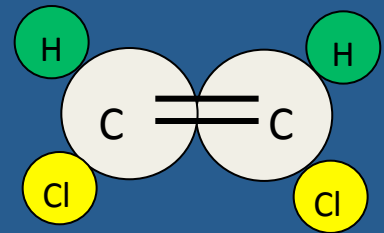
β elimination (abiotic) pathway



PCE

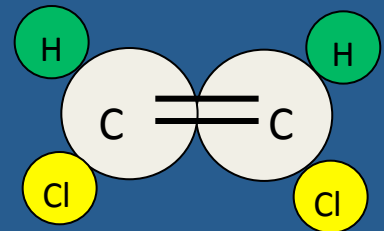
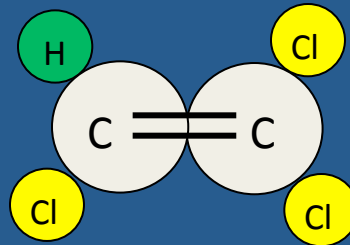
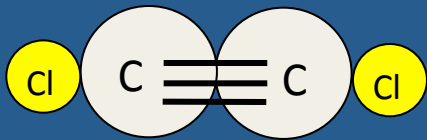
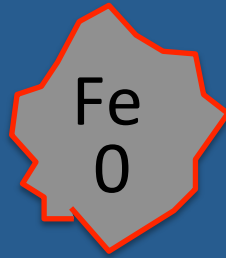


TCE



DCE

β elimination (abiotic) pathway

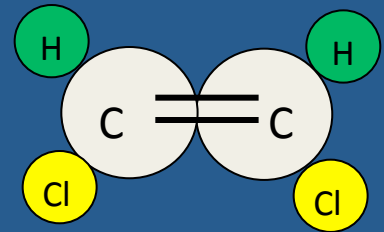
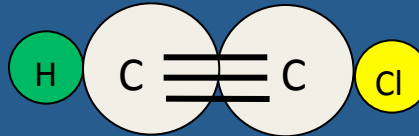
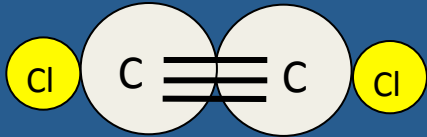


Dichloroacetylene

TCE

DCE

β elimination (abiotic) pathway

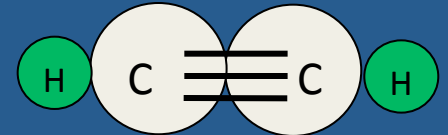
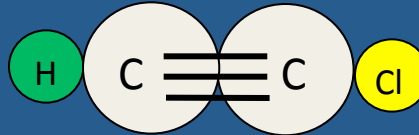
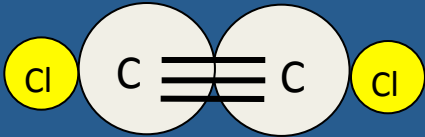


Dichloroacetylene

Chloroacetylene

DCE

β elimination (abiotic) pathway



Dichloroacetylene

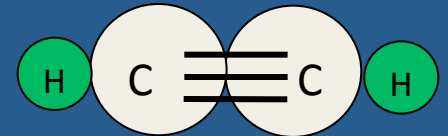
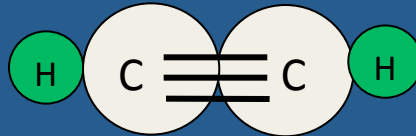
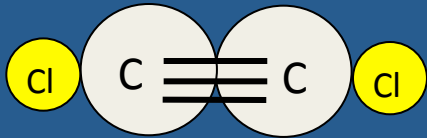
Chloroacetylene

Acetylene

β elimination (abiotic) pathway



Hydrogenolysis



Dichloroacetylene

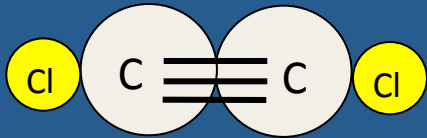
Acetylene

Acetylene

β elimination (abiotic) pathway



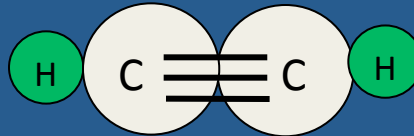
Hydrogenolysis



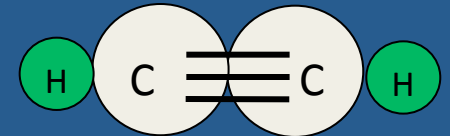
Dichloroacetylene



Acetylene



Hydrogenation

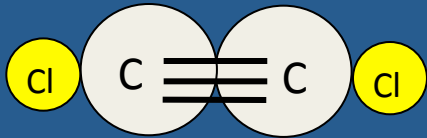


Acetylene

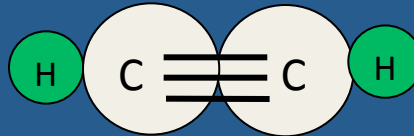
β elimination (abiotic) pathway



Hydrogenolysis



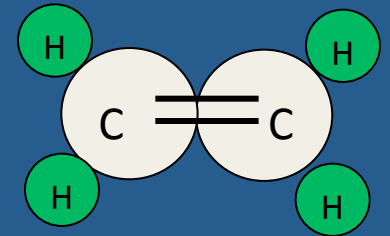
Dichloroacetylene



Acetylene



Hydrogenation

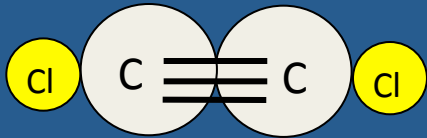


Ethene

β elimination (abiotic) pathway



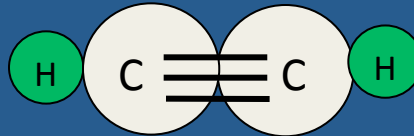
Hydrogenolysis



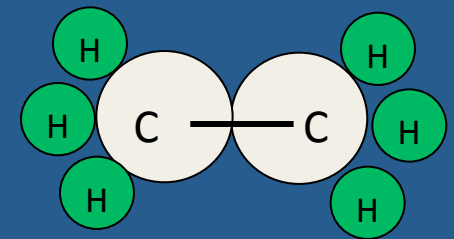
Dichloroacetylene



Hydrogenation



Acetylene



Ethane

Biotic – ISCR Field Comparison

Two Pilot Tests Conducted at Concord Naval Weapon Station

Biotic Only – (2011 – 2012)

In Situ Chemical Reduction (ISCR) – (2013 – 2014)

Biotic Only Approach:

- Direct push, high pressure injection – 6 foot radius
- Injection water preconditioned with sodium lactate
- Emulsified vegetable oil ~6 grams/Liter, (buffered)
- Bioaugmentation (SDC-9™)
- H₂ added to one well

In Situ Chemical Reduction (ISCR) Approach:

- Direct push, fracking and high pressure injection - 10 ' & 15 feet Radius
- Injection water preconditioned with sodium lactate
- Emulsified Lecithin Substrate (ELS) ~3 grams/Liter
- Bioaugmentation (SDC-9™)
- Zero Valent Iron (ZVI) suspended in guar

Design Optimization Test (DOT)

- IL5** Injection Location 15' ROI – 70' TD
- IL4** Injection Location 10' ROI – 98' TD
- IL1** Injection Location 10' ROI – 70' TD

ISCR Well
S29MW01

TCE Plume

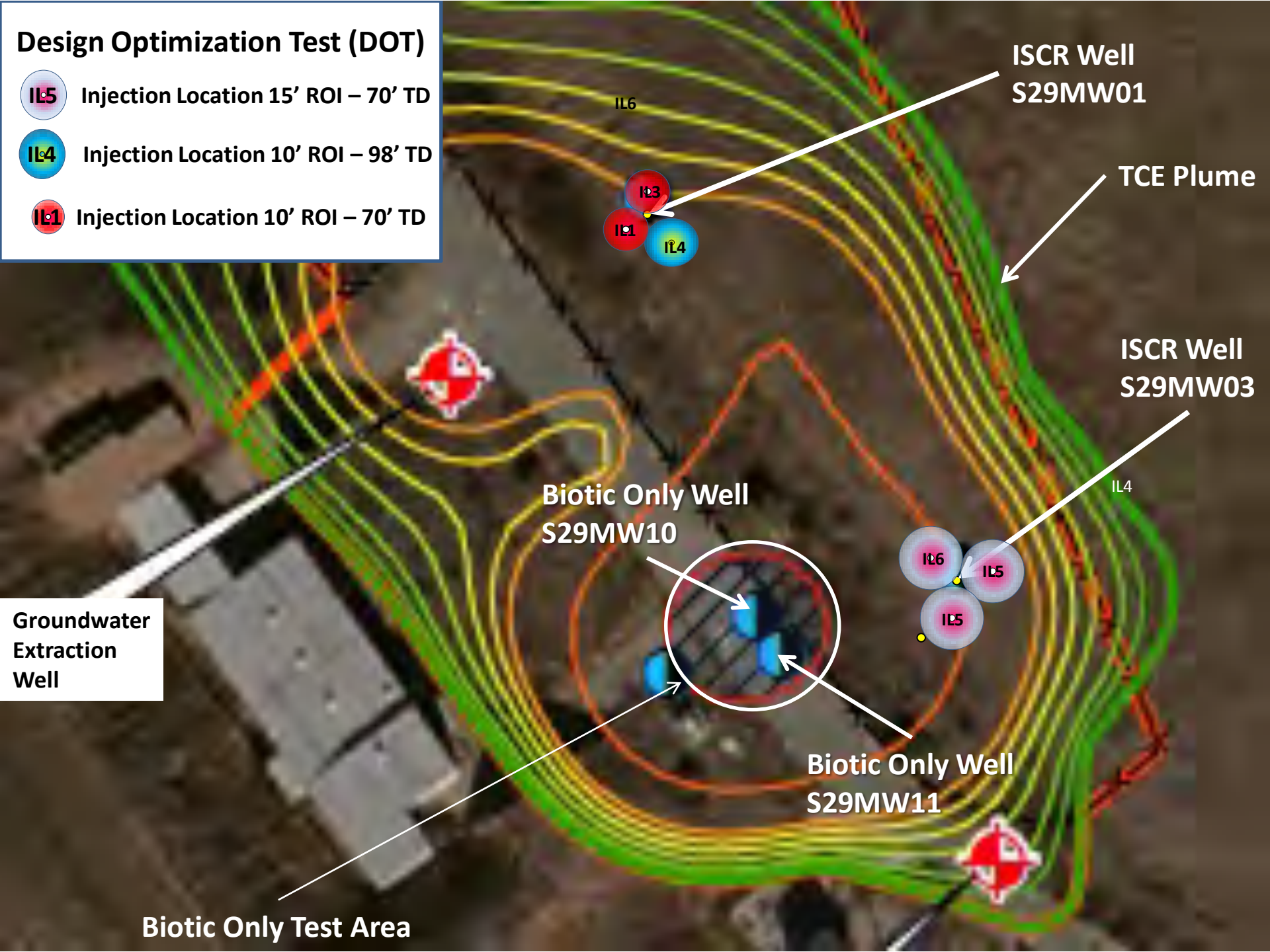
ISCR Well
S29MW03

Biotic Only Well
S29MW10

Biotic Only Well
S29MW11

Groundwater
Extraction
Well

Biotic Only Test Area



Organic Reducing Substrate –ELS – Biotic



Chemical Reductant - Zero Valent Iron - Abiotic

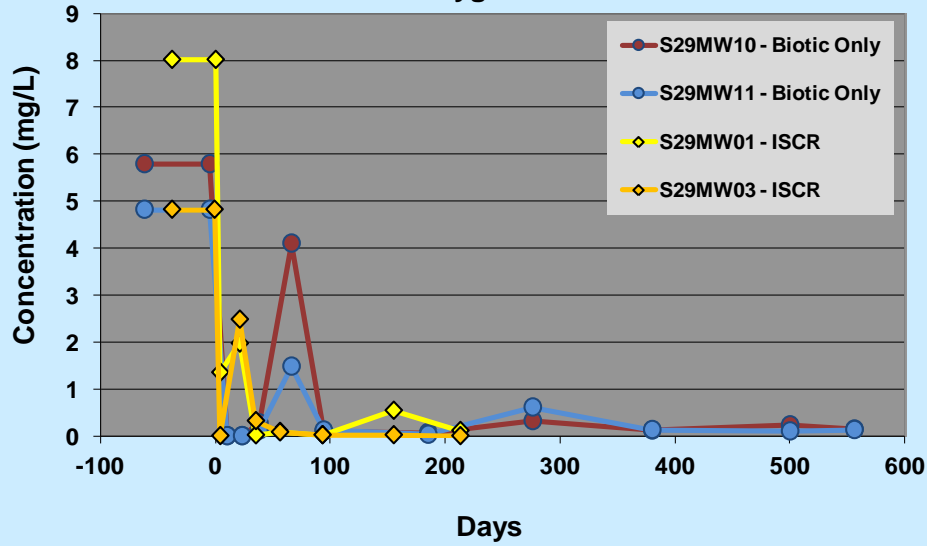
ZVI added to:

- Maintain pH in range favorable for biological degradation
- Bypass generation of toxic daughter products
- Reduction of daughter products more rapidly achieves goals
- Provide long term process for continued dechlorination.

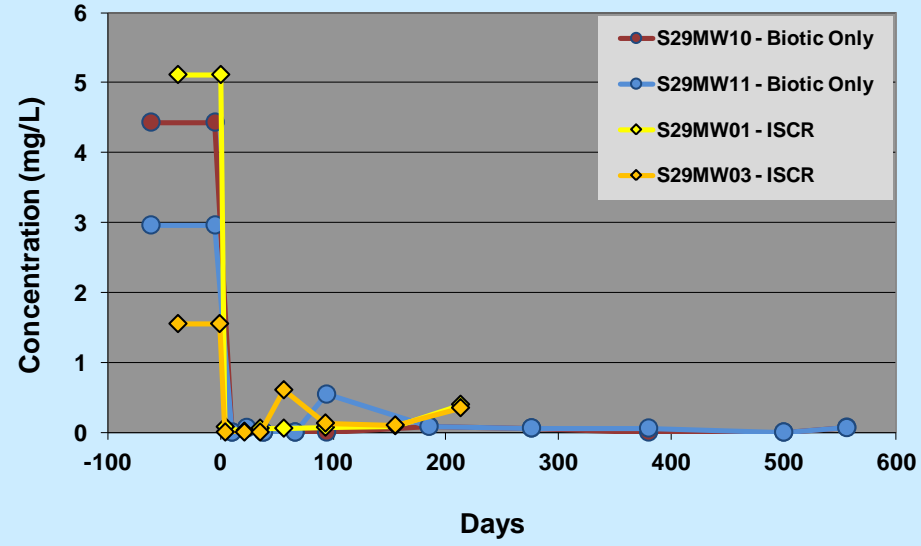


Analytical Results

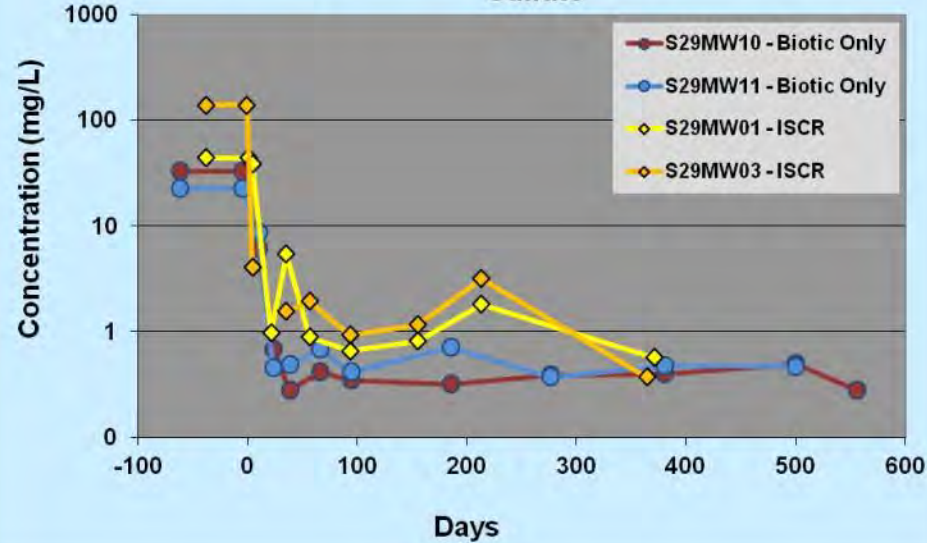
ISCR vs Biotic Only Treatment Comparison Oxygen



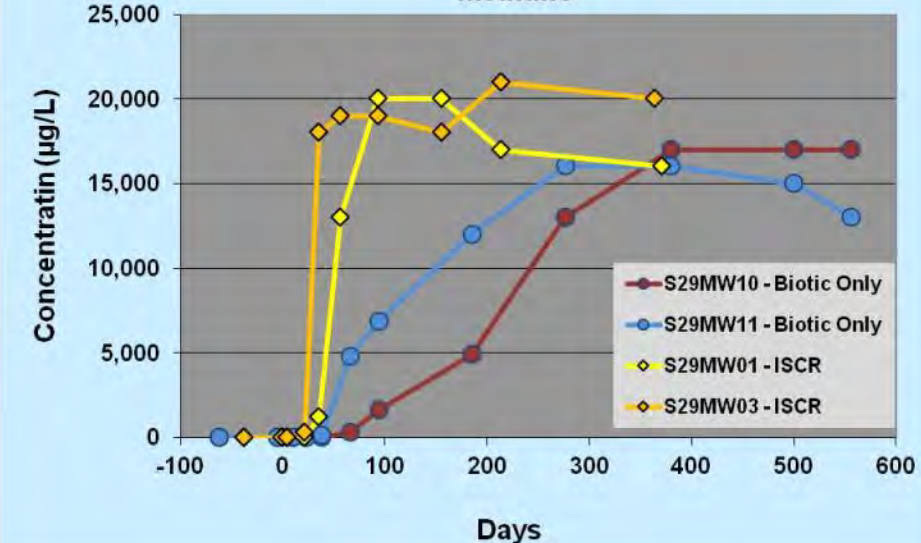
ISCR vs Biotic Only Treatment Comparison Nitrate



ISCR vs Biotic Only Treatment Comparison Sulfate

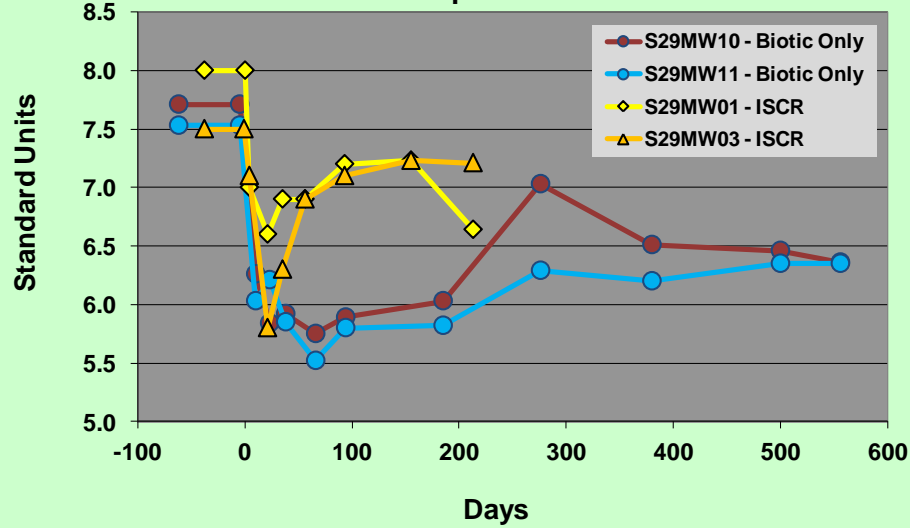


ISCR vs Biotic Only Treatment Comparison Methane

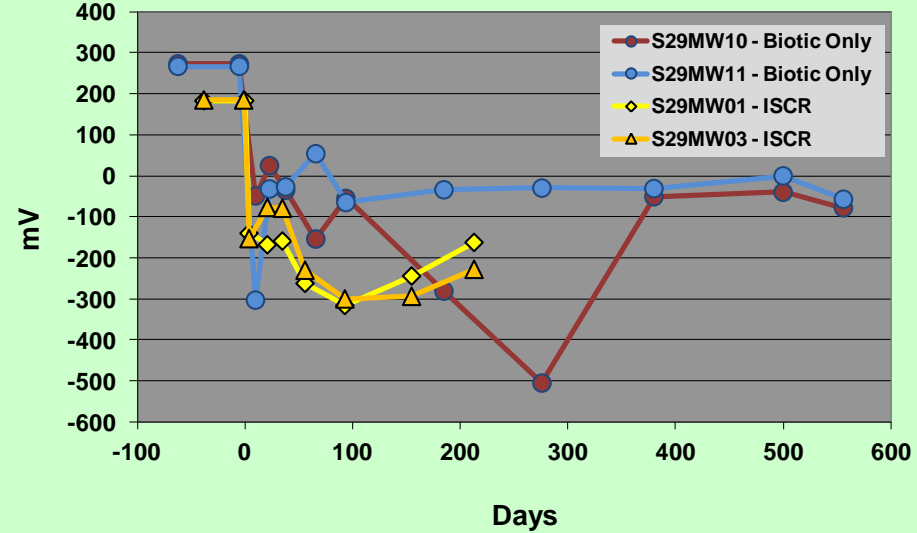


Analytical Results

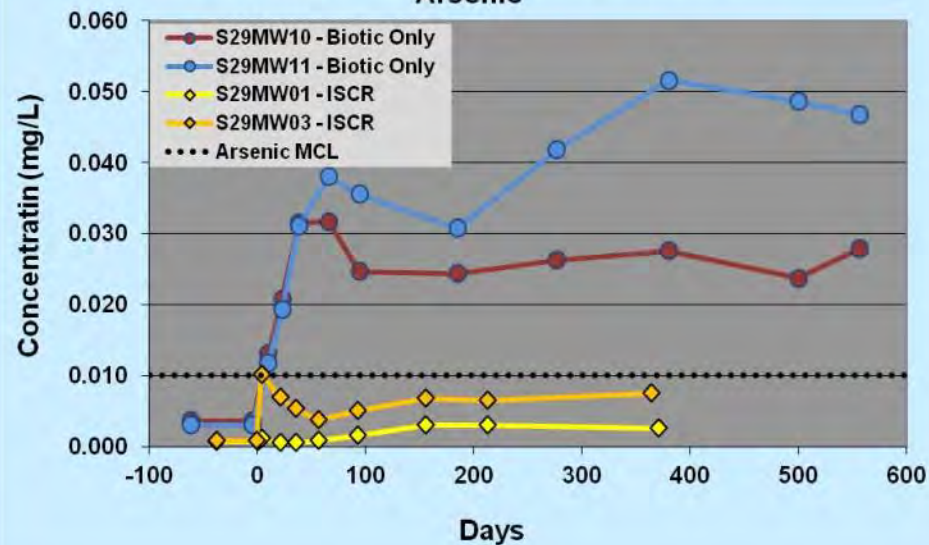
ISCR vs Biotic Only Treatment Comparison
pH



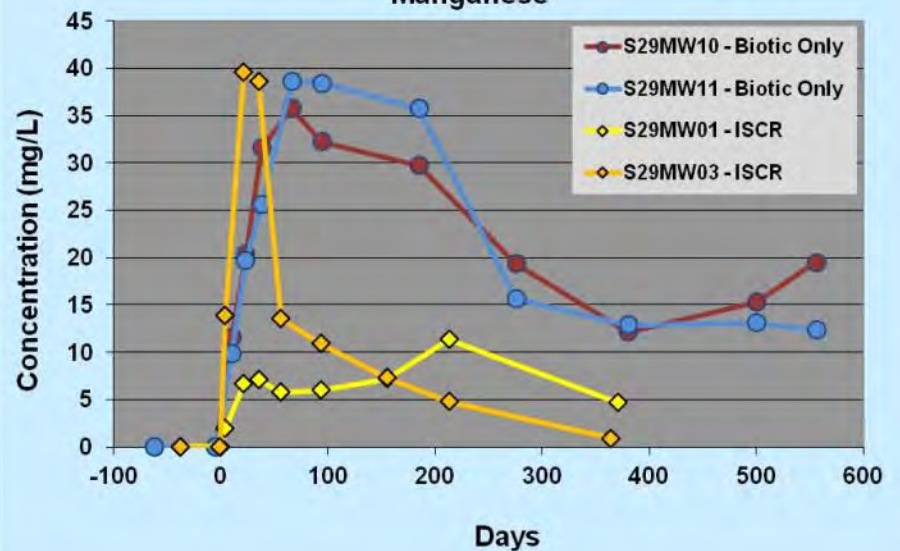
ISCR vs Biotic Only Treatment Comparison
Oxidation-Reduction Potential



ISCR vs Biotic Only Treatment Comparison
Arsenic

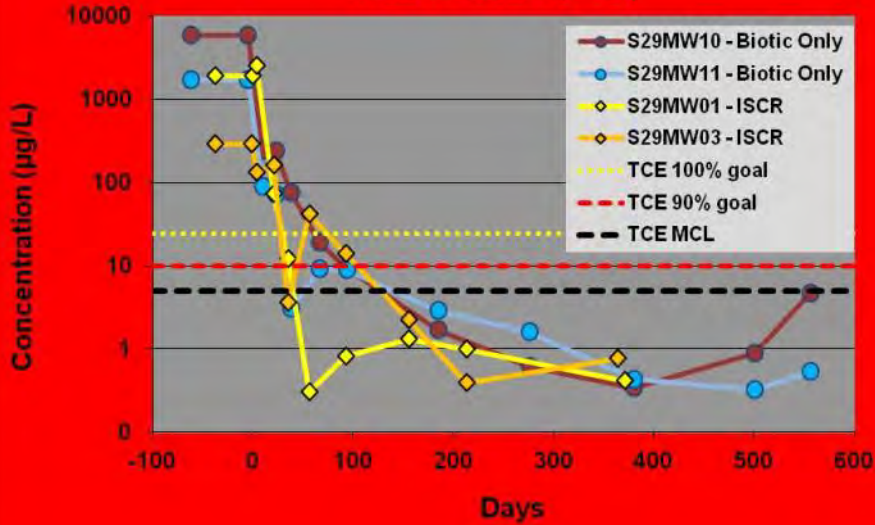


ISCR vs Biotic Only Treatment Comparison
Manganese

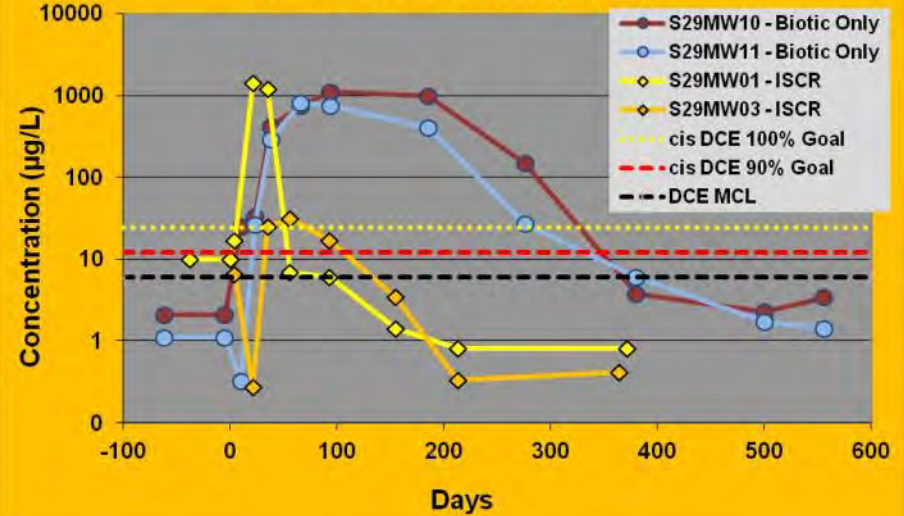


Analytical Results

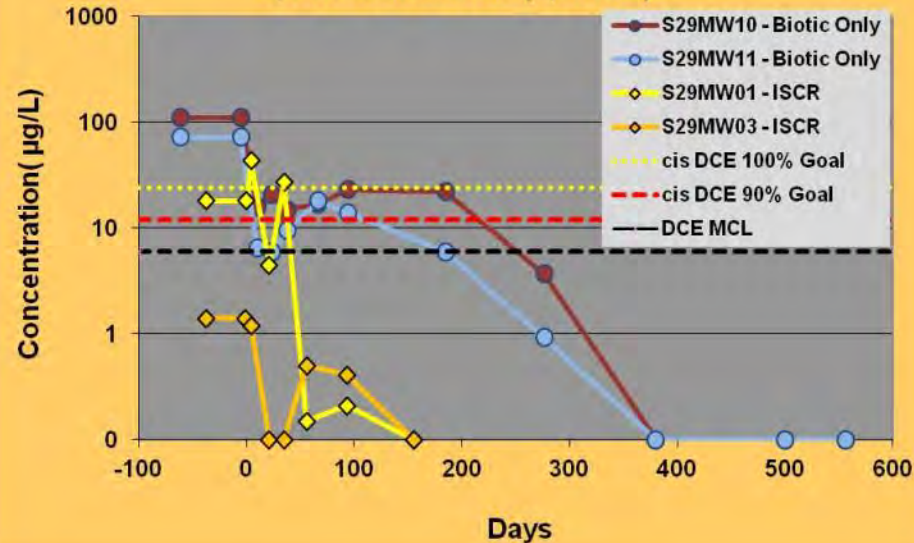
ISCR vs Biotic Only Treatment Comparison Trichloroethene (TCE)



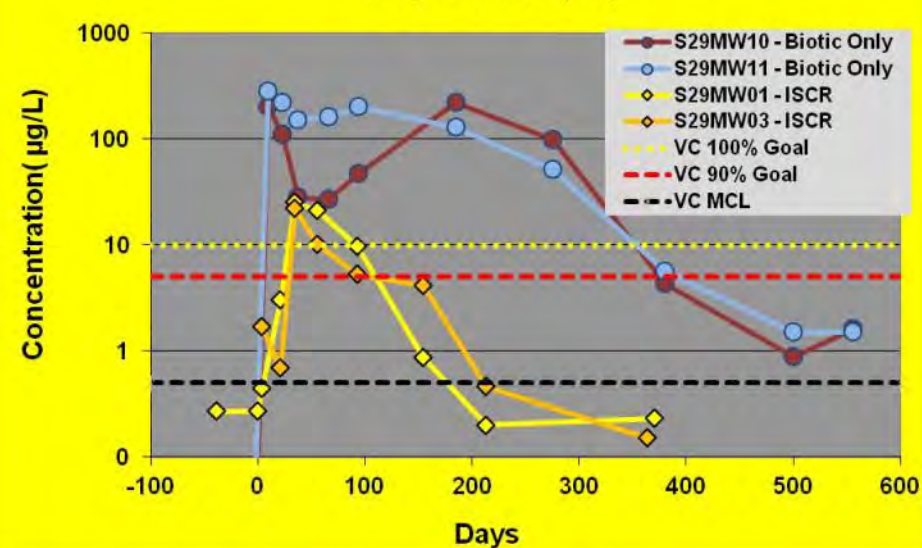
ISCR vs Biotic Only Treatment Comparison cis 1,2-Dichloroethene (cDCE)



ISCR vs Biotic Only Treatment Comparison 1,1-Dichloroethene (1,1-DCE)

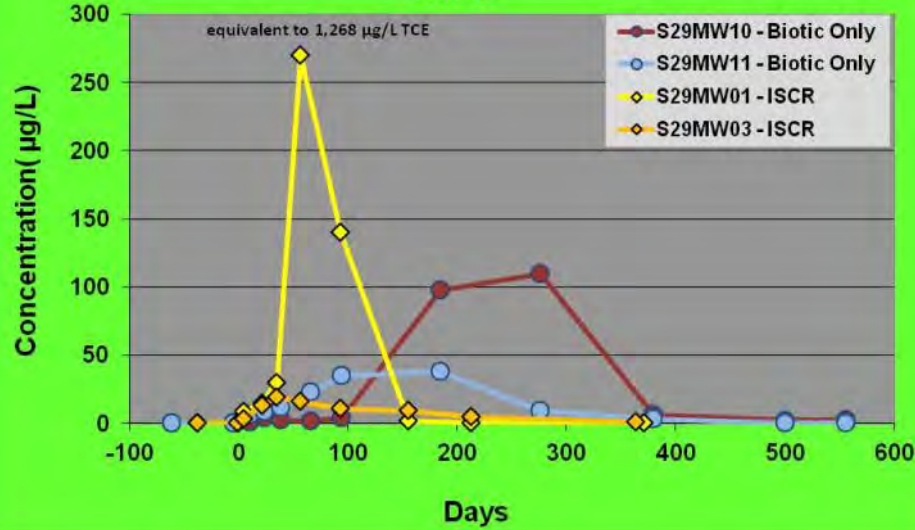


ISCR vs Biotic Only Treatment Comparison Vinyl Chloride (VC)

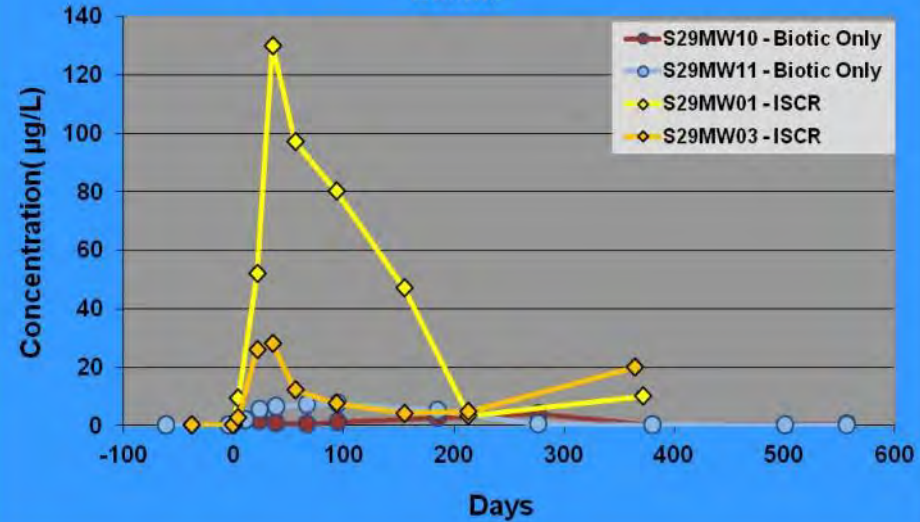


Analytical Results

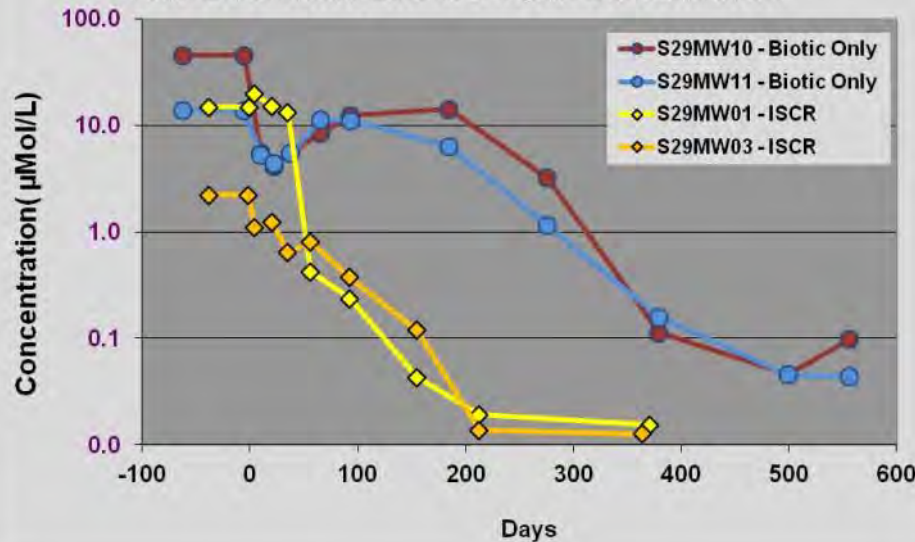
ISCR vs Biotic Only Treatment Comparison
Ethene



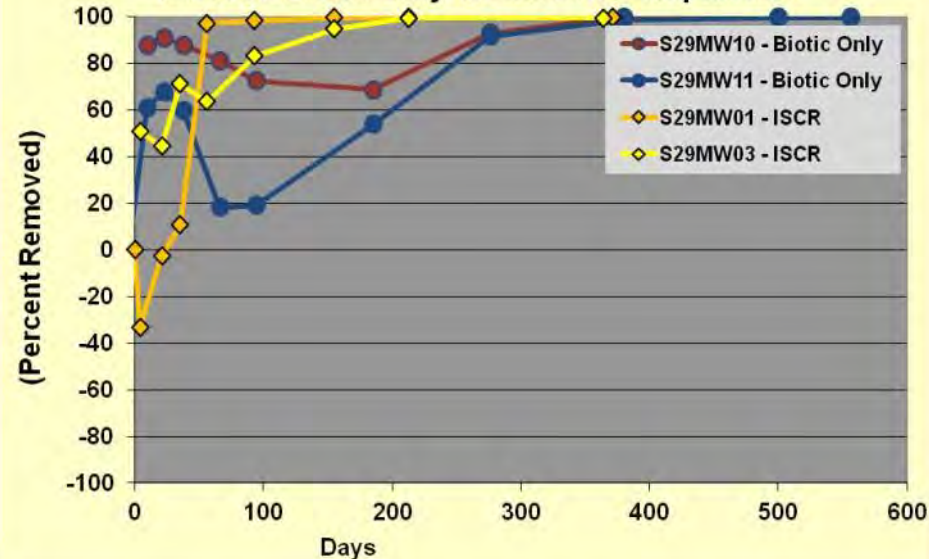
ISCR vs Biotic Only Treatment Comparison
Ethane



ISCR vs Biotic Only Treatment Comparison
Total Chlorinated Ethenes - Molar Concentration



Chlorinated Ethene Molar Removal
ISCR vs Biotic Only Treatment Comparison



Considerations when applying biotic and abiotic reductive processes.

- Difficult to achieve equal distribution so changes in GW geochemistry are not the same everywhere
- Addition of water will tend to push the plume.
- Potable water has different geochemistry than site groundwater, consider DO, pH, chlorine,
- Adding organic substrate will drop the pH ~ 1 to 2 SU
- Distribution of organic substrate in highly heterogeneous aquifers through wells may only treat permeable zones.
- Distribution of substrate in low permeability zones difficult, may require fracturing or exotic technology (electrokinetics)

Considerations when applying bioremediation processes.

- Substrates do not release hydrogen at the same rate
- Substrates do not transport the same rates
- Consider changes in substrate concentration by dilution and dispersion when injecting substrates
- Difficult to determine population of organisms in situ
- Every site is different so don't get used to applying the same processes just because it worked last time.
- Consider combining substrates, approaches and technologies

Questions?

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