PeroxyChem

Design Considerations for Enhanced Reductive Dechlorination

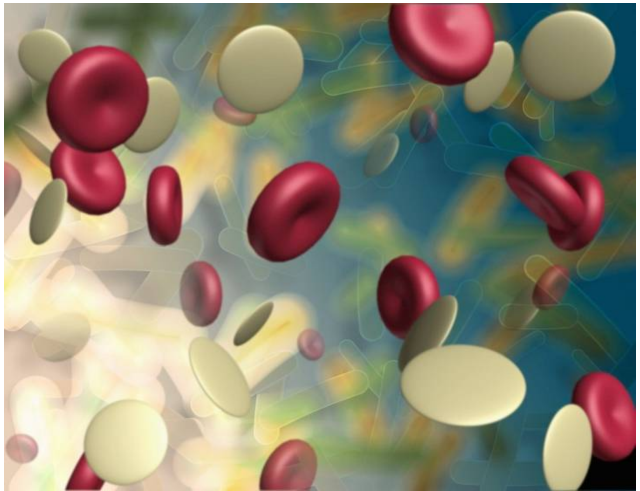
Dan Leigh PG, CHg

Webinar May 13, 2015

Presentation Outline

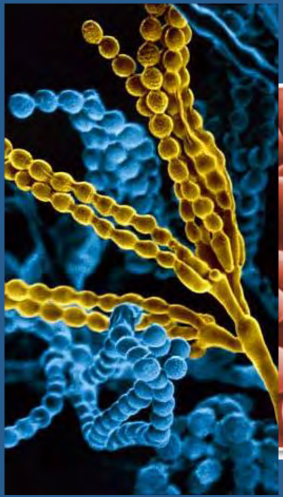
Introduction Dan Leigh P.G., C. Hg. – Peroxychem Environmental Solutions

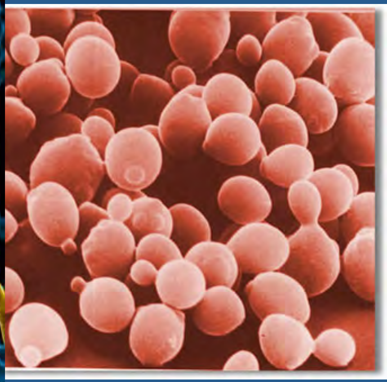
- **Basic concepts of biological and geochemical processes**
  - Respiration, fermentation, co metabolism
  - Electron acceptors and donors
  - Biotic and abiotic anaerobic degradation pathways of chlorinated ethenes
  - Enhancing aerobic and anaerobic bioremediation
  - Calculating substrate requirements
- **Site conditions considered not conducive to anaerobic bioremedation**
  - 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)

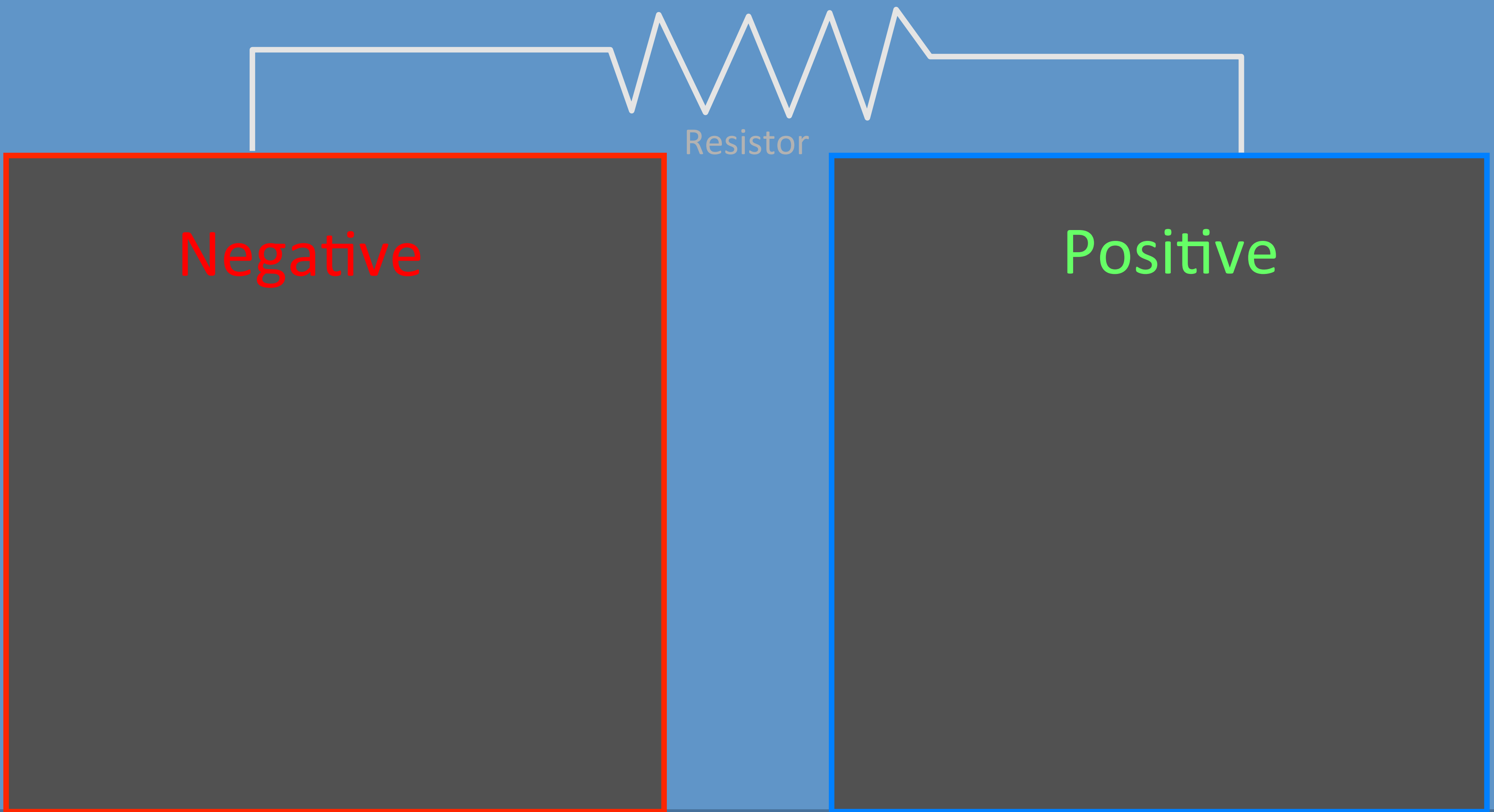
- Biotic and abiotic reductive degradation processes occur in distinct identifiable pathways.

Biologically Mediated Oxidation - Reduction

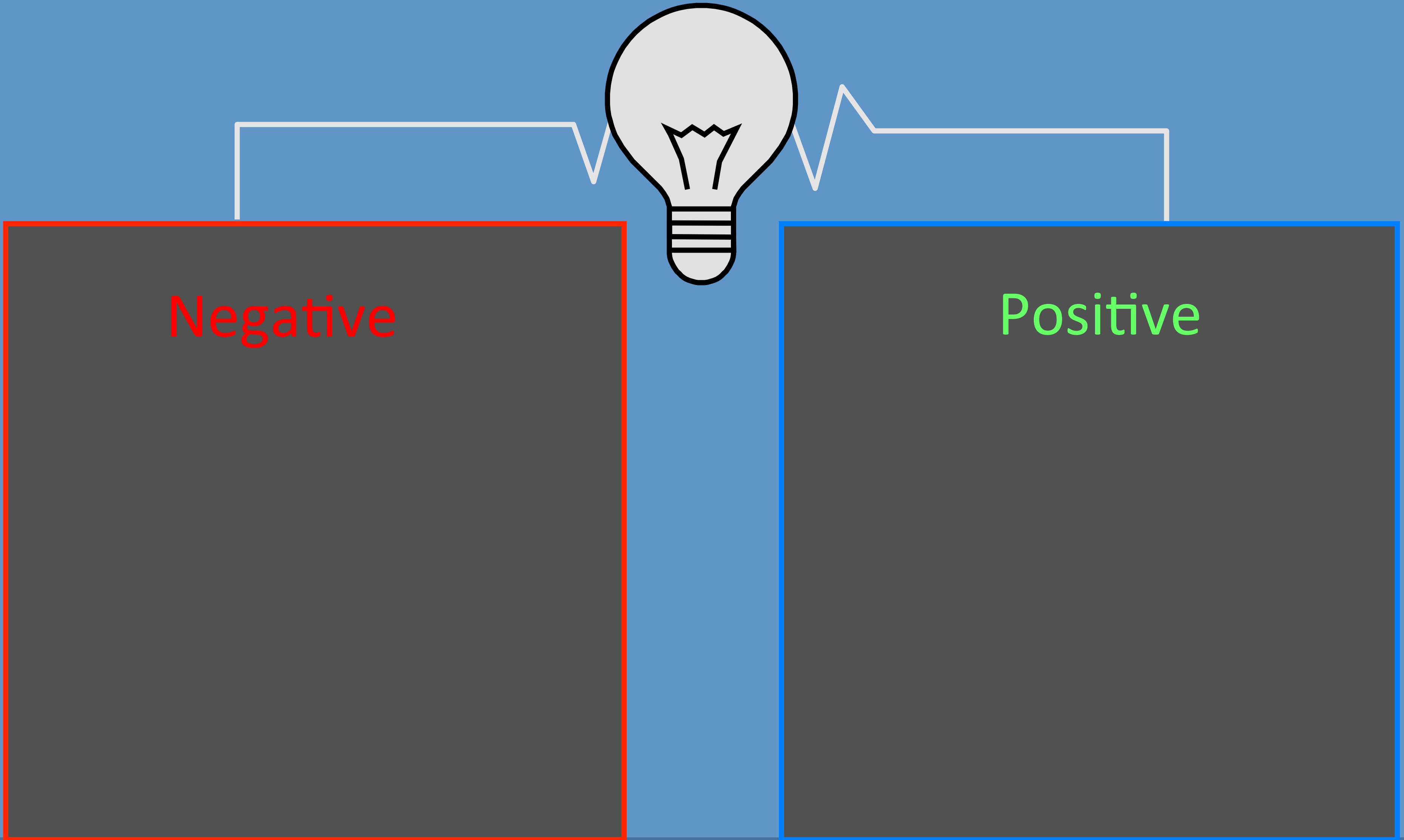
Negative

Positive

Biologically Mediated Oxidation - Reduction



Biologically Mediated Oxidation - Reduction



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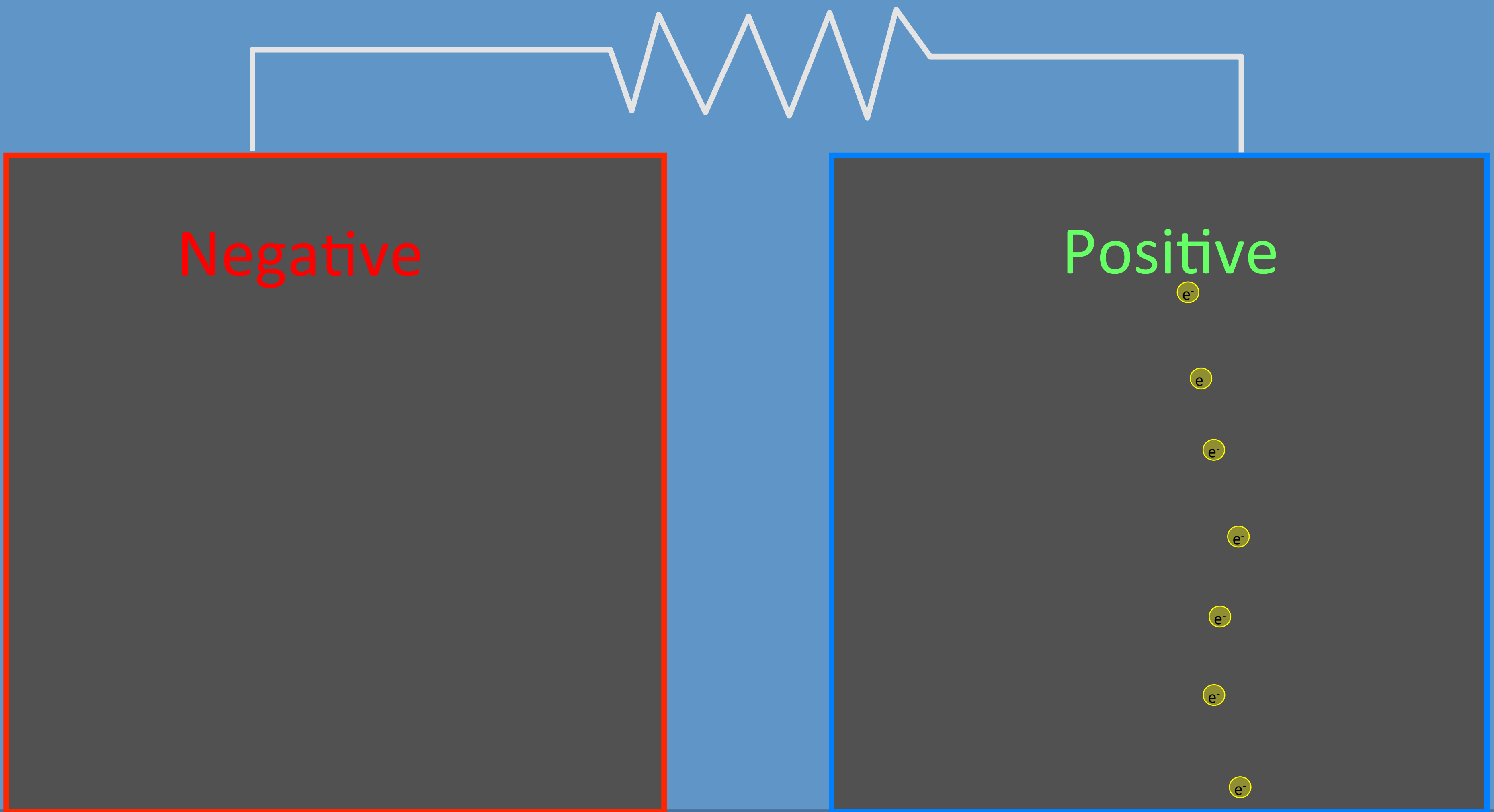
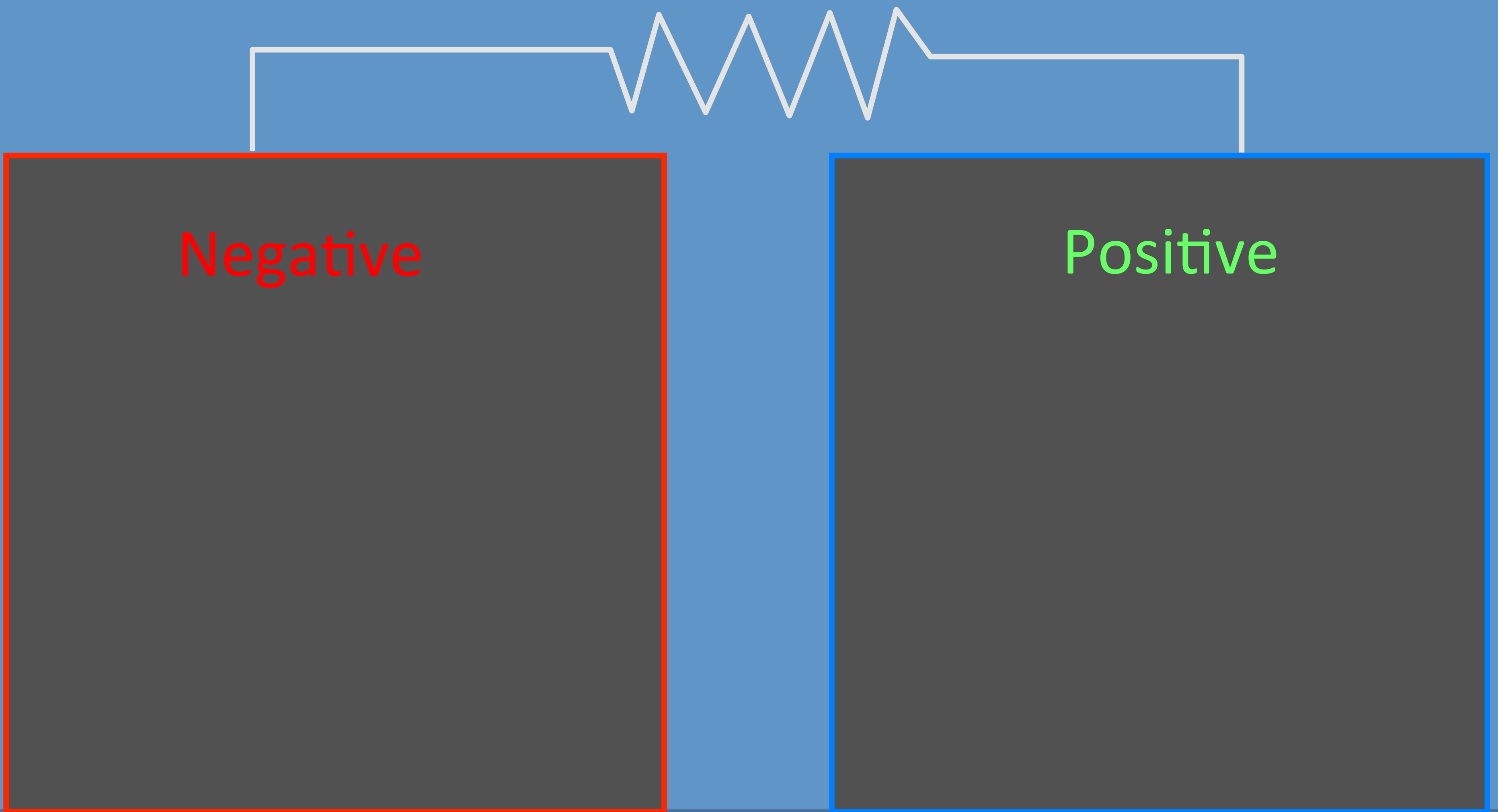


Biologically Mediated Oxidation - Reduction



Biologically Mediated Oxidation - Reduction

Negative

Positive

Biologically Mediated Oxidation - Reduction

Electron Donor

Reduced

C_nH_n

HNO_2

As(III)

Mn(II)

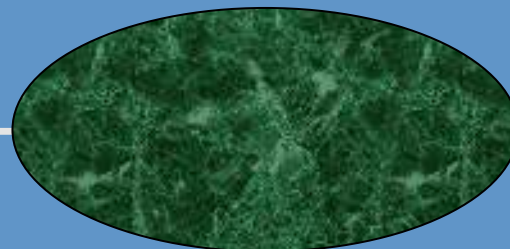
Fe(II)

H_2S

H_2

Electron Acceptor

Biologically Mediated Oxidation - Reduction



Electron Donor

Reduced

C_nH_n

HNO_2

As(III)

Mn(II)

Fe(II)

H_2S

H_2

Electron Acceptor

Oxidized

O_2

NO_3

As(V)

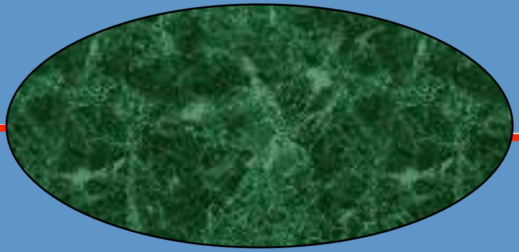
Mn(IV)

Fe (III)

SO_4

CO_2

Biologically Mediated Oxidation - Reduction



Electron Donor

Reduced | Oxidized

C_nH_n e⁻

HNO_2 e⁻

As(III) e⁻

Mn(II) e⁻

Fe(II) e⁻

H_2S e⁻

H_2 e⁻

Electron Acceptor

Reduced | Oxidized

O_2

NO_3

As(V)

Mn(IV)

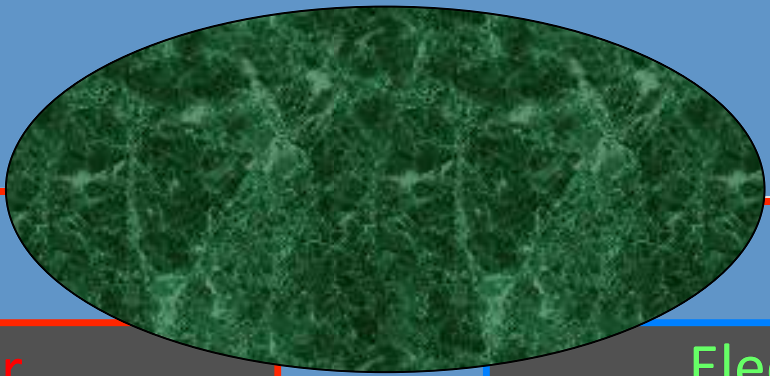
Fe (III)

SO_4

CO_2

Biologically Mediated Oxidation - Reduction

Growth
Protein Synthesis
Reproduction



Electron Donor

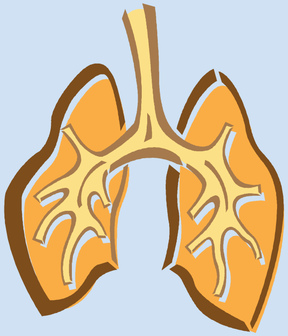
Reduced		Oxidized
C_nH_n	→	$CO_2 + H_2O$
HNO_2	→	NO_3
As(III)	→	As(V)
Mn(II)	→	Mn(IV)
Fe(II)	→	Fe(III)
H_2S	→	$H_2O + SO_4$
H_2	→	H_2O

Electron Acceptor

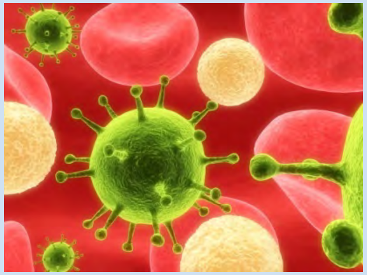
Reduced		Oxidized
$H_2O + CO_2$	←	e^- O_2
HNO_2	←	e^- NO_3
As(III)	←	e^- As(V)
Mn(II)	←	e^- Mn(IV)
Fe (II)	←	e^- Fe (III)
$H_2S^- + H_2O$	←	e^- SO_4
CH_4	←	e^- CO_2

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.**

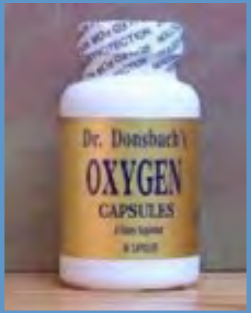
- **Fermentation uses a reduced carbon source (e.g. cellulose, lecithin, lactose, sugars).**
  - **to generate volatile fatty acids (VFAs e.g. lactic, acetic, propionic, valeric, butyric acids)**
  - **and gases (e.g. H_2, CO_2, CH_4)**

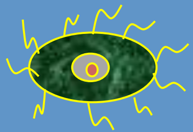
- **H_2 is used by dechlorinating bacteria to degrade chlorinated organics by chlororespiration.**

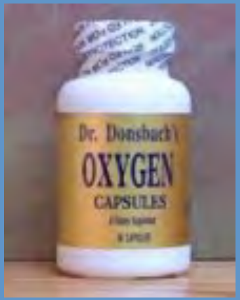
Aerobic Respiration Process

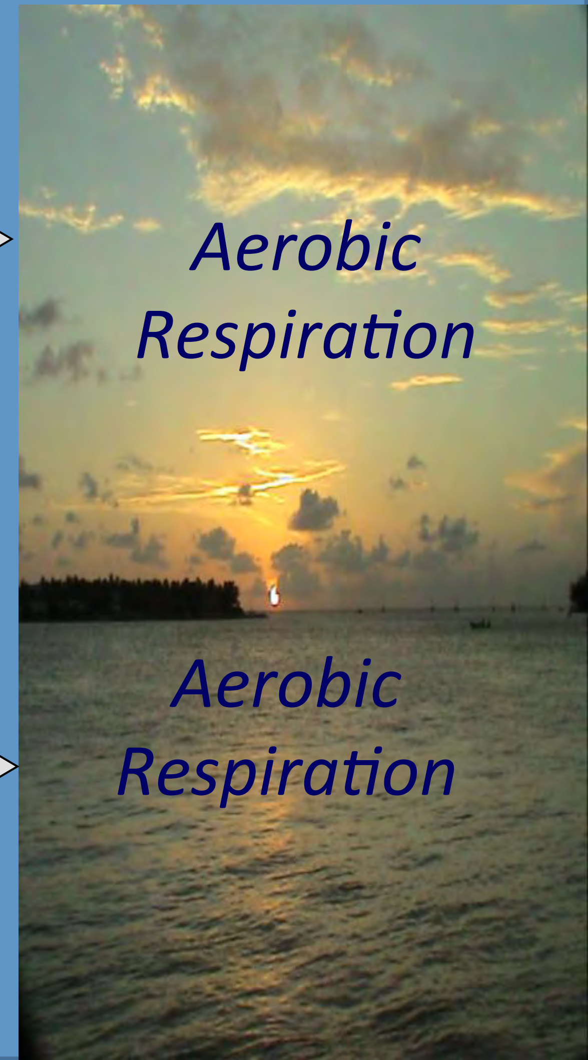
$C_6 H_6 + 12 O_2 \rightarrow 6 CO_2 + 6 H_2O$

Eat & Breathe

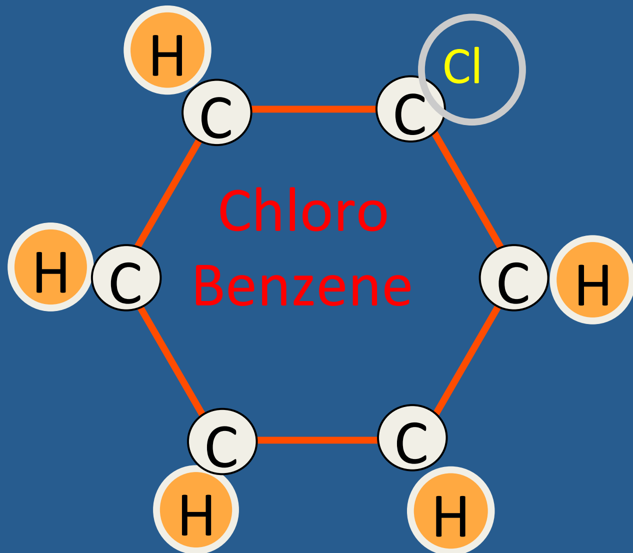


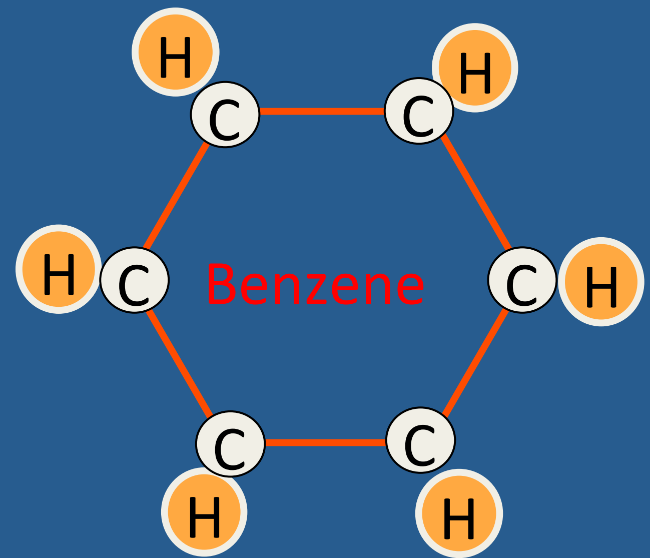


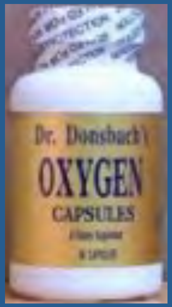




Direct Oxidation –
Aerobic Biodegradation of Benzene and Chlorobenzene







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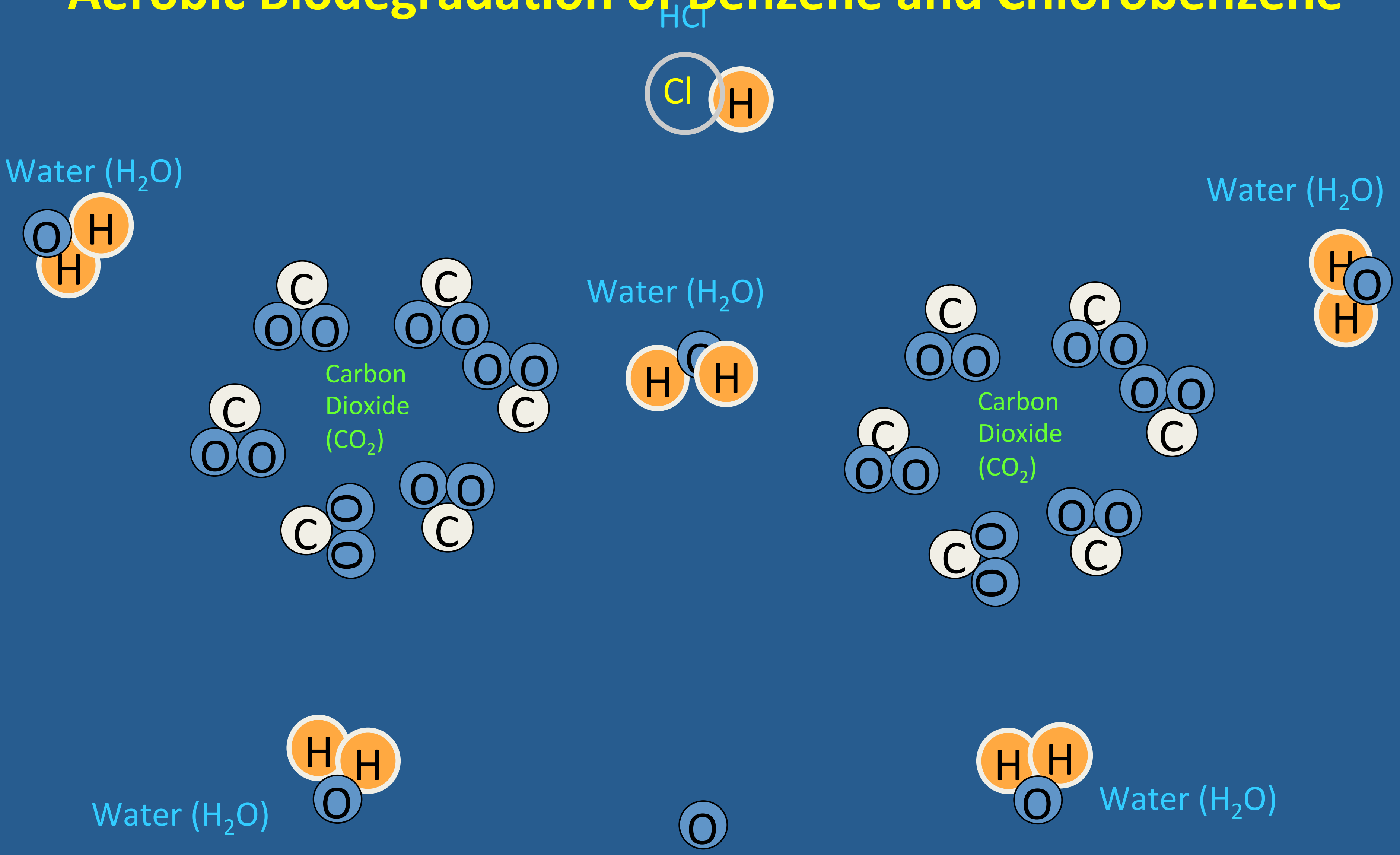
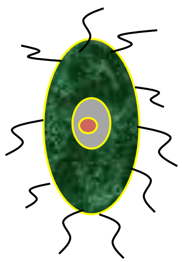


Anaerobic and aerobic respiration are similar

Biota + Electron Donor + Electron Acceptor → *Respiration*

 + 

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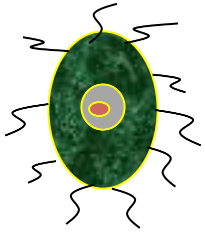
→ *Anaerobic Respiration*

 + 

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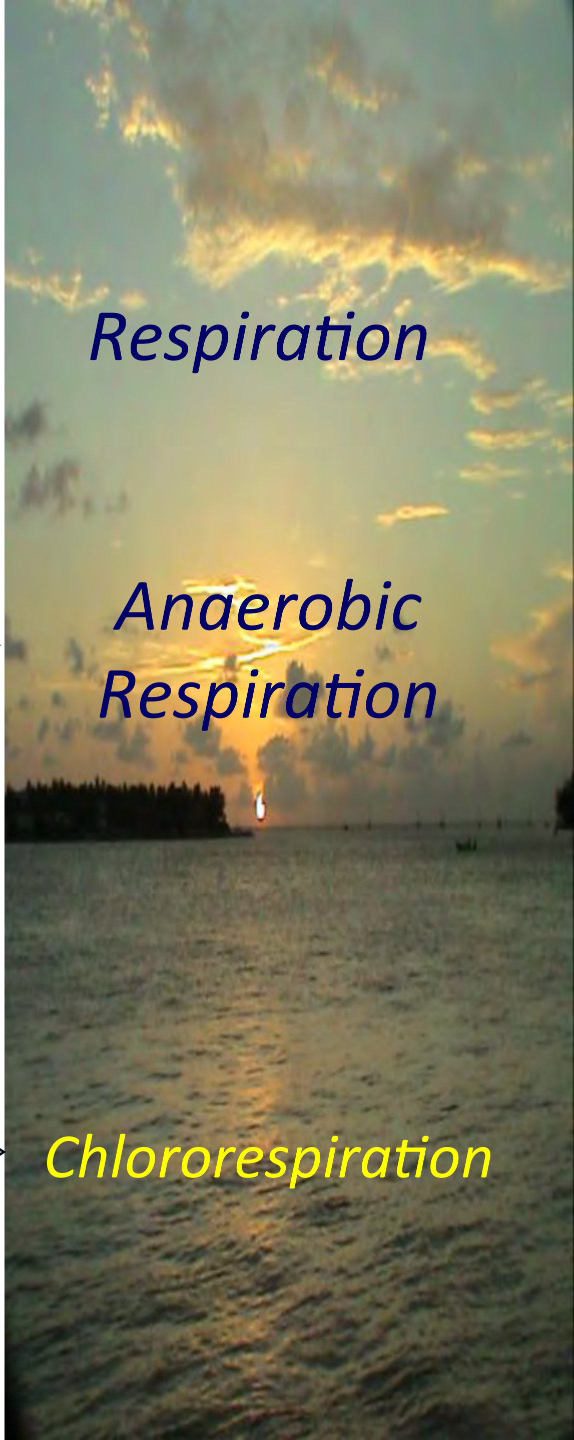
→ *Chlororespiration*



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

1000

Anaerobic

Aerobic

Anaerobic

500

0 0

-250

Chromium (VI) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ $(Eh^0 = +1330)$

Oxygen $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $(Eh^0 = +820)$

Nitrate $2NO_3^- + 12H^+ + 10e^- \longrightarrow N_{2(g)} + 6H_2O$ $(Eh^0 = +740)$

Perchlorate $ClO_4^- + 4H_2O + 8e^- \rightarrow Cl^- + 8OH^-$ $(Eh^0 560)$

Arsenic (V) $H_3AsO_4 + 2H^+ + 2e^- \longrightarrow H_3AsO_3 + H_2O$ $(Eh^0 = +559)$

Manganese (IV) $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_20$ $(Eh^0 = {}^{+}520)$

Redox Potential (Eh^0) in Millivolts @ pH = 7 and T = 25^{0}C

Range for Effective Chlorinated Ethene Degradation (chlororespiration)

PCE → **TCE**

Iron $FeOOH(s) + HCO_3^- + 2H + e^- \longrightarrow FeCO_3 + 2H_2O$ $(Eh^0 = {}^{-}50)$

TCE → **DCE**

DCE → **VC**

Sulfate $SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS- + 4H_2O$ $(Eh^0 = {}^{-}220)$

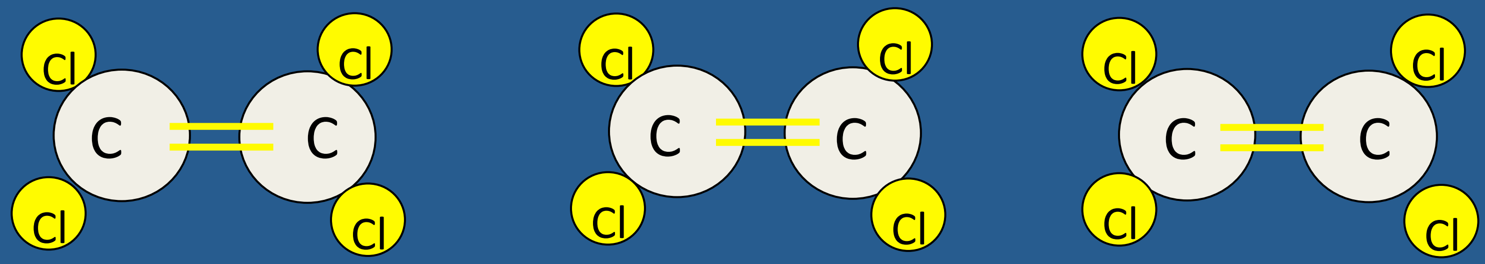
VC → **Ethene**

Methanogenesis $CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$ $(Eh^0 = {}^{-}240)$

Biological Reductive Dechlorination of Chlorinated Ethenes

ORP

0



PCE PCE PCE

Biological Reductive Dechlorination of Chlorinated Ethenes

ORP

0

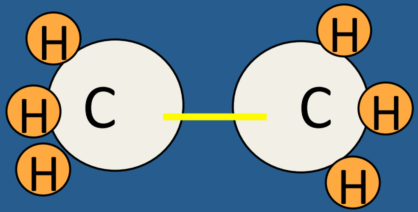
- 50

- 150

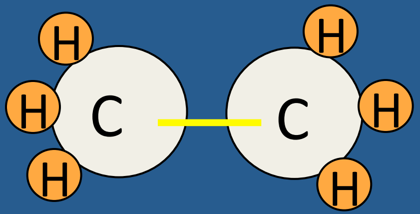
- 200

- 250

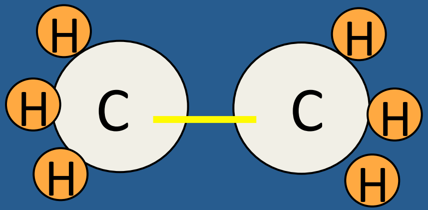
-300



Ethane



Ethane

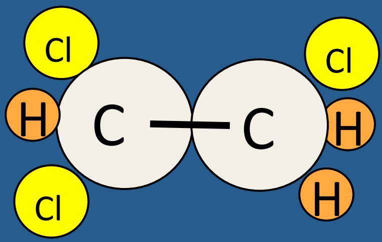


Ethane

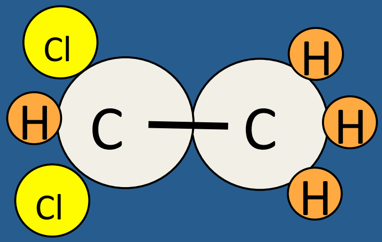
Dichloroelimination of Chlorinated Ethanes

ORP

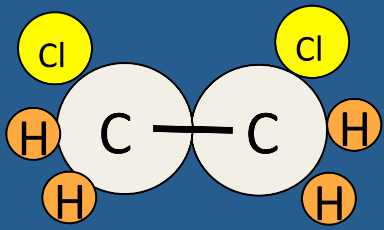
0



1,1,2-TCA

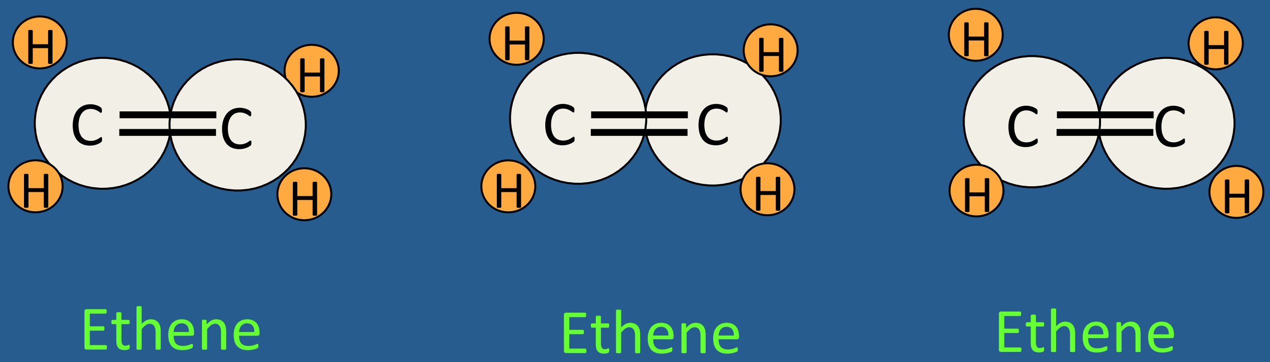


1,1-DCA

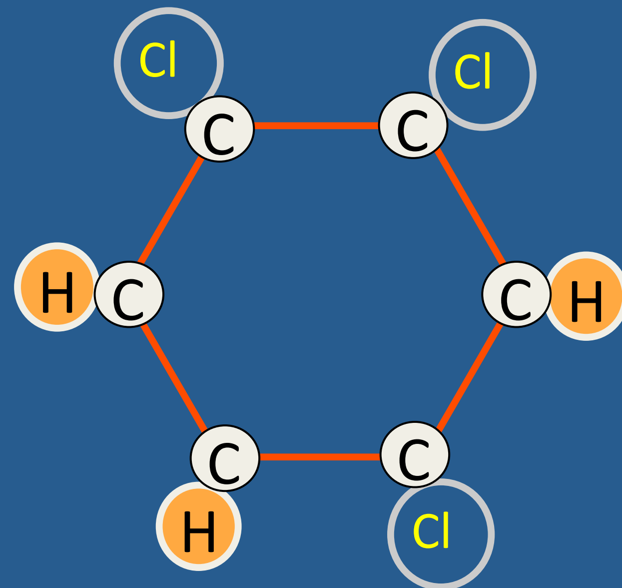


1,2-DCA

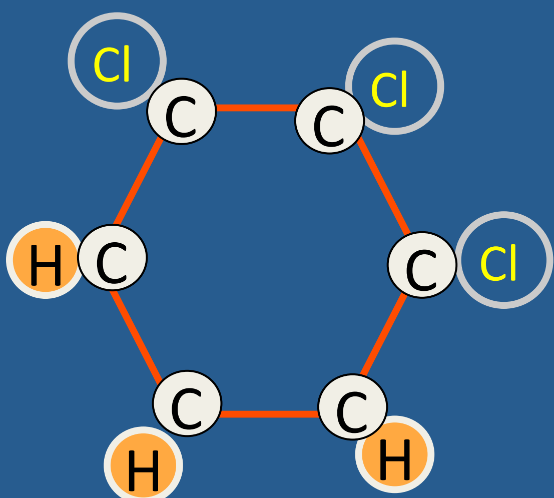
Dichloroelimination of Chlorinated Ethanes



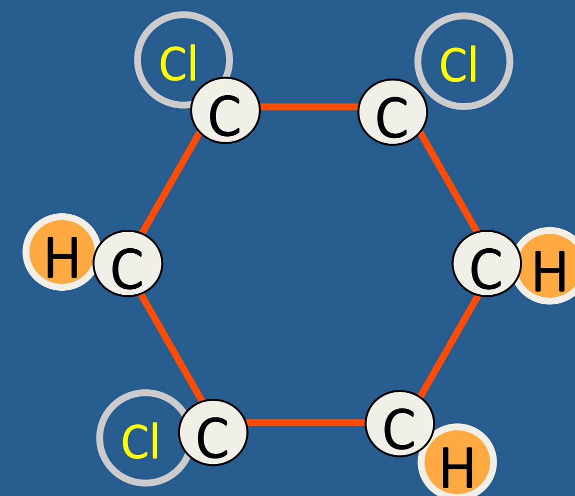
Reductive Dechlorination of Chlorinated Benzenes



1,2,4-TCB

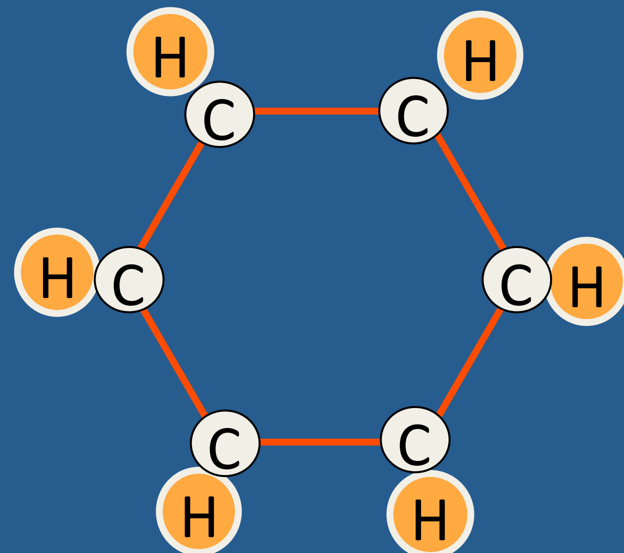


1,2,3-TCB

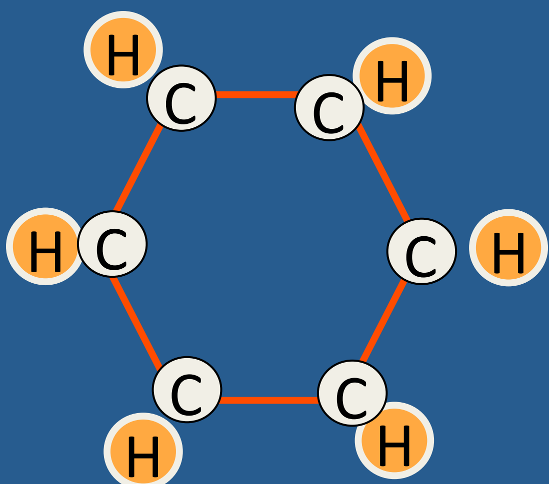


1,2,5-TCB

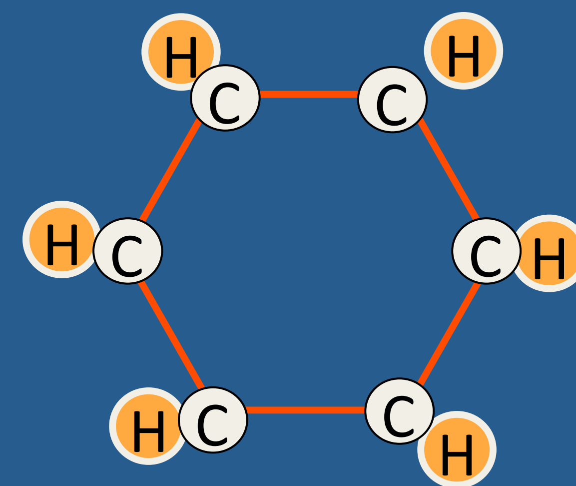
Reductive Dechlorination of Chlorinated Benzenes



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 (H_2), 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 H_2 production

Molasses

Starch

Cheese whey

Emulsified vegetable oil

Corn syrup

Lactose

Glucose

Ethanol

Methanol

Propanol

Lecithin

Glycerol, xylitol, sorbitol

Molecular H_2

Acetic acid and its salts

Lactic acid and its salts

Propionic acid and its salts

Citric acid and its salts

Various Bean Oils (soy, guar)

Benzoic acid and its salts

Oleic acid and its salts

Polylactate esters of fatty acids (e.g.., Glycerol tripolylactate)

Food process byproducts including milk whey or yeast extract

Complex organic material such as wood chips

Complex sugars

Only H_2 has been shown to be an electron donor for cis 1,2-DCE and vinyl chloride conversion to ethene

Draft General Waste Discharge Requirements for
In Situ Groundwater Remediation – Santa Ana Water Quality Control Board CA, 2013

Theoretical H_2 Production by Donor Substrate

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

H_2 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 – $CaSO_4 \cdot 2H_2O$**
- **Anhydrite – $CaSO_4$**
- **Hannebachite – $CaSO_3 \cdot 0.5H_2O$**
- **Anglesite ($PbSO_4$)**
- **Magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$ or Fe_3O_4)**
- **Hematite (Fe_2O_3)**

Reducing/reductive degradation enhancement compounds

Ferrous Chloride

Ferrous Carbonate

Ferrous Gluconate

Sorbitol Cysteinate

Sodium Sulfide

Sodium Dithionite

Calcium Polysulfide

Zero-Valent Iron
- Granular
- Emulsified
- Micro-scale
- Nano-scale

Draft General Waste Discharge Requirements for *In Situ Groundwater Remediation – Santa Ana Water Quality Control Board CA, 2013*

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

	Values	Range	Units
Width (Perpendicular to predominant groundwater flow direction)	175	1-10,000	feet
Length (Parallel to predominant groundwater flow)	900	1-1,000	feet
Saturated Thickness	24	1-100	feet
Treatment Zone Cross Sectional Area	4200	--	ft^2
Treatment Zone Volume	3,780,000	--	ft^3
Treatment Zone Total Pore Volume (total volume x total porosity)	8,484,588	--	gallons
Design Period of Performance	4.0	.5 to 5	year

2. Treatment Zone Hydrogeologic Properties

	Values	Range	Units
Total Porosity	0.3	.05-50	
Effective Porosity	0.3	.05-50	
Average Aquifer Hydraulic Conductivity	5.08	.01-1000	ft/day
Average Hydraulic Gradient	0.006939	0.1-0.0001	ft/ft
Average Groundwater Seepage Velocity through the Treatment Zone	0.12	--	ft/day
Average Groundwater Seepage Velocity through the Treatment Zone	42.9	--	ft/yr
Average Groundwater Flux through the Treatment Zon 0	404,316	--	gallons/year
Soil Bulk Density	1.7	1.4-2.0	gm/cm^3
Soil Fraction Organic Carbon (foc)	0.0005	0.0001-0.1	

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

A. Aqueous-Phase Native Electron Acceptors	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Oxygen	5.0	354.00	7.94	44.58	4
Nitrate (denitrification)	2.0	141.60	12.30	11.51	5
Sulfate	10	708.00	11.91	59.45	8
Carbon Dioxide (estimated as the amount of methane produced)	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)	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Manganese (IV) (estimated as the amount of Mn (II) produced)	1.0	84.30	27.25	3.09	2
Iron (III) (estimated as the amount of Fe (II) produced)	1.0	84.30	55.41	1.52	1
Solid-Phase Competing Electron Acceptor Demand (lb.)				**4.61**	

C. 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	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**	

Total Soluble Contaminant Electron Acceptor Demand (lb.) 4.04

D. Sorbed Contaminant Electron Acceptors (Soil Concentration = Koc x foc x Cgw)	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**	

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. Acronyns and Abbreviations

- °C =degrees celsius
- µs/cm = microsiemens per centimeter
- cm/day = centimeters per day
- cm/sec = centimeters per second
- ft^2 = square feet
- ft/day = feet per day
- ft/ft = foot per foot
- ft/yr = feet per year
- gm/cm^3 = 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 meters
- mV = millivolts
- m/yr = meters per year
- su = standard pH units
- wt/wt H2 = concetration 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	RETURN TO COVER PAGE

NOTE: Open cells are user input.

1. Treatment Zone Physical Dimensions	Values	Range	Units
Width (Perpendicular to predominant groundwater flow direction)	175	1-10,000	feet
Length (Parallel to predominant groundwater flow)	900	1-1,000	feet
Saturated Thickness	24	1-100	feet
Treatment Zone Cross Sectional Area	4200	--	ft^2
Treatment Zone Volume	3,780,000	--	ft^3
Treatment Zone Total Pore Volume (total volume x total porosity)	8,484,588	--	gallons
Design Period of Performance	4.0	.5 to 5	year

2. Treatment Zone Hydrogeologic Properties

Total Porosity		0.3	.05-50	
Effective Porosity		0.3	.05-50	
Average Aquifer Hydraulic Conductivity		5.08	.01-1000	ft/day
Average Hydraulic Gradient		0.006939	0.1-0.0001	ft/ft
Average Groundwater Seepage Velocity through the Treatment Zone		0.12	--	ft/day
Average Groundwater Seepage Velocity through the Treatment Zone		42.9	--	ft/yr
Average Groundwater Flux through the Treatment Zon	0	404,316	--	gallons/year
Soil Bulk Density		1.7	1.4-2.0	gm/cm^3
Soil Fraction Organic Carbon (foc)		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) 1X - 3X

Design Factor	10.0
Total Life-Cycle Hydrogen Requirement with Design Factor (lb)	5,719.3

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- mg/L = milligrams per liter
- m/m = meters per meters
- mV = millivolts
- m/yr = meters per year
- su = standard pH units
- wt/wt H2 = concetration 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

	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Oxygen	5.0	354.00	7.94	44.58	4
Nitrate (denitrification)	2.0	141.60	12.30	11.51	5
Sulfate	10	708.00	11.91	59.45	8
Carbon Dioxide (estimated as the amount of methane produced)	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)

	Concentration (mg/L)	Mass (lb)	Stoichiometric demand (wt/wt h_2)	Hydrogen Demand (lb)	Electron Equivalents per Mole
Manganese (IV) (estimated as the amount of Mn (II) produced)	1.0	84.30	27.25	3.09	2
Iron (III) (estimated as the amount of Fe (II) produced)	1.0	84.30	55.41	1.52	1
Solid-Phase Competing Electron Acceptor Demand (lb.)				**4.61**	

C. 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	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**	

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)	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)	[illegible]	[illegible]	22.06	[illegible]	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. Acronyns and Abbreviations

^{o}C =degrees celsius
μs/cm = microsiemens per centimeter
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kg of CaCO3 per mg = kilograms of calcium carbonate per milligram
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meq/100 g = milliequivalents per 100 grams
mg/kg = milligrams per kilogram
mg/L = milligrams per liter
m/m = meters per meters
mV = millivolts
m/yr = meters per year
su = standard pH units
wt/wt H2 = concetration molecular hydrogen, weight per weight

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
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Trichloromethane (or chloroform) (CF)	0.000	0.00	19.74	0.00	6
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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
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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. Acronyns and Abbreviations

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gm/cm^3 = 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 meters
mV = millivolts
m/yr = meters per year
su = standard pH units
wt/wt H2 = concetration molecular hydrogen, weight per weight

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
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Dichloroethene (cis-DCE, trans-DCE, and 1,1-DCE)	0.546	1.84	24.05	0.08	4
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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**

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ft/day = feet per day
ft/ft = foot per foot
ft/yr = feet per year
gm/cm^3 = 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 = milligran
m/m = meters p
mV = millivolts
m/yr = meters p
su = standard p
wt/wt H2 = conc

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**

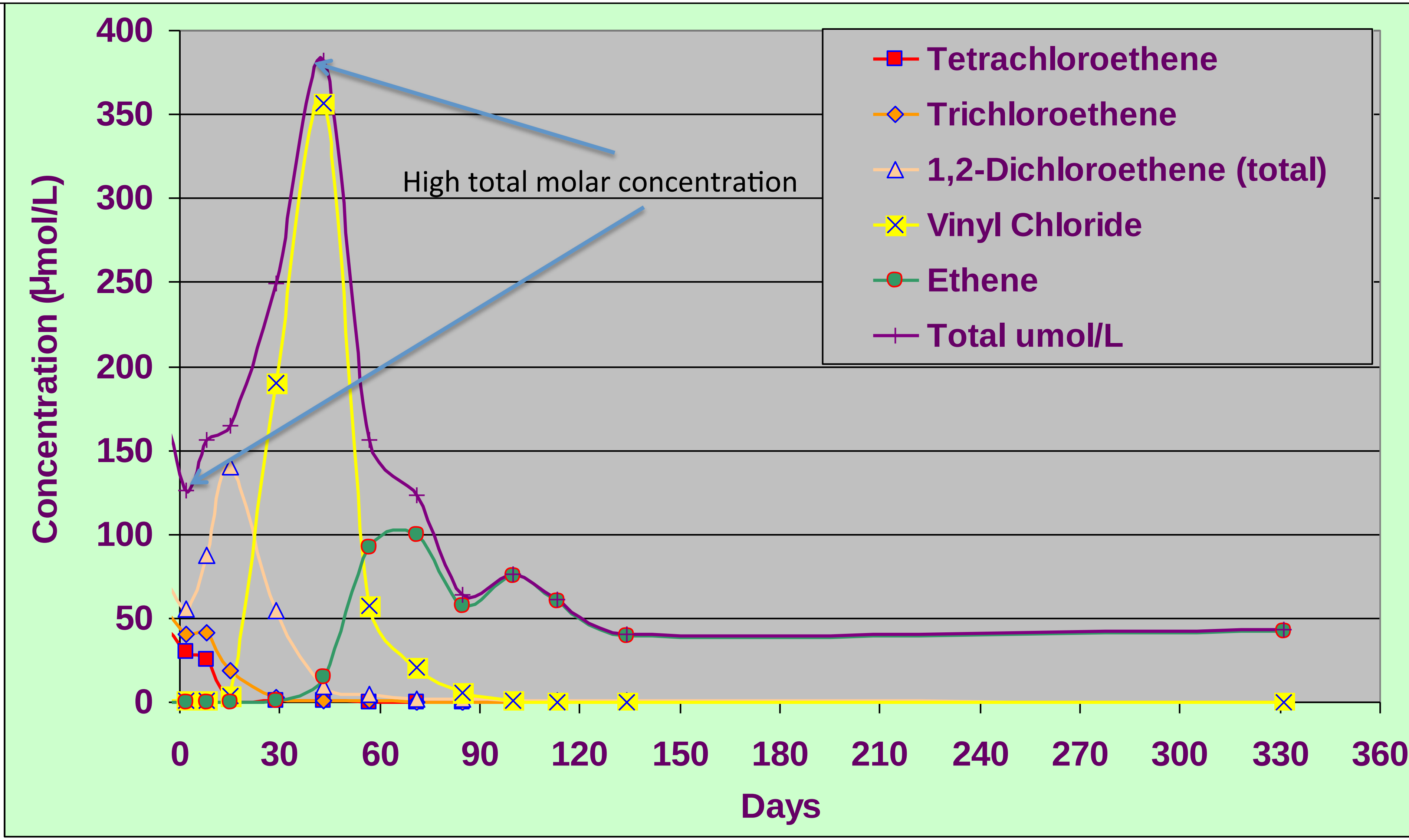
Contaminants disappear without generation of daughter products

- **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**

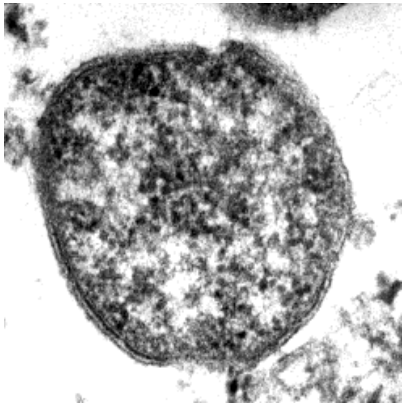
Increased Dissolved Phase Chlorinated Ethenes During Bioremediation



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



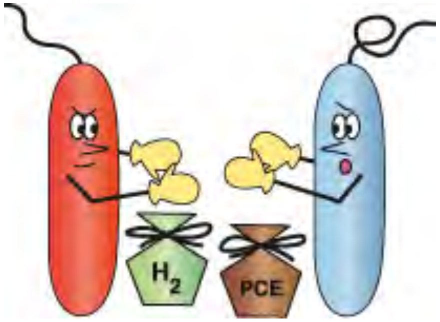
Various organisms approved for bioaugmentation

Dehalococcoides (Dhc)
Dehalobacter
Dehalogenimonas
Desulfuromonas
Desulfitobacterium
Desulfovbrio
Sulfurospirillum
Alcaligenes faecalis
Arthrobacter

Geobacter
Corynebacterium
Nitrosomonas
Nitrobacter
Rhodococcus
Pseudomonas fluorescens
Methylibium petroleiphilum
Methanotrophs
Methylosinus

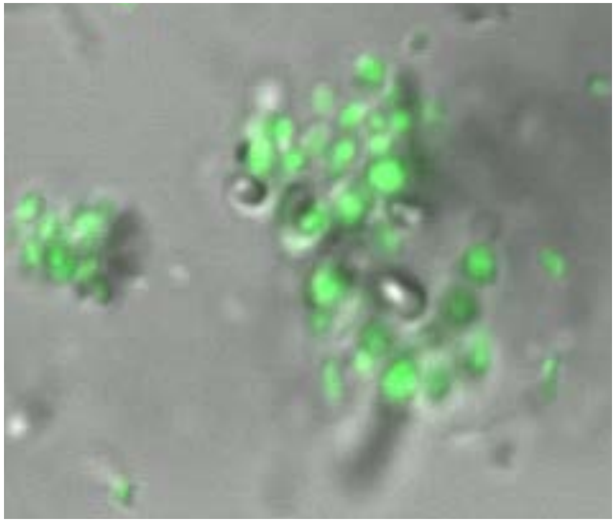
Is ‘Bioaugmentation Necessary?

- **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.**
  - > $1x10^7$ 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.**



www.mdsg.umd.edu/CQ/v05n1/main/

Bioaugmentation in Aerobic Aquifers

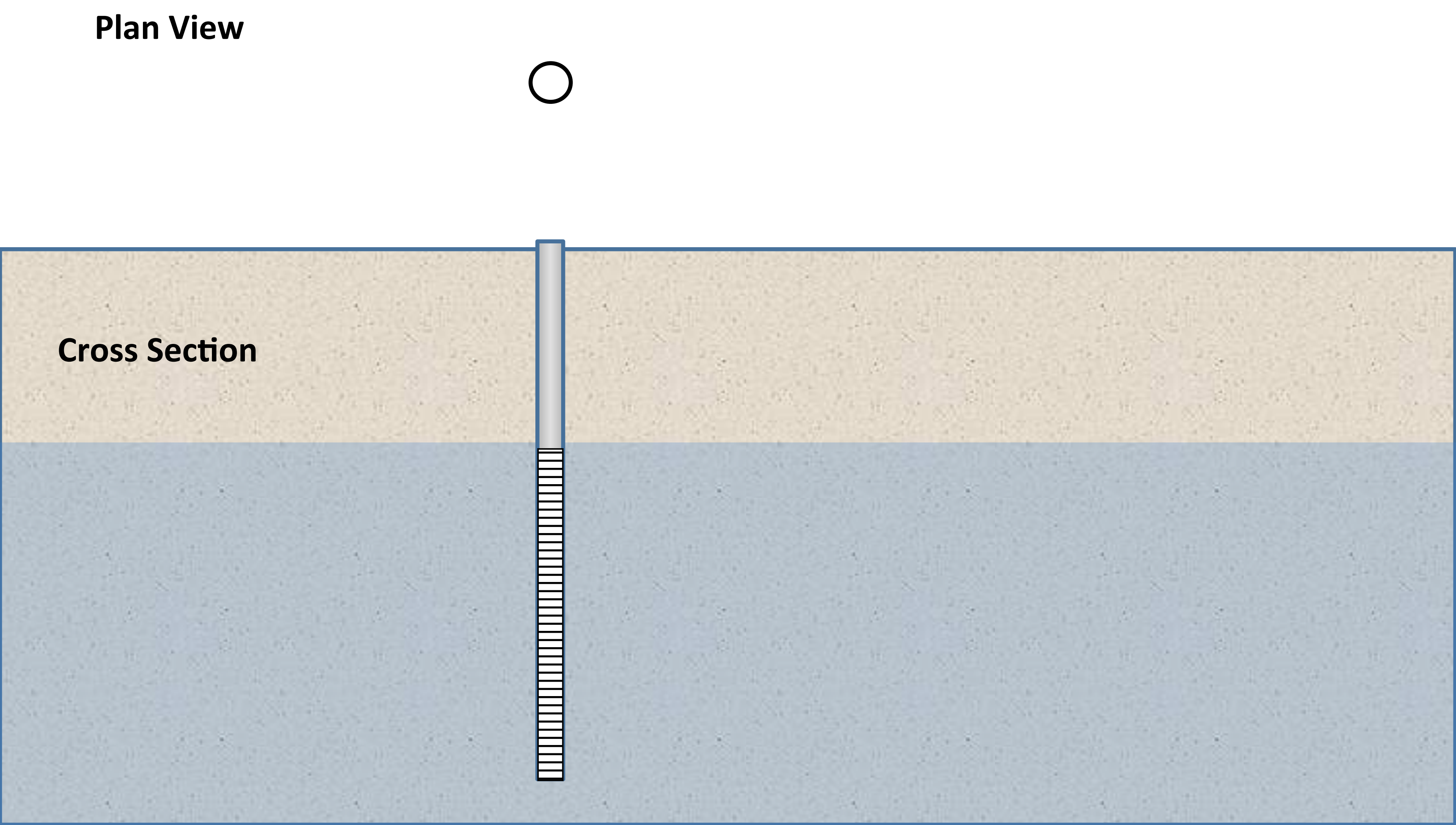


- **Dhc is an obligate anaerobe.**
- **Does not grow in presence of 0_2**
- **Aerobic aquifers contain little, if any, Dhc.**
- **Aerobic aquifers often not considered appropriate for biological ERD.**
- **Substantial effort considered necessary to bioaugment in aerobic aquifers but not necessarily true.**
- **Bioaugmentation probably necessary treat CEs biologically in aerobic aquifers.**

Considerations when Bioaugmenting

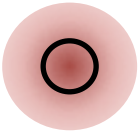
- Establishment of reducing conditioning of the aquifer prior to bioaugmentation, although helpful, is costly and may not be necessary
- The addition of organic substrate to aerobic water usually sufficient to protect culture from oxygen.
- Preferable to use site groundwater for injection.
- Potable (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



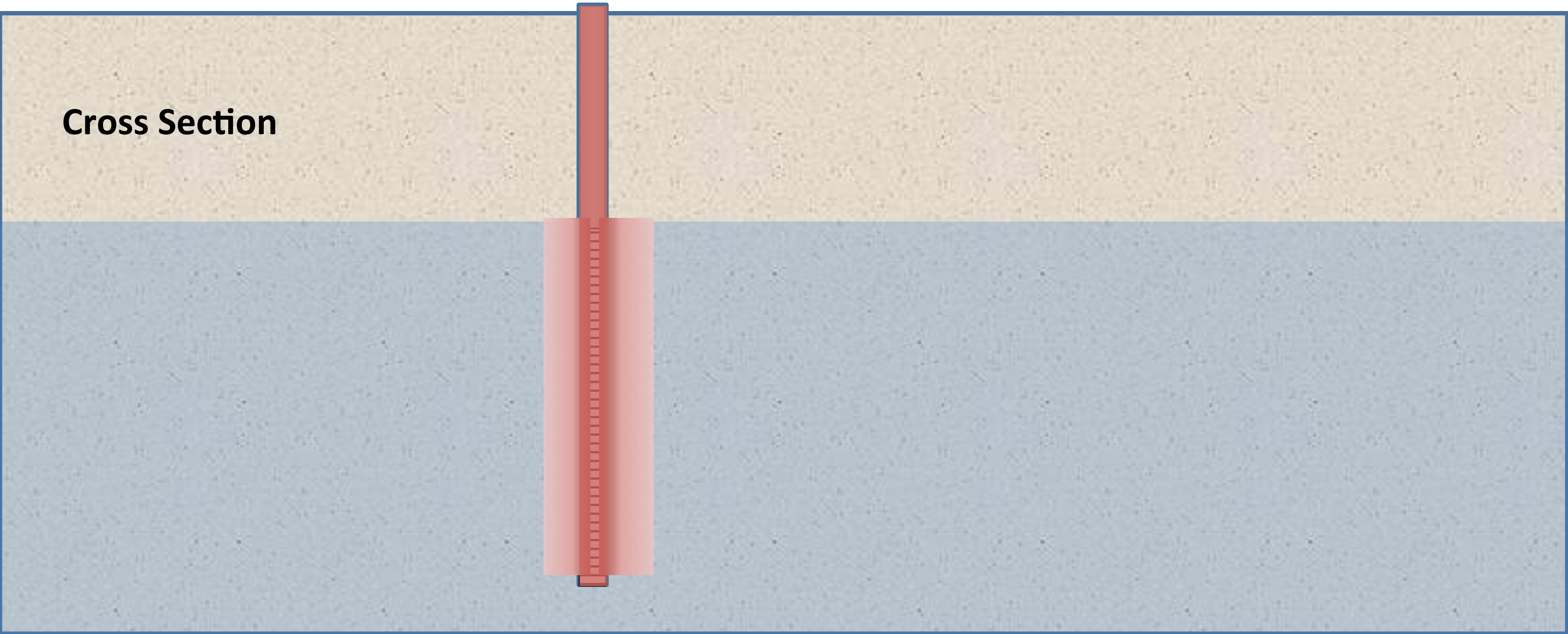
Bioaugmentation methods applied to overcome aerobic conditions

Plan View

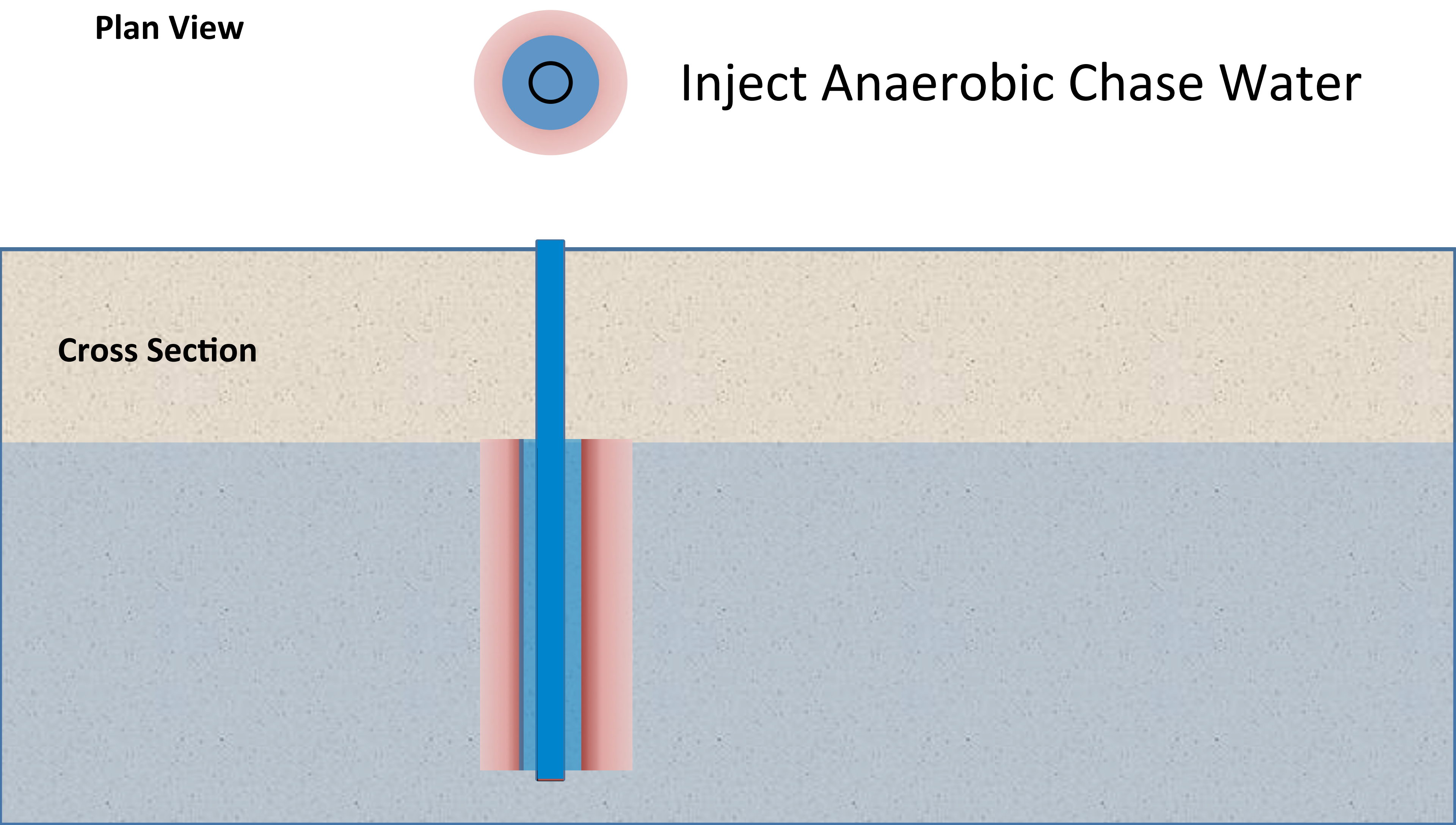


Inject 25% Substrate

Cross Section

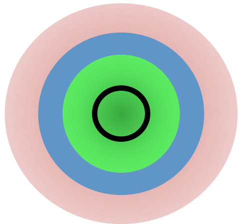


Bioaugmentation methods applied to overcome aerobic conditions



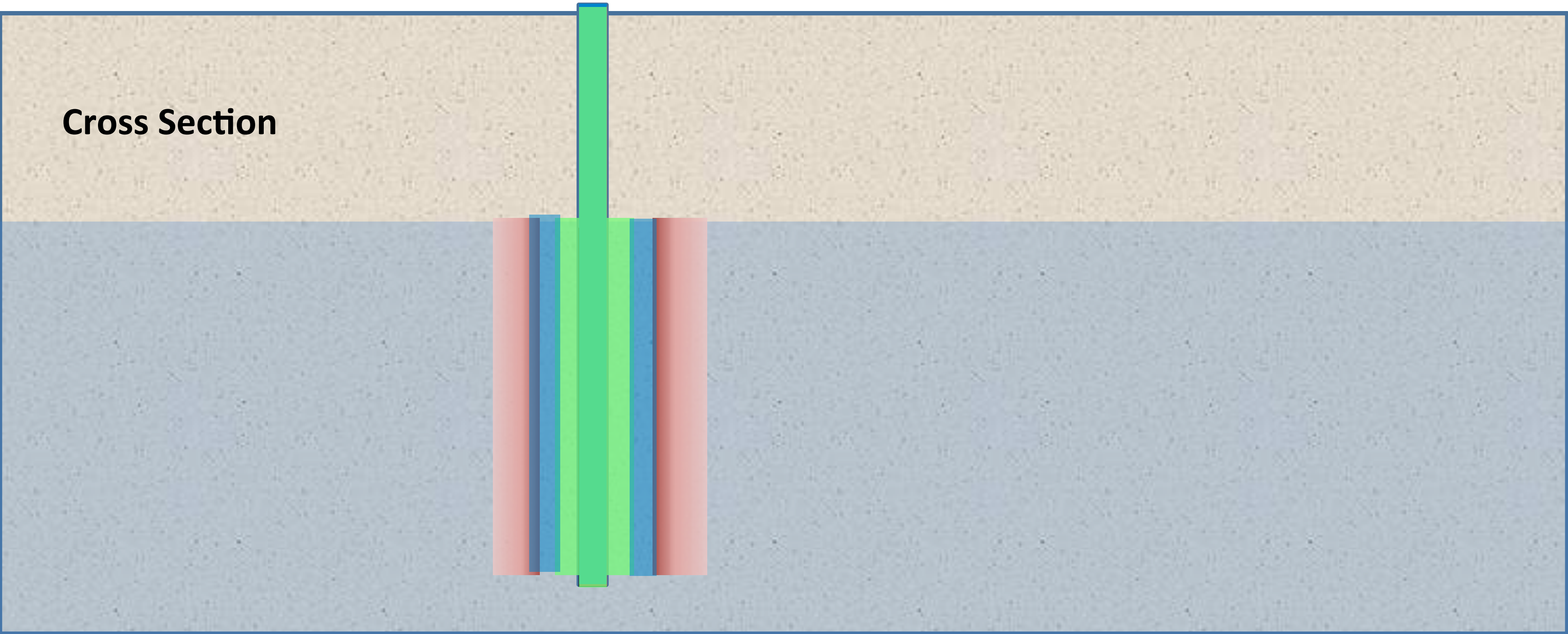
Bioaugmentation methods applied to overcome aerobic conditions

Plan View



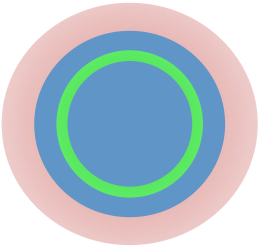
Inject Bioaugmentation Culture

Cross Section



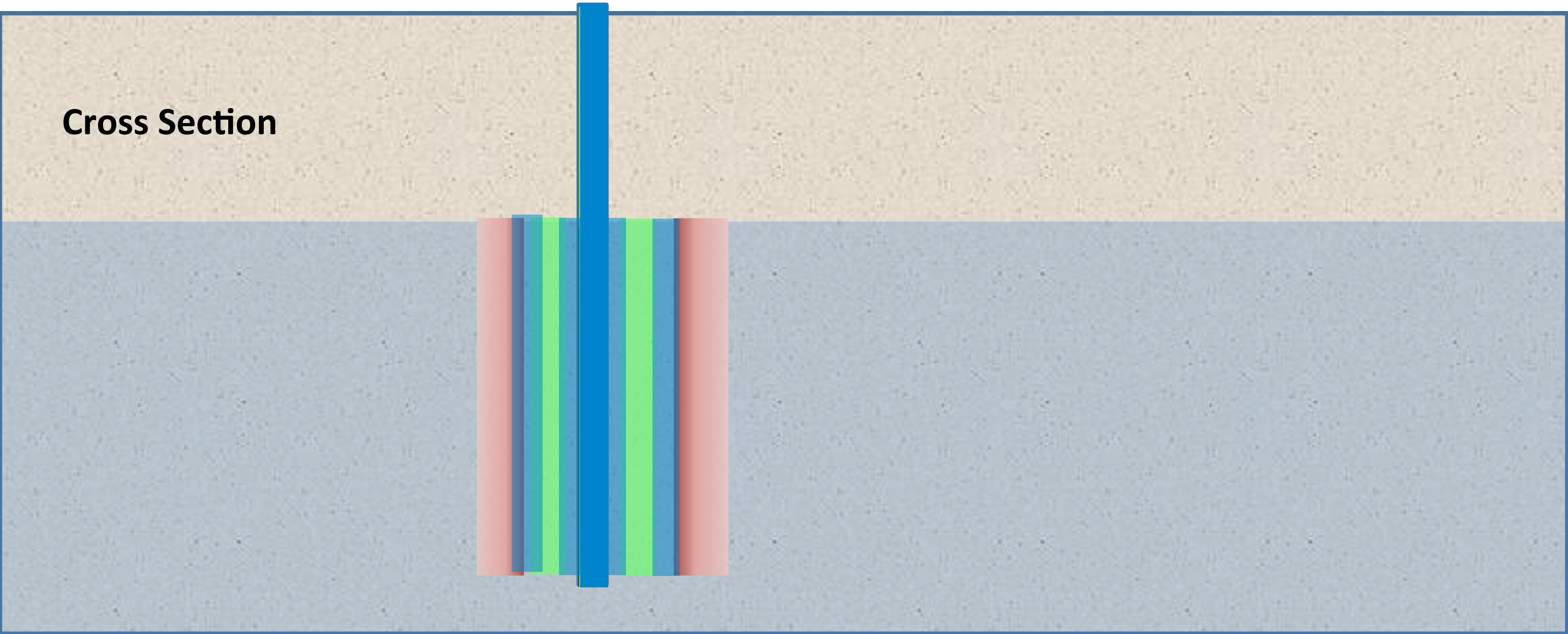
Bioaugmentation methods applied to overcome aerobic conditions

Plan View

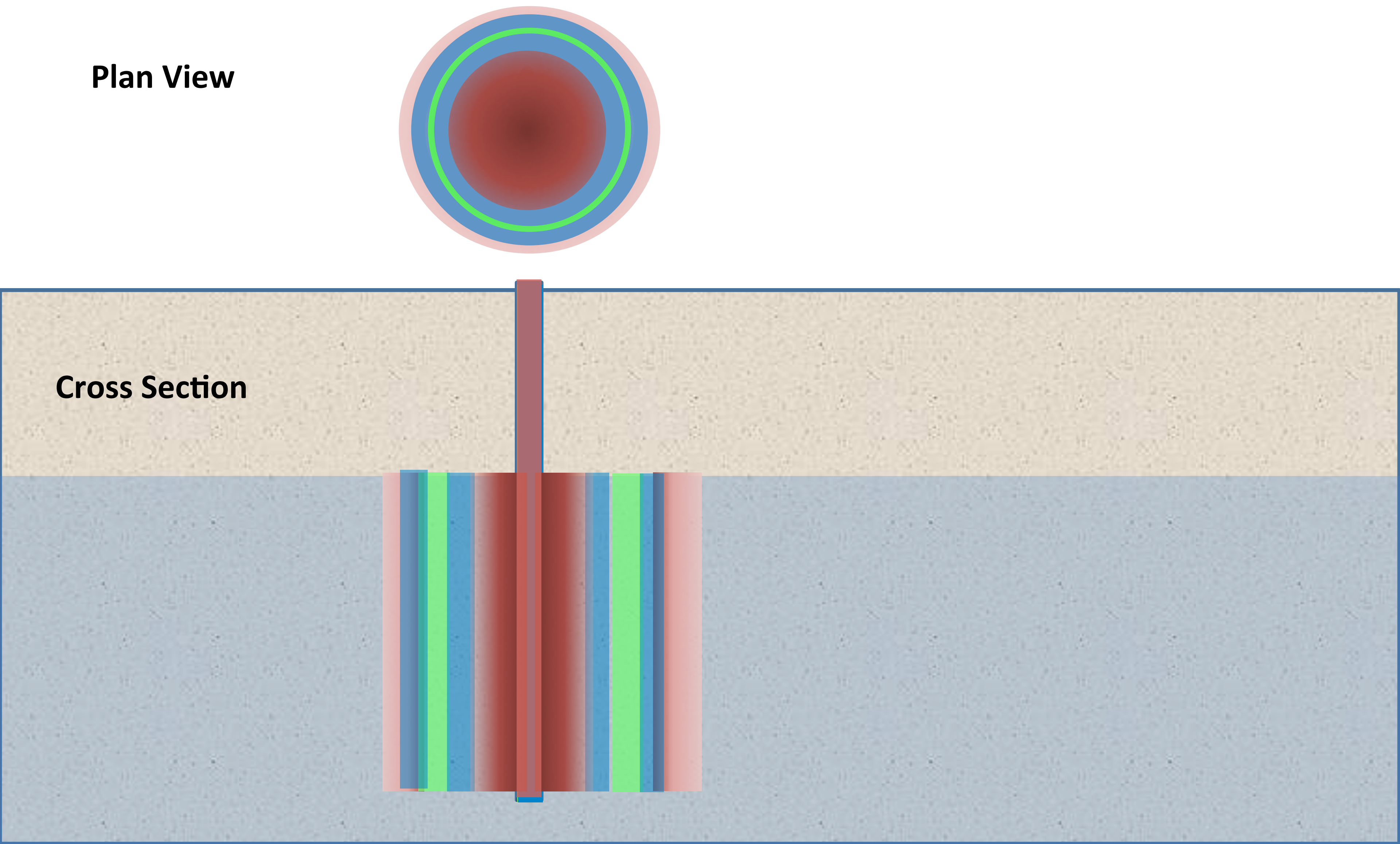


Inject Chase Water

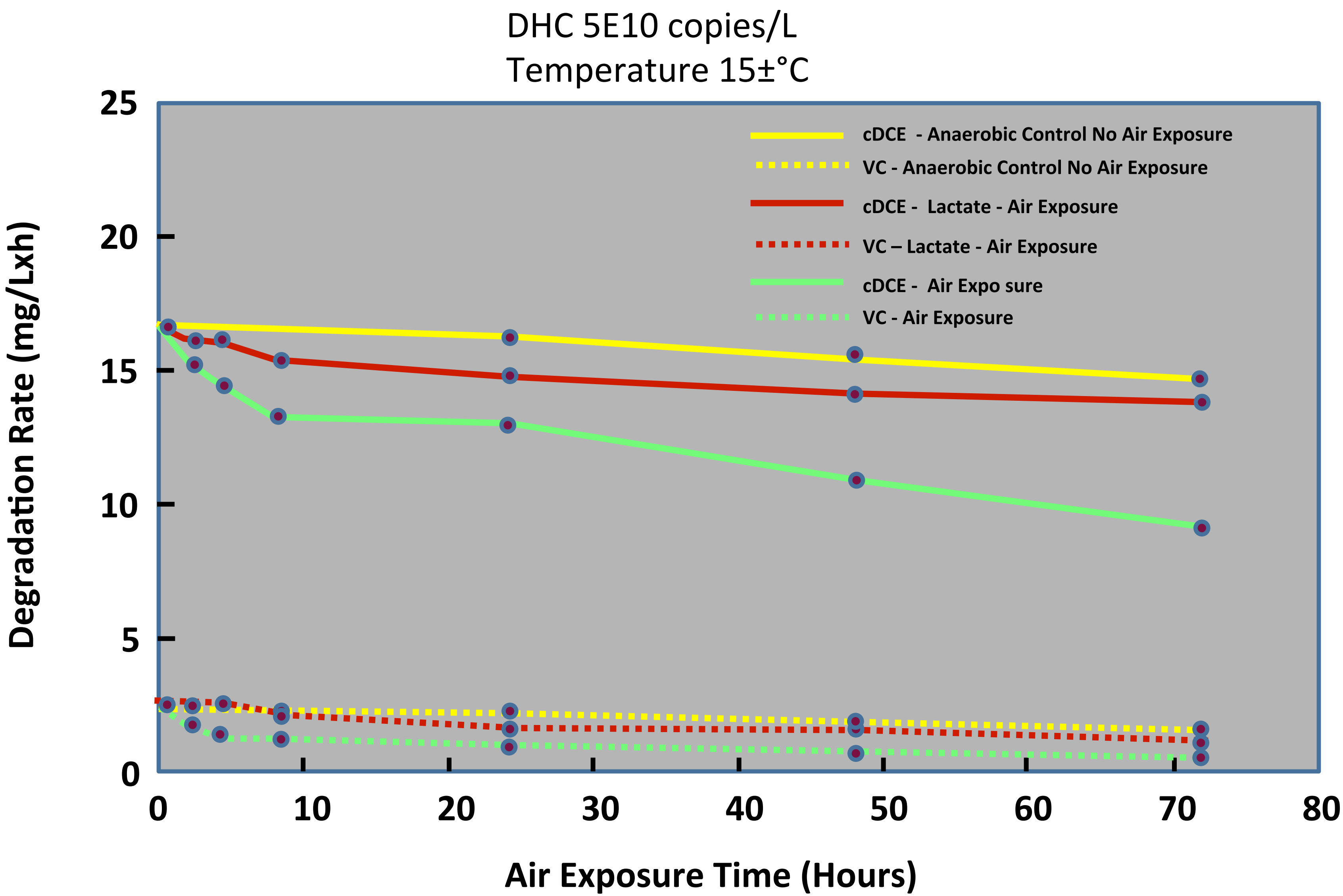
Cross Section



Bioaugmentation methods applied to overcome aerobic conditions



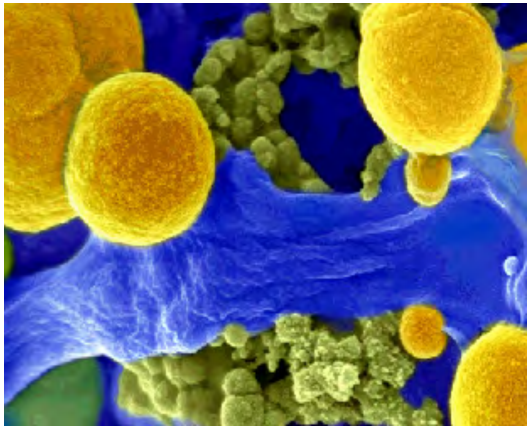
cDCE and VC Degradation Rates of SDC-9™ Exposed to Air (With and Without Organic Substrate)



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

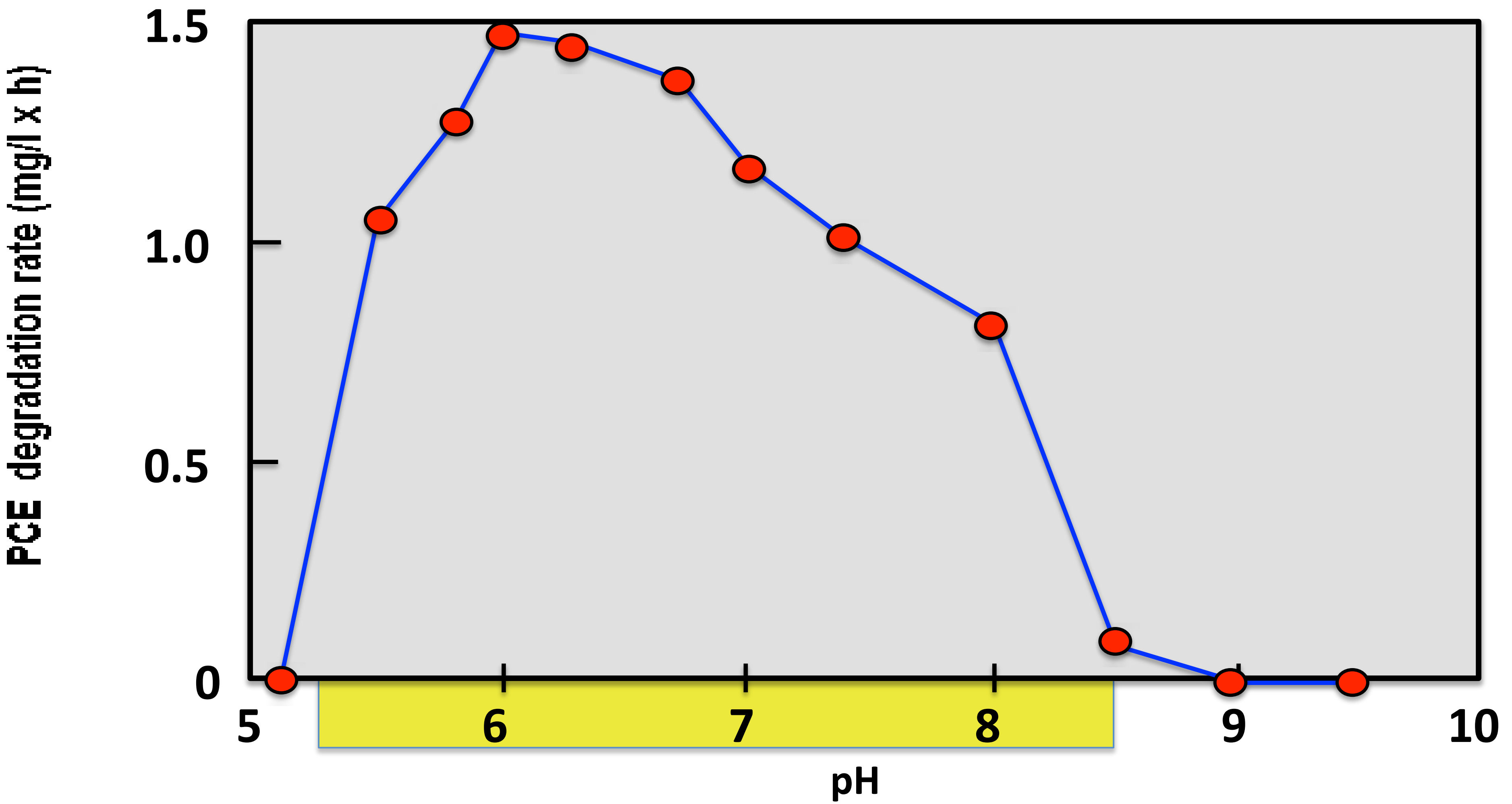
- **Dhc are very sensitive to pH**

- **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



Vainberg, S., C.W. Condee, R.J. Steffan. 2009. Large scale production of *Dehalococcoides sp.*-containing cultures for bioaugmentation. J. Indust. Microbiol. Biotechnol. 36:1189-1197.

Solution to Elevated pH

Buffers:

- Sodium Bicarbonate
- Potassium Bicarbonate
- Sodium hydroxide
- Calcium Carbonate

Remember Dhc sensitive to high pH as well

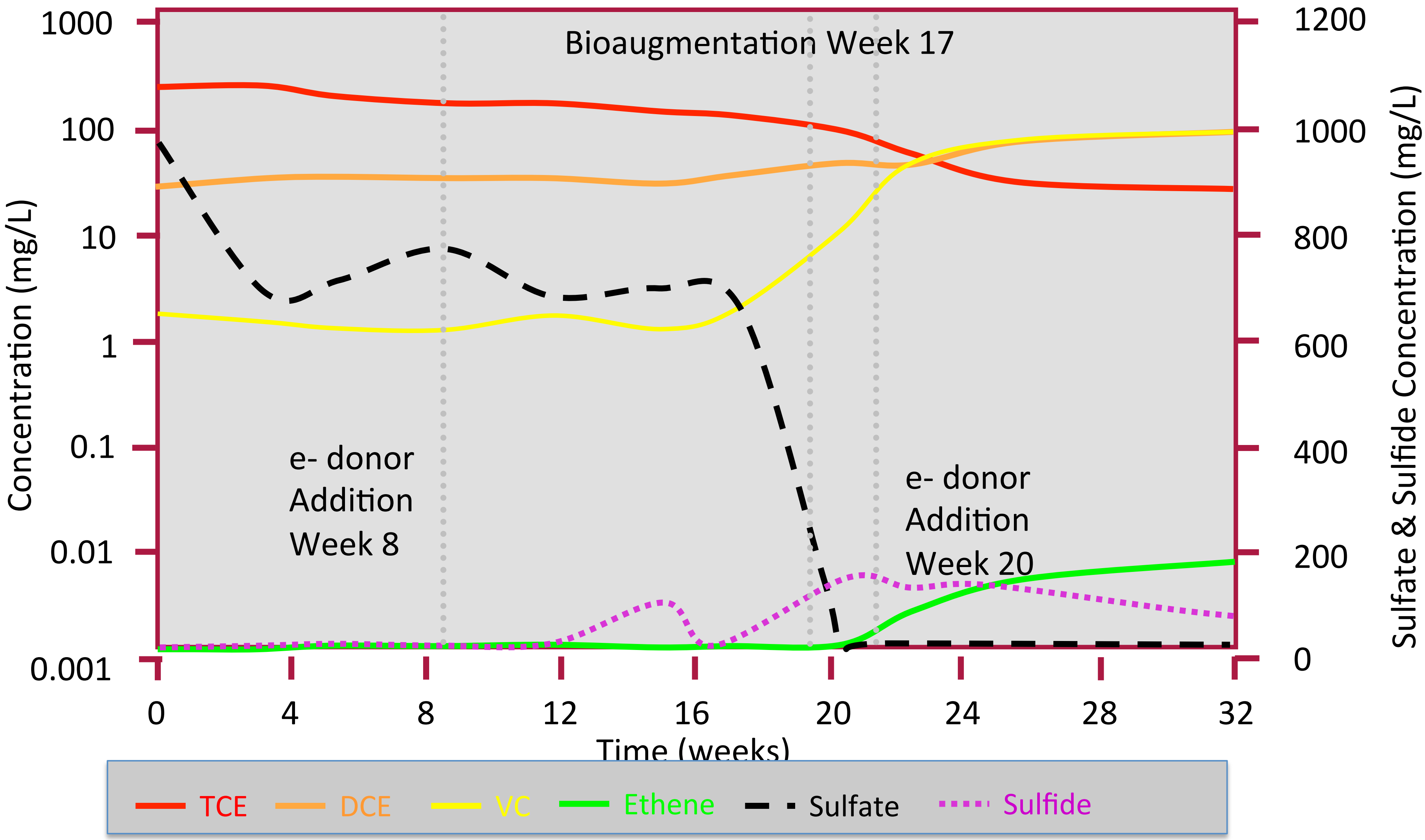
ZVI also buffers pH - ISCR

Sulfide Toxicity

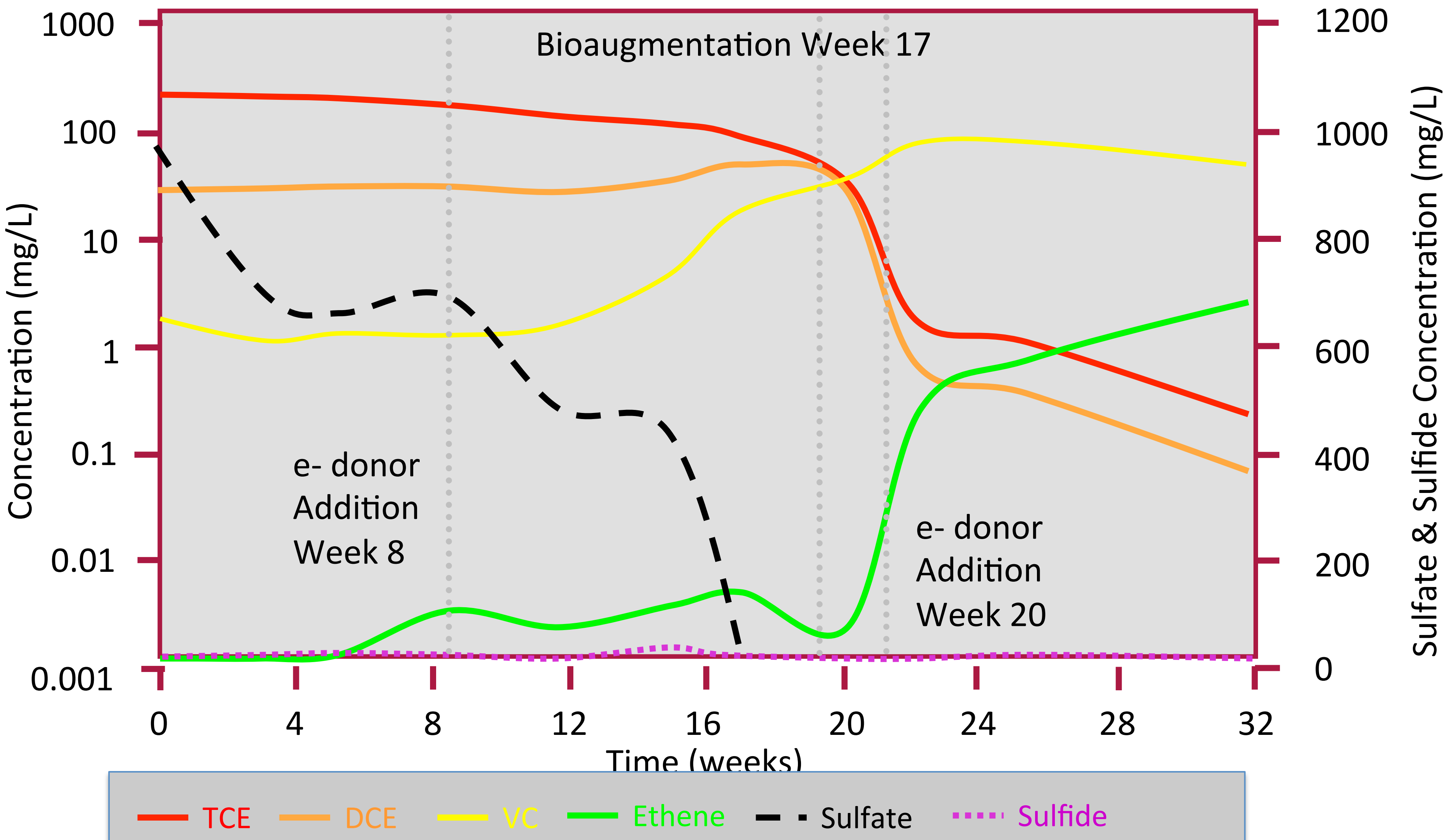
Elevated concentrations of sulfide can inhibit anaerobic biodegradation

- **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 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



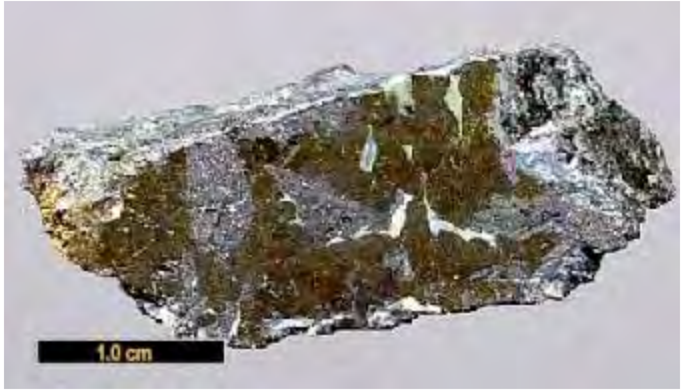
Biogeochemical Transformation

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)

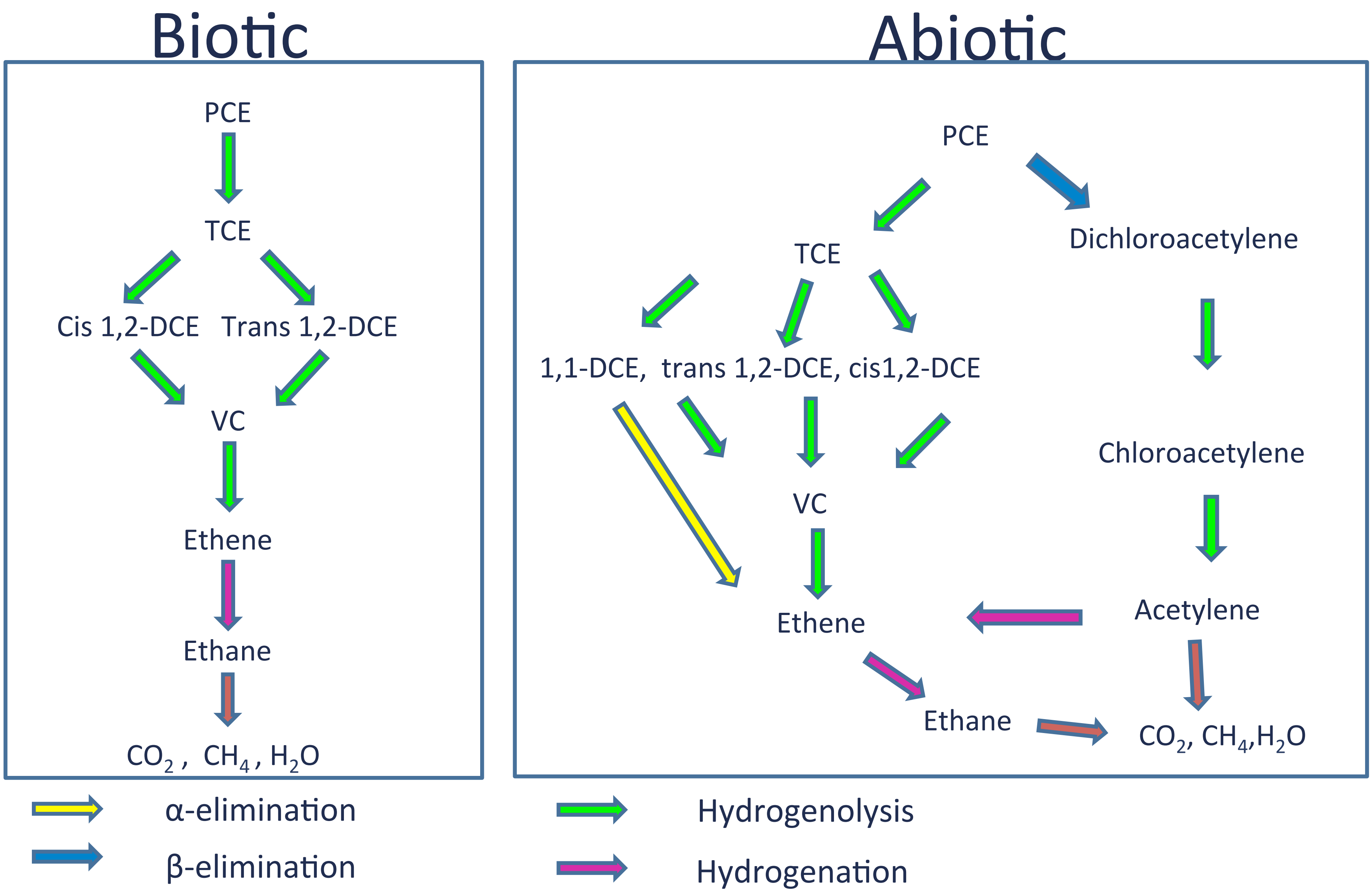
Magnetite(Fe_3O_4)



Mackinawite ($Fe_{(1+x)}S$

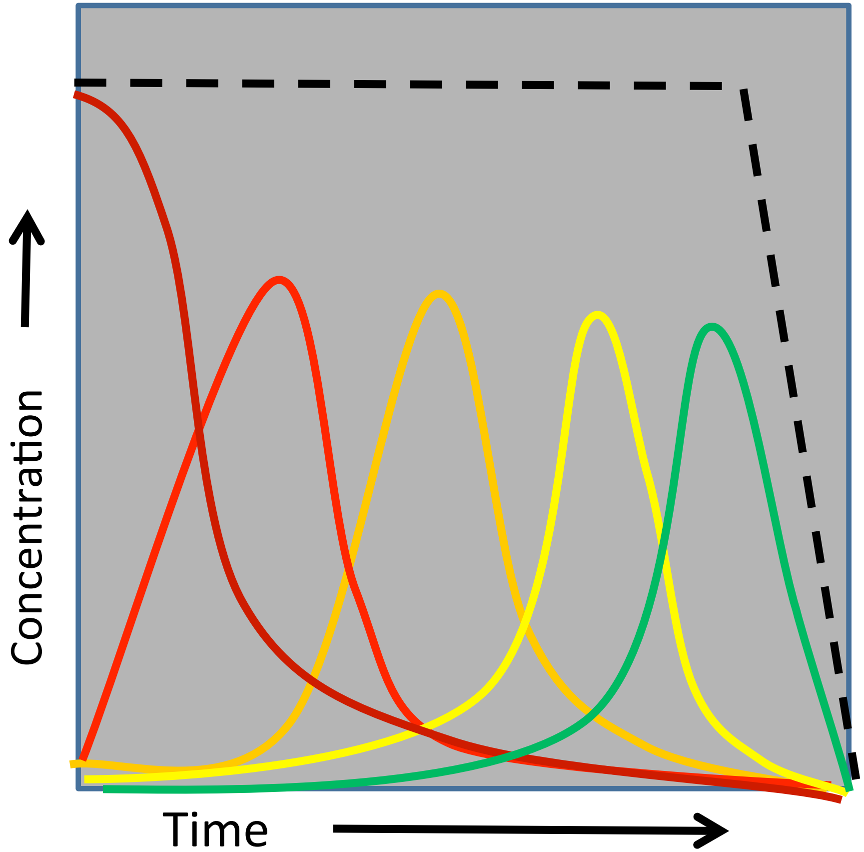
ß–Elimination does not generate stable toxic daughter products

Biogeochemical Degradation Pathways

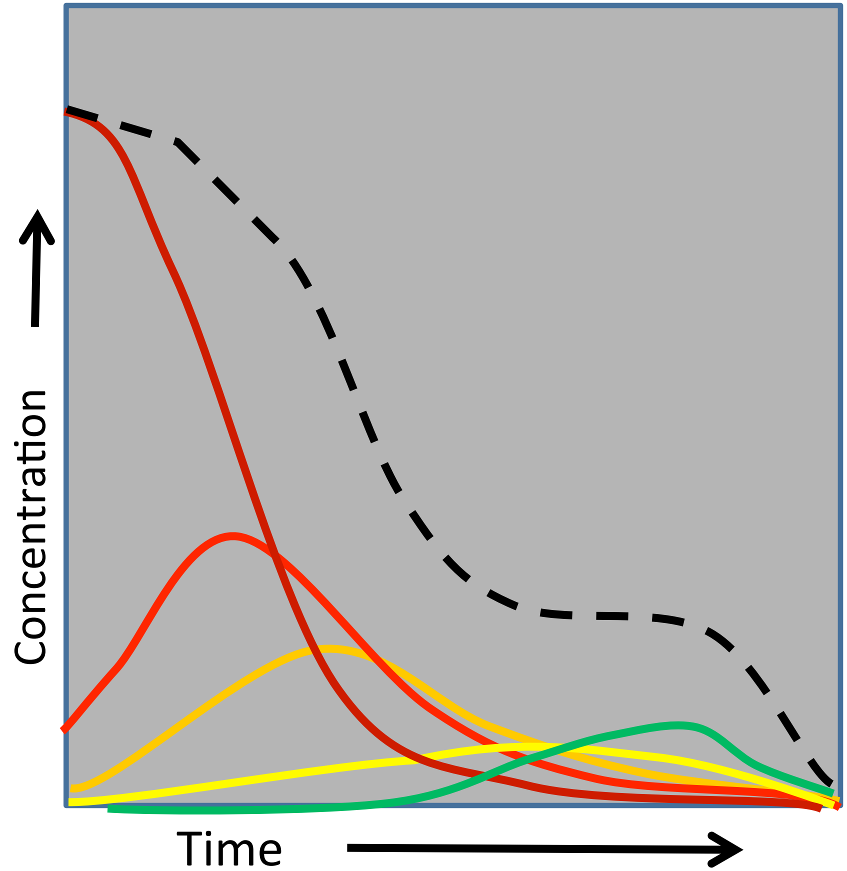


Anticipated Change in CE Molar Concentration

Biological Degradation (Chlororespiration)

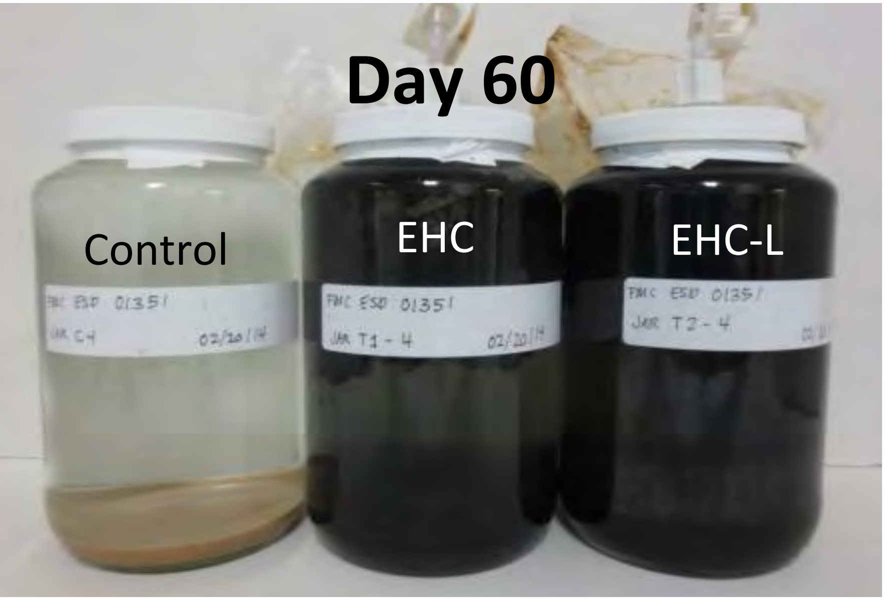


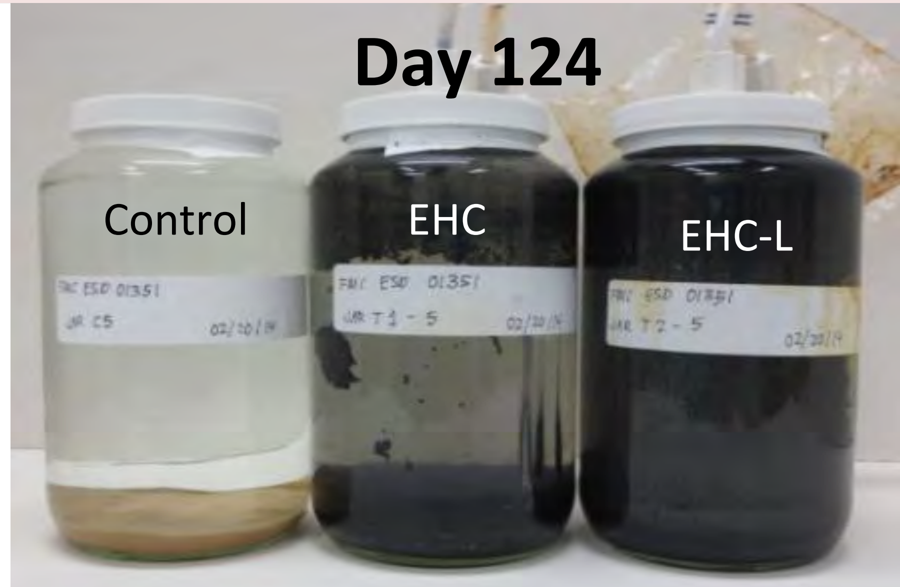
Abiotic Degradation (β elimination)

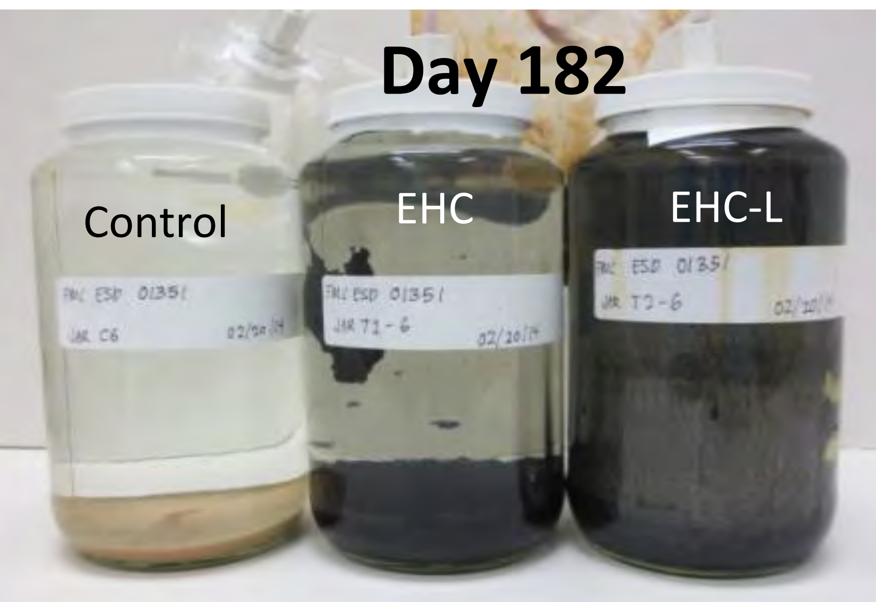


PCE TCE DCE VC Ethene Total

Sulfide Precipitation



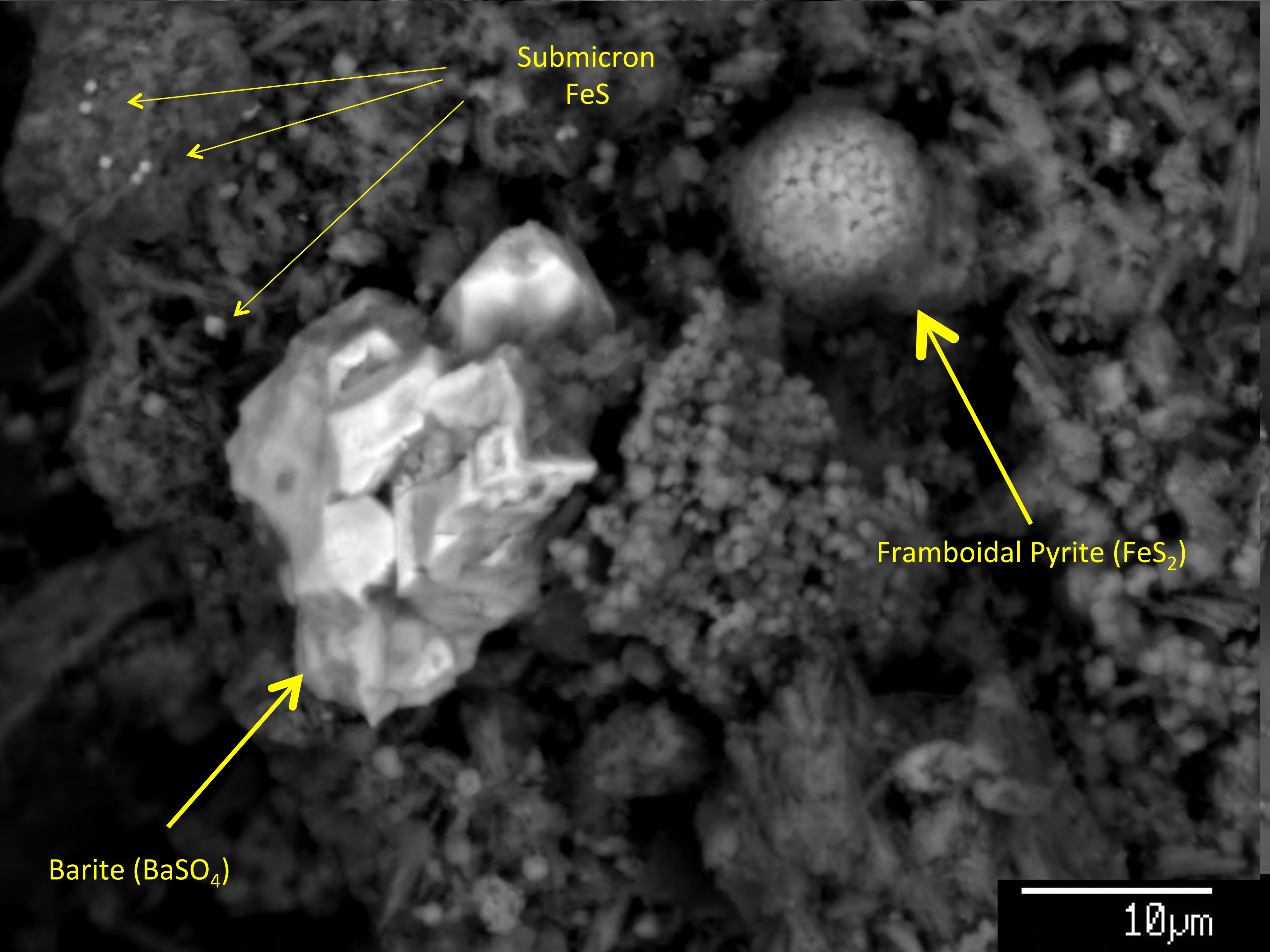




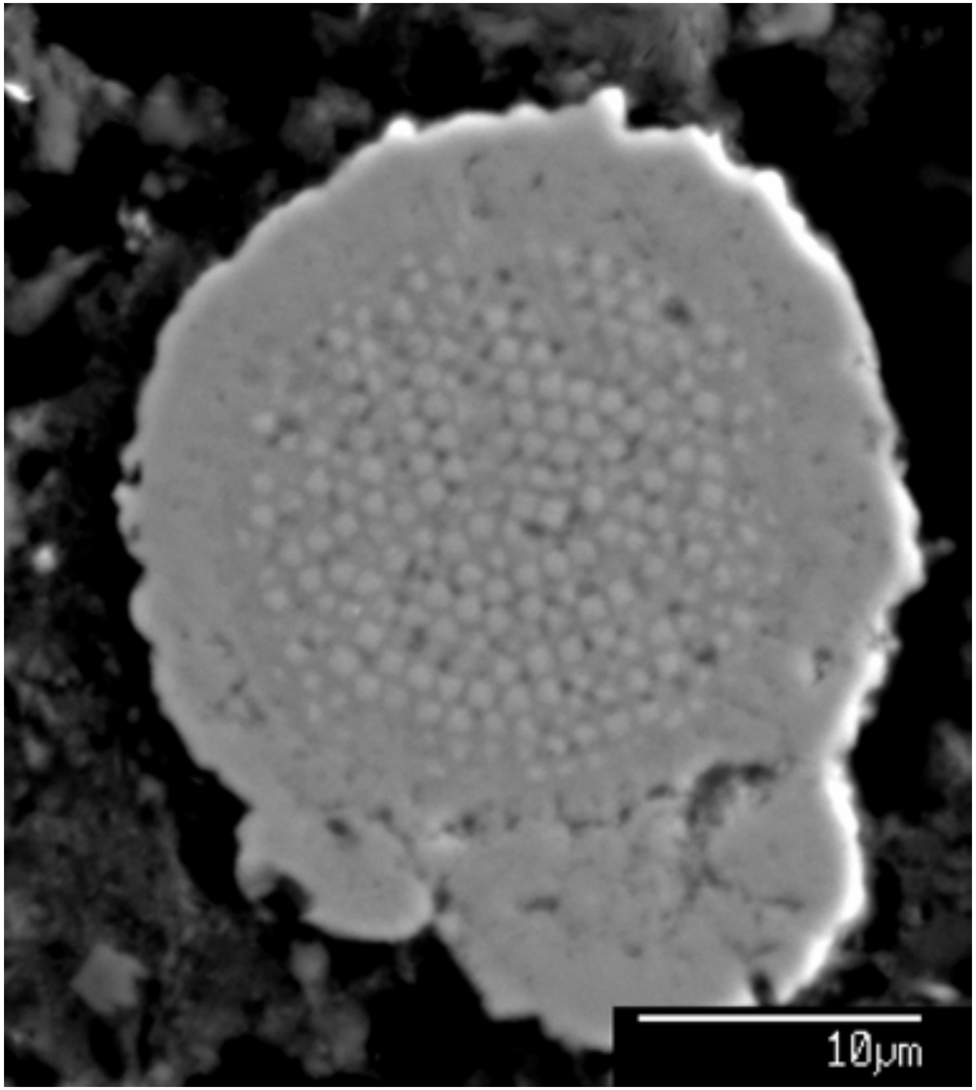
EHC Precipitate		
mg/Kg	Sulfide	31000
	Total Fe	210000
mMol/Kg	Sulfide	967
	Total Fe	3760

EHC-L + Iron Precipitate		
mg/Kg	Sulfide	42000
	Total Fe	130000
Mmol/Kg	Sulfide	1310
	Total Fe	2328

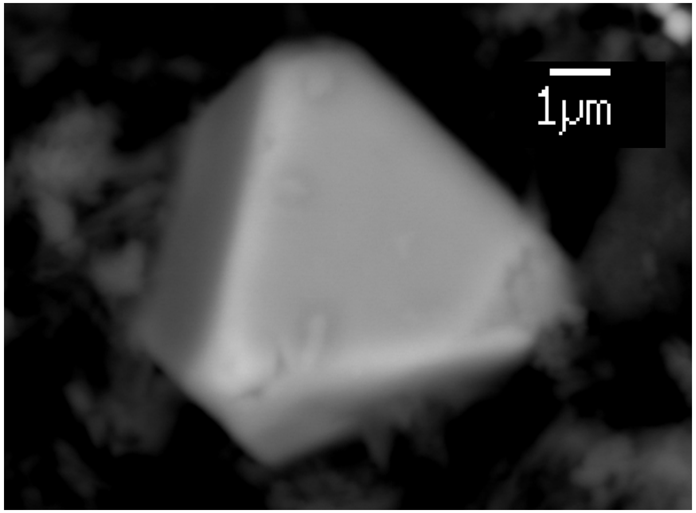

Well PFA-1
Quartz, Calcium Carbonate
Back Scatter Electron Image
10μm


Submicron
FeS
Framboidal Pyrite (FeS_2)
Barite ($BaSO_4$)
10μm

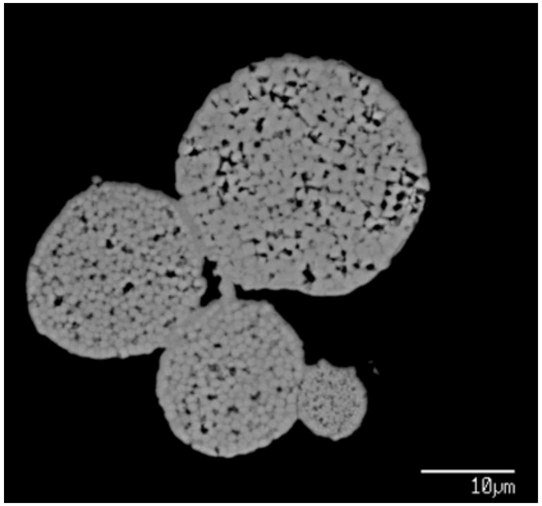
FeS_2 Occurs as Euhedral and Framboidal Pyrite



Framboidal FeS_2 and FeS

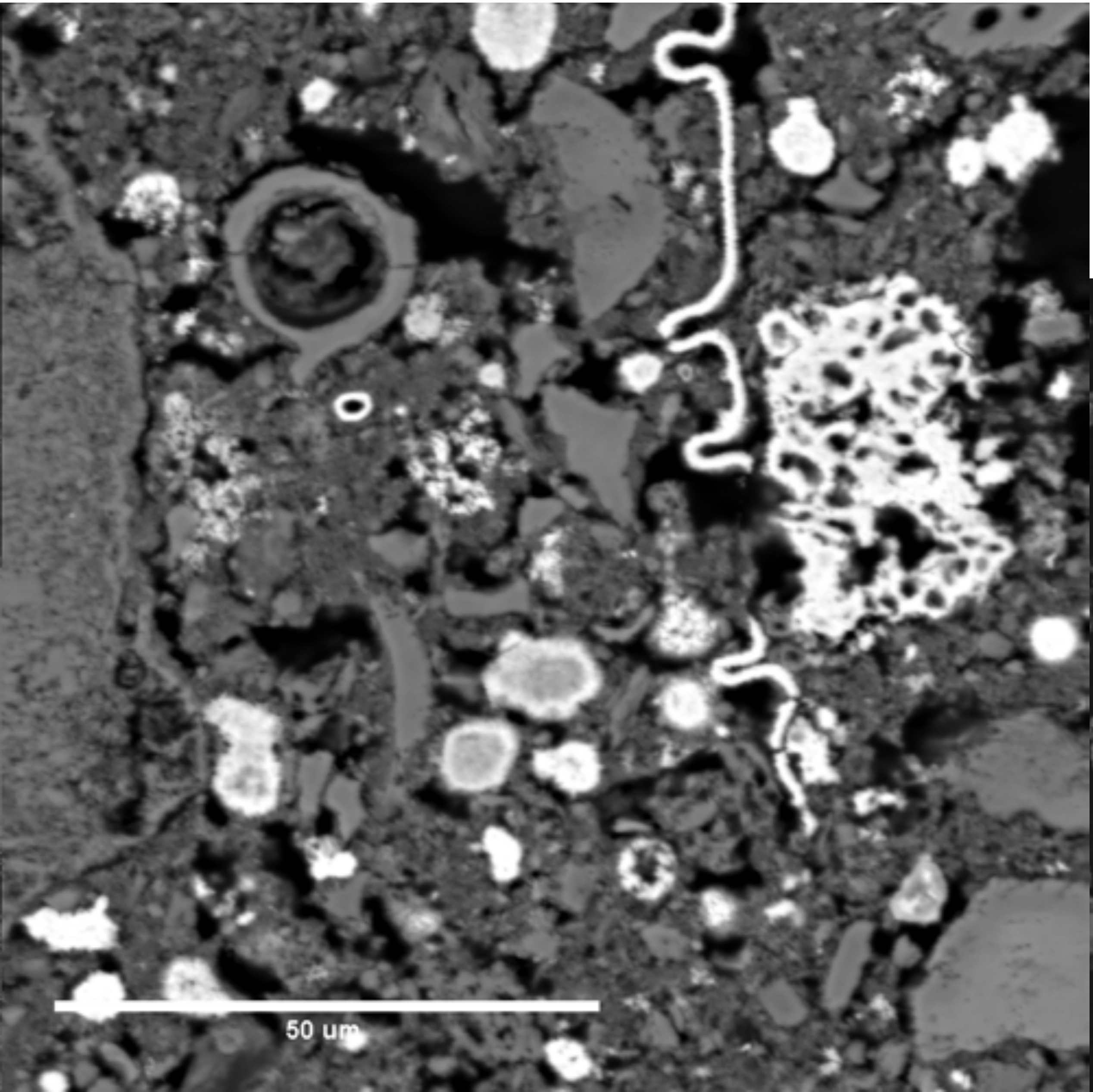


Euhedral Pyrite (FeS_2)

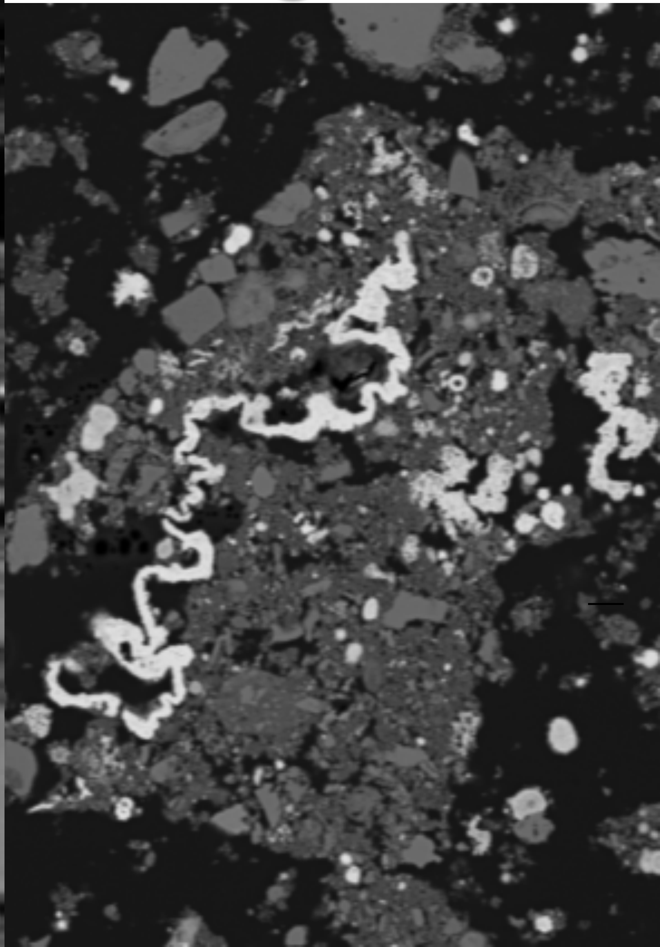


Framboidal Pyrite (FeS_2)

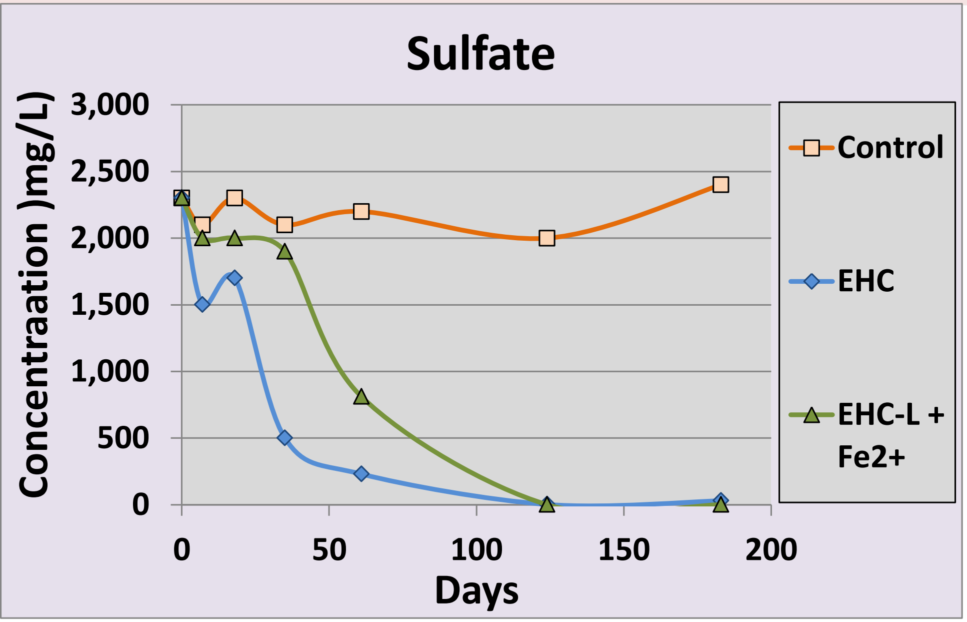
Electron Microprobe - Fe + S Spectra



FeS present as fine (~ 3 - 5 μm) coating



Sulfide Precipitation Analytical Results



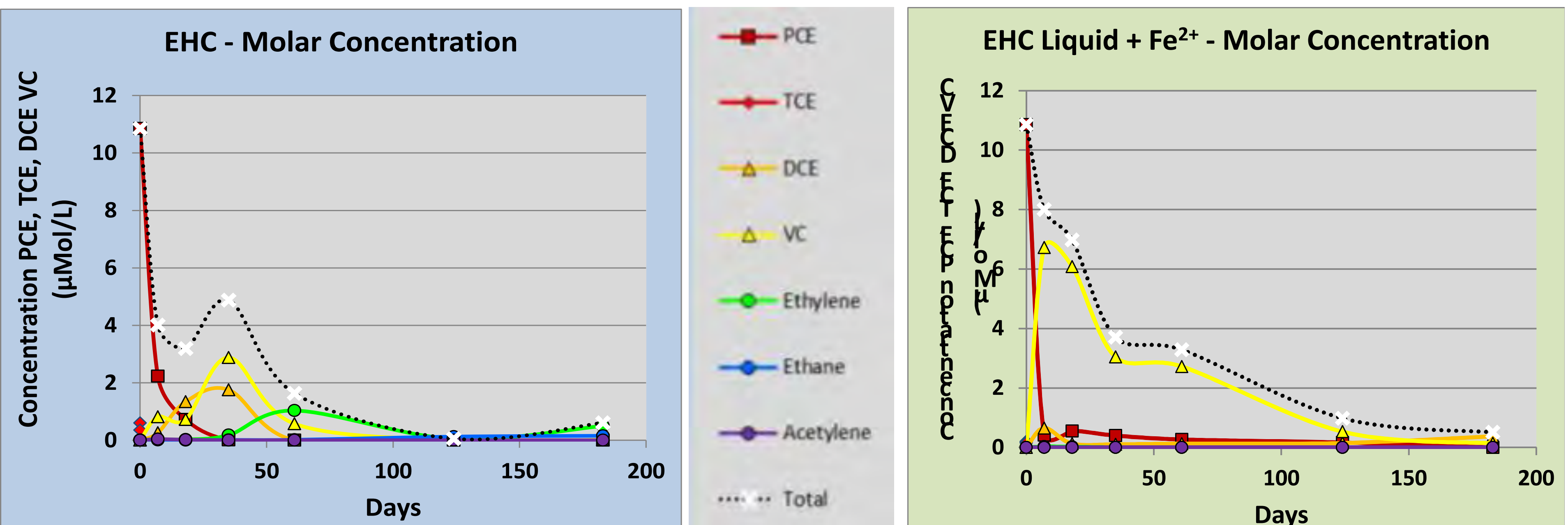
High sulfate concentrations can be reduced

Requires additional electron donor

May require Fe to precipitate sulfide

Electrons are not wasted but stored as FeS

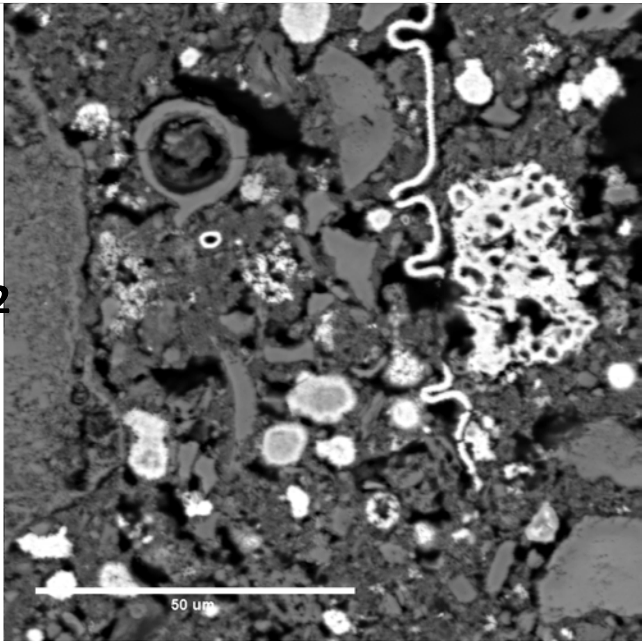
Iron sulfides establish an abiotic pathway

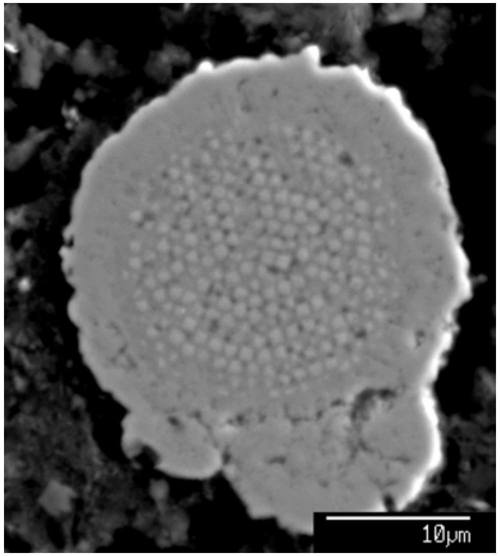


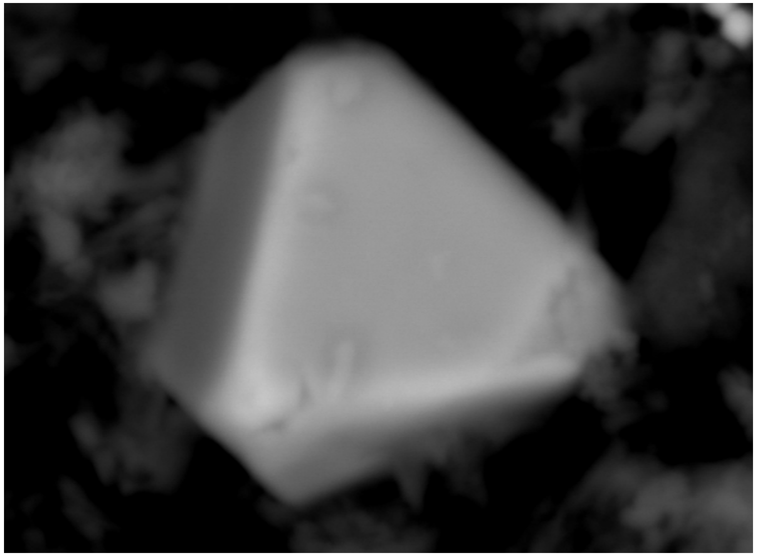
Process generates reactive FeS

3,000 mg/L sulfate + Fe^{2+}:

- Produces framboidal and euhedral pyrite
- Produces a 1 to 5 µM thick FeS coating 1.2 ft^2
- Large surface area increases rate of biogeochemical degradation







FeS Precipitation

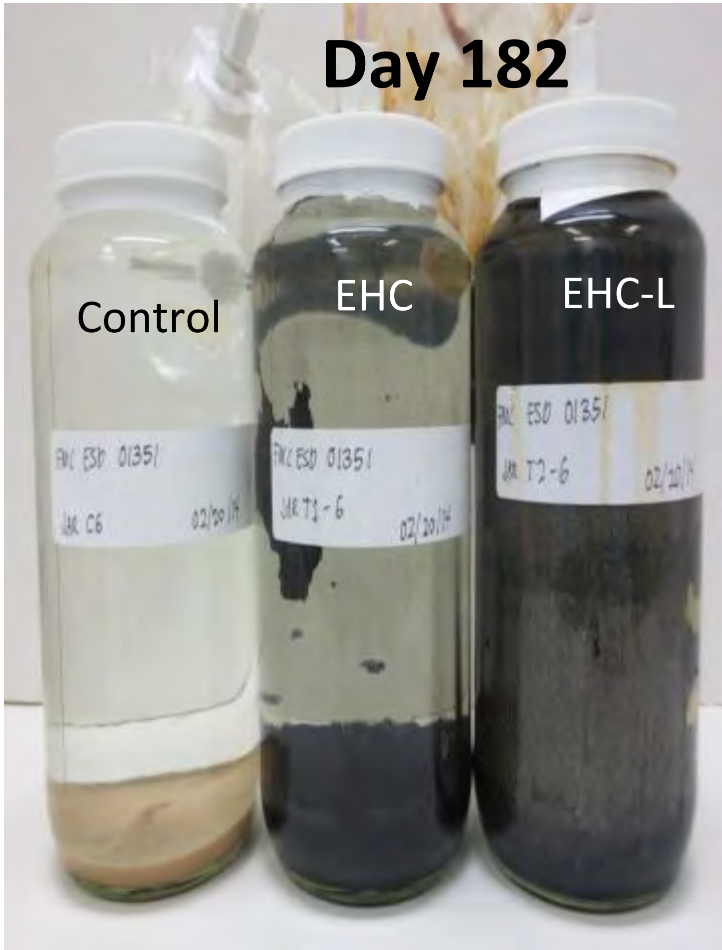
FeS does not fill pore space

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

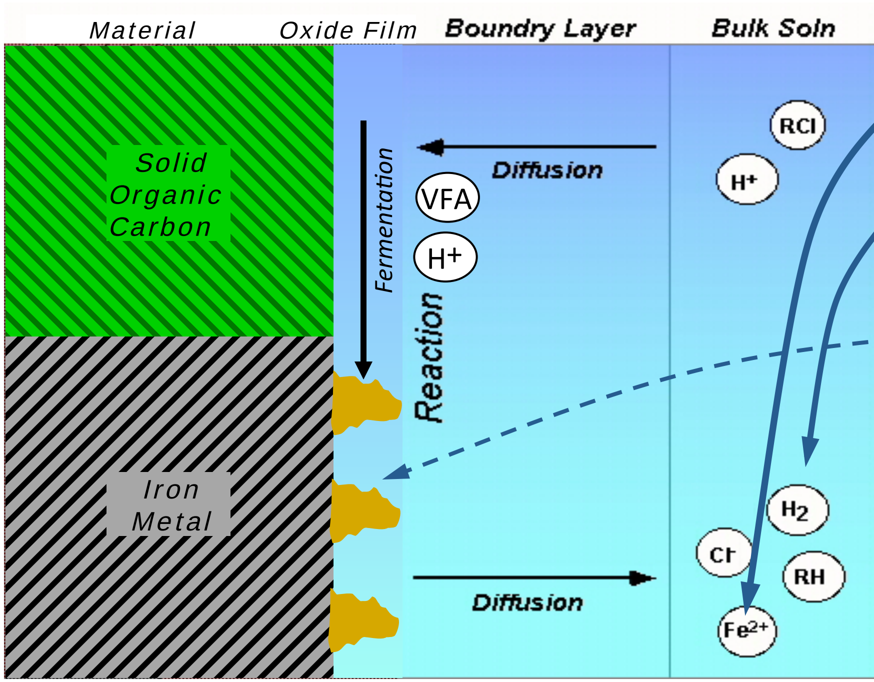
0.56 cm^3 Mackinawite (FeS, 4.9 g/cm^3)
~0.05% of volume of pore space

0.38 cm^3 Pyrite (FeS_2, 4.8 to 5.0 g/cm^3)
~ 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

H_2 generation

ZVI Reactions:

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

$2H_2O \rightarrow 2H^+ + 2OH^-$

$2H^+ + 2e^- \rightarrow H_{2(g)}$

$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$

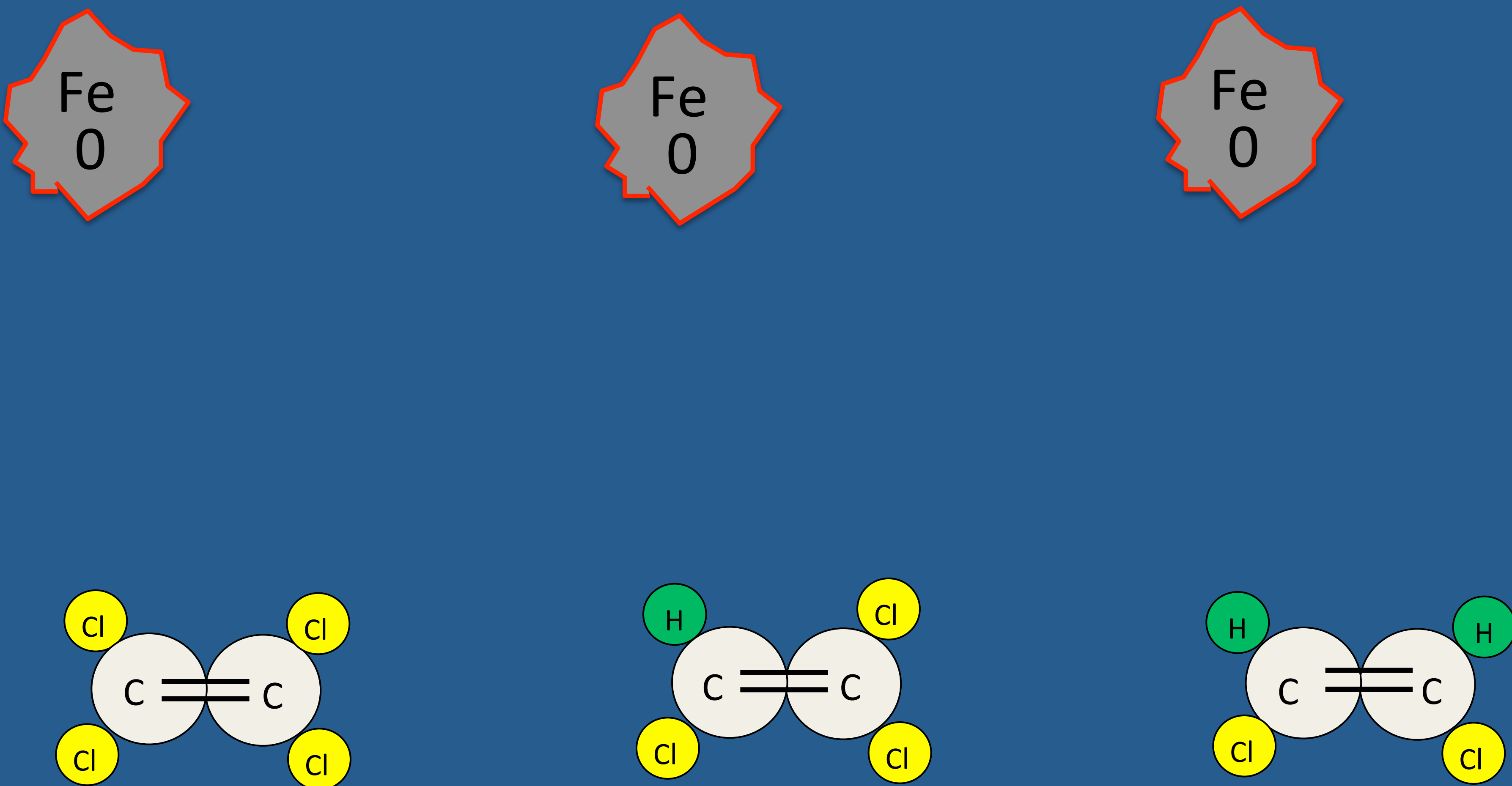
Favorable thermodynamic conditions for dechlorination:

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

Production of organic acids (VFAs):

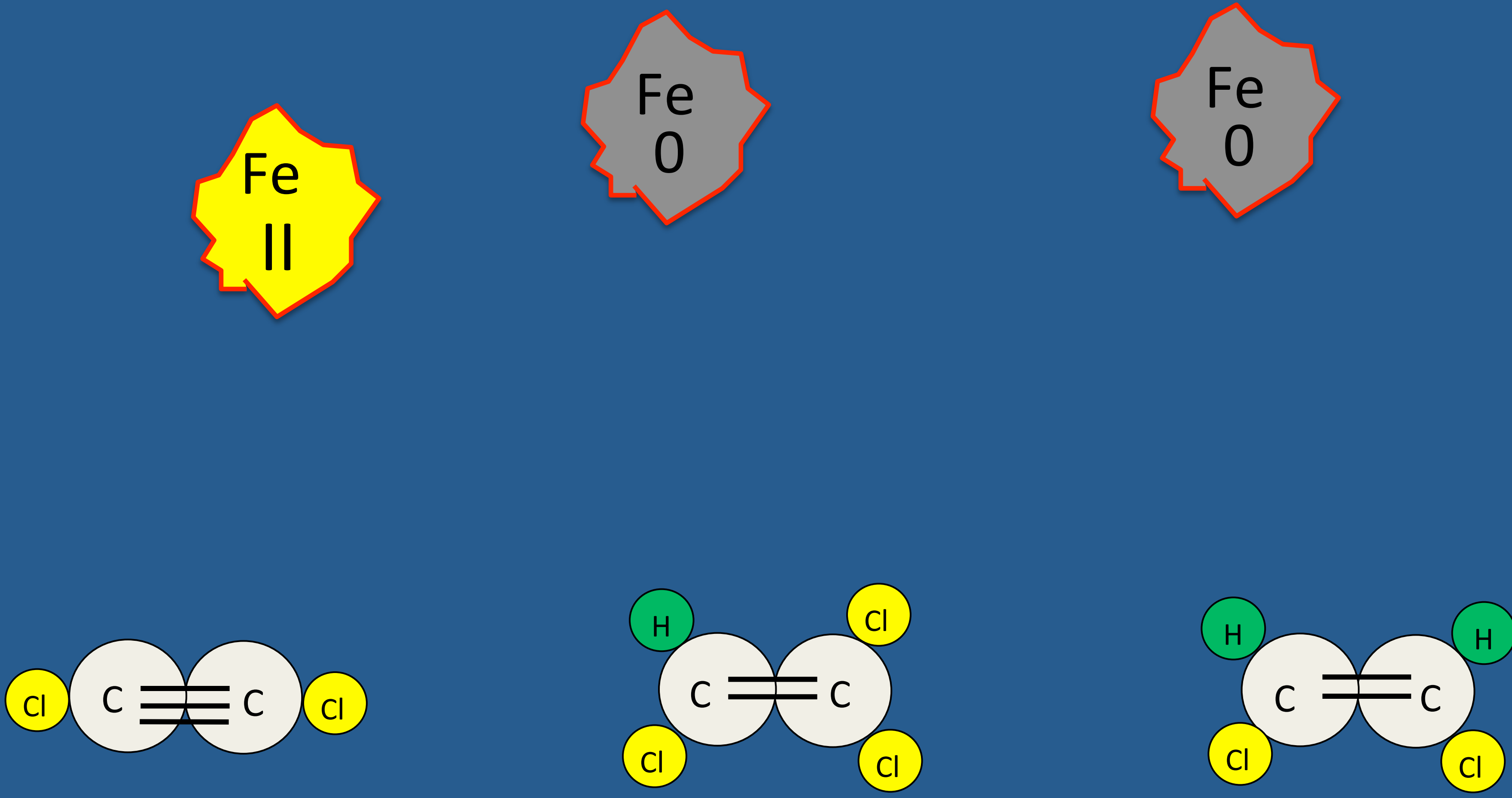
- Serves as electron donor for microbial reduction of CVOCs and other oxidized species such as O_2, NO_3, SO_4
- The release of acids keeps the pH down and thereby serve to reduce precipitate formation on ZVI surfaces to increase reactivity
- Increase rate of iron corrosion/H_2 generation

β elimination (abiotic) pathway



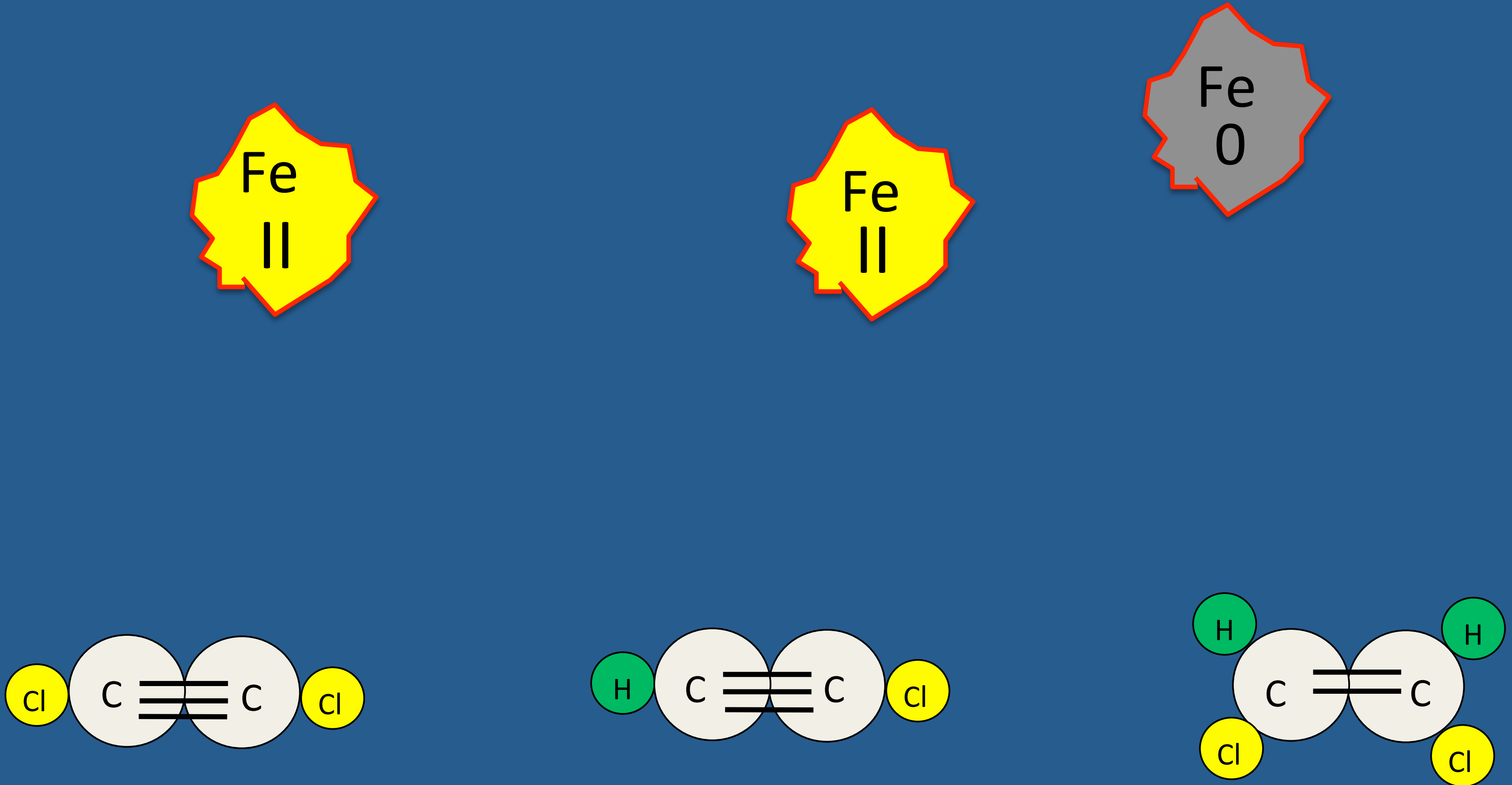
PCE TCE DCE

β elimination (abiotic) pathway



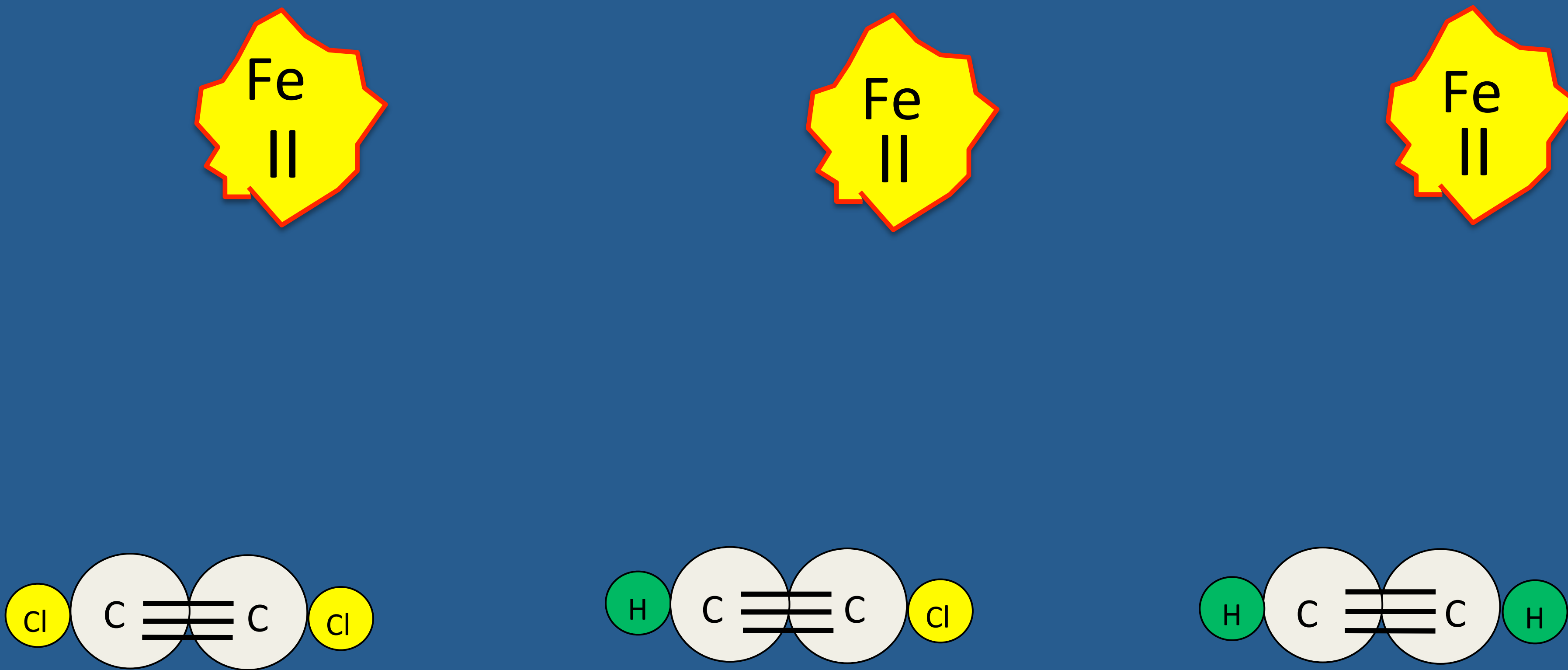
Dichloroacetylene TCE DCE

β elimination (abiotic) pathway



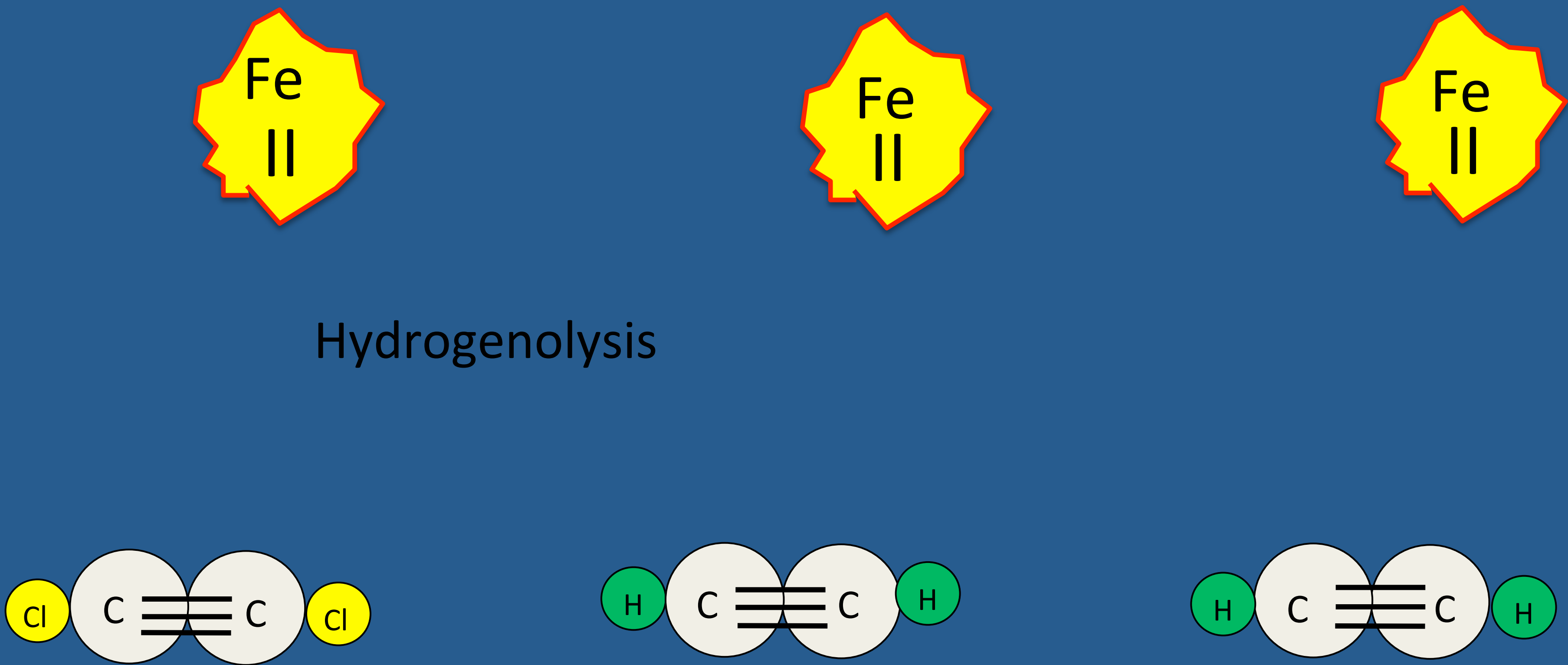
Dichloroacetylene Chloroacetylene DCE

β elimination (abiotic) pathway



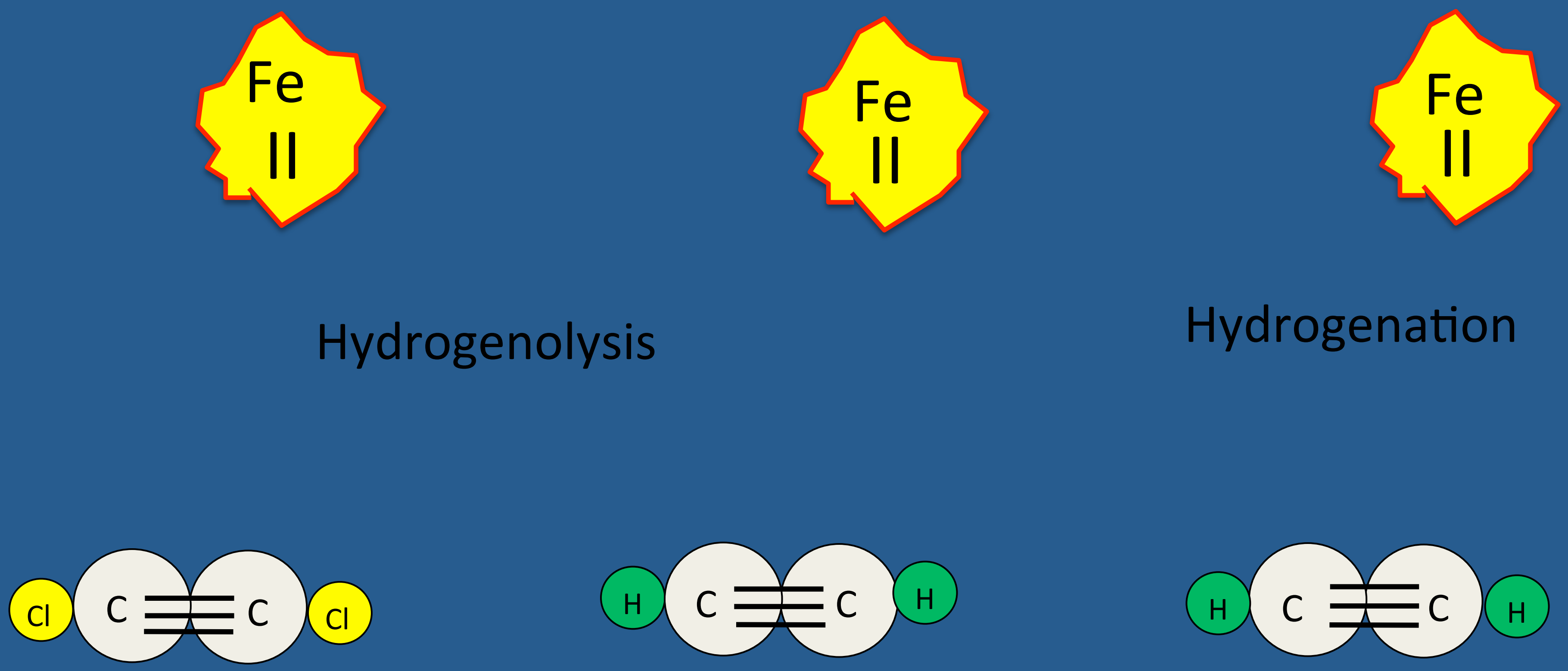
Dichloroacetylene Chloroacetylene Acetylene

β elimination (abiotic) pathway



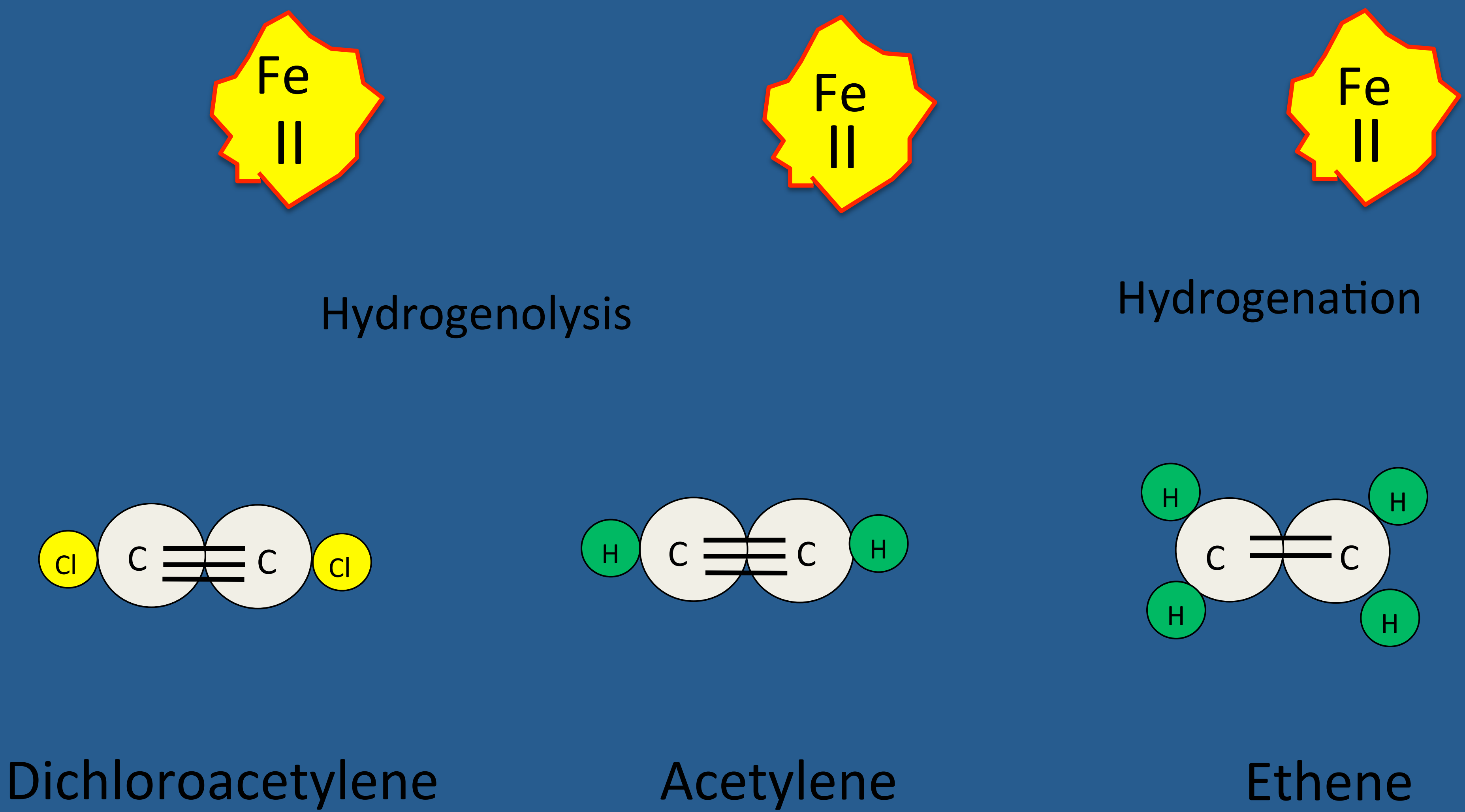
Dichloroacetylene Acetylene Acetylene

β elimination (abiotic) pathway



Dichloroacetylene   Acetylene   Acetylene

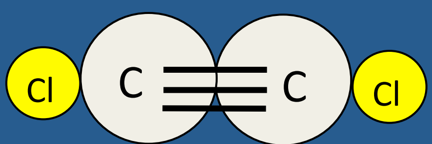
β elimination (abiotic) pathway

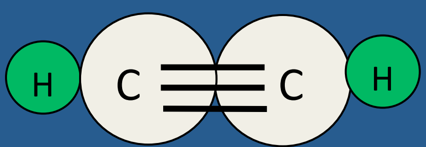


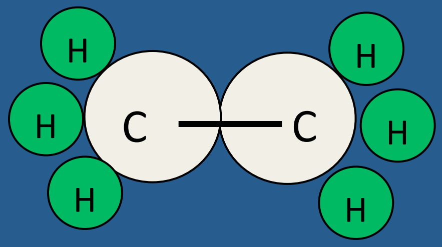
β elimination (abiotic) pathway

Hydrogenolysis

Hydrogenation







Dichloroacetylene

Acetylene

Ethane

Biotic – ISCR Field Comparison

Two Pilot Tests Conducted at Concord Naval Weapon Station

Biotic Only – (2011 – 2012)

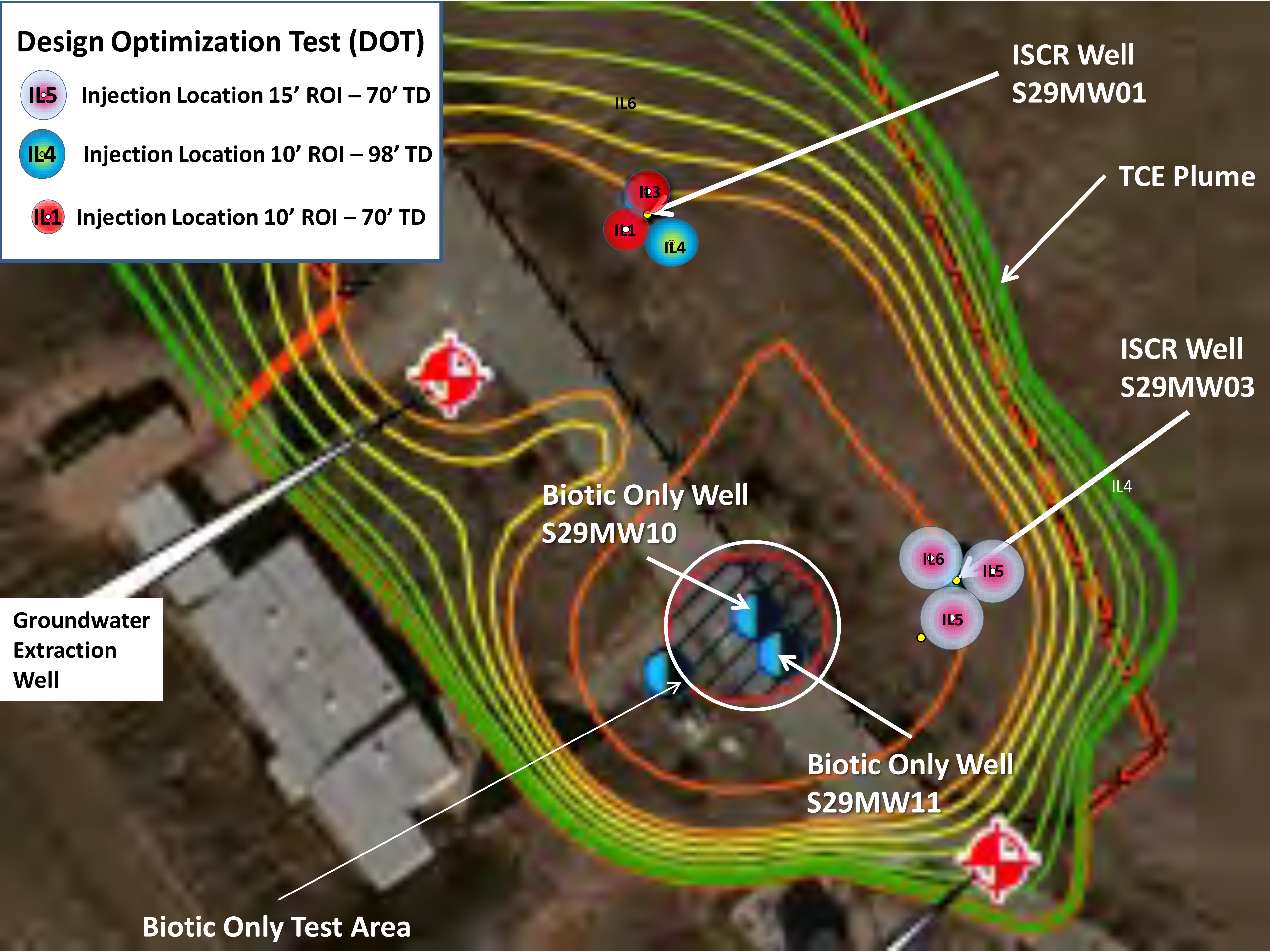
In Situ Chemical Reduction (ISCR) – (2013 – 2014)

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™)**
- **H_2 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
IL6
IL3
IL1
IL4
TCE Plume
ISCR Well
S29MW03
IL4
Biotic Only Well
S29MW10
IL6
IL5
IL5
Groundwater
Extraction
Well
Biotic Only Well
S29MW11
Biotic Only Test Area

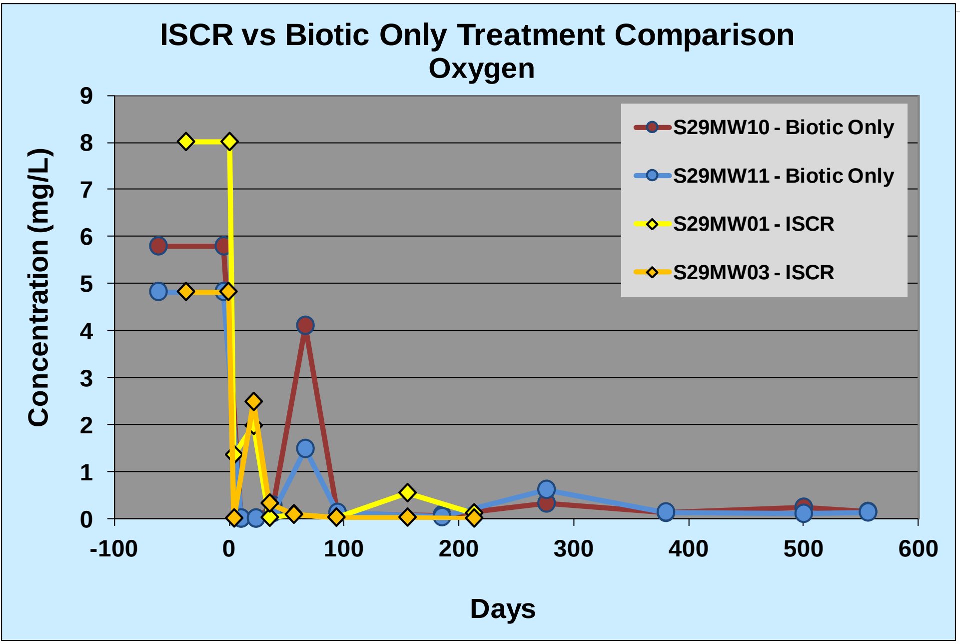
Organic Reducing Substrate –ELS – Biotic

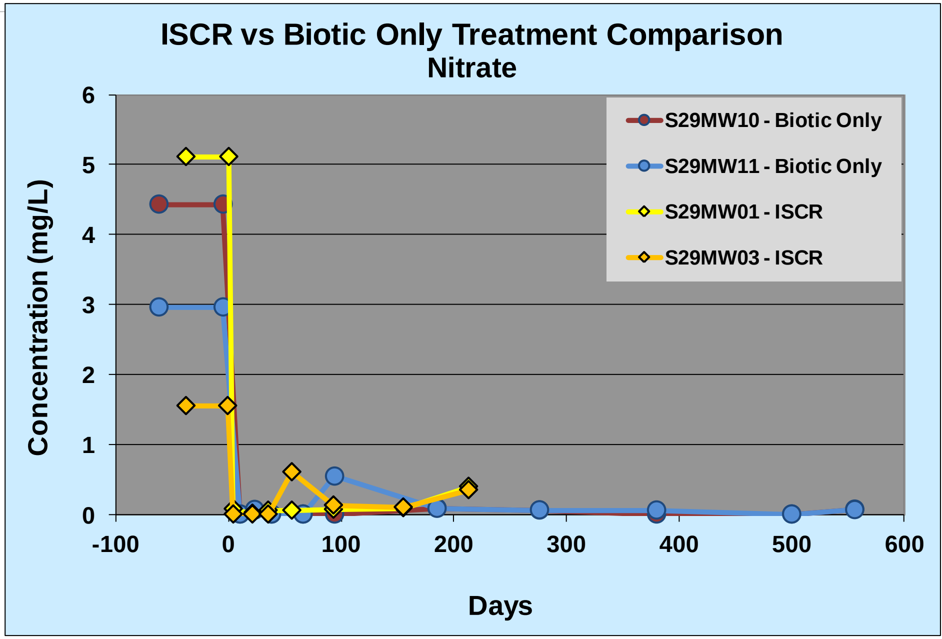
Chemical Reductant - Zero Valent Iron - Abiotic

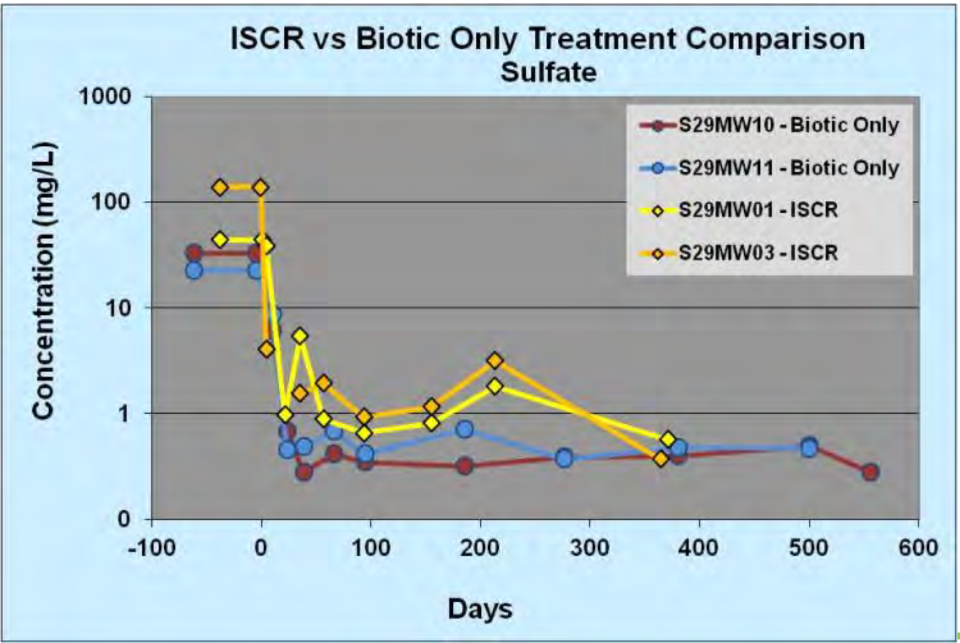
ZVI added to:

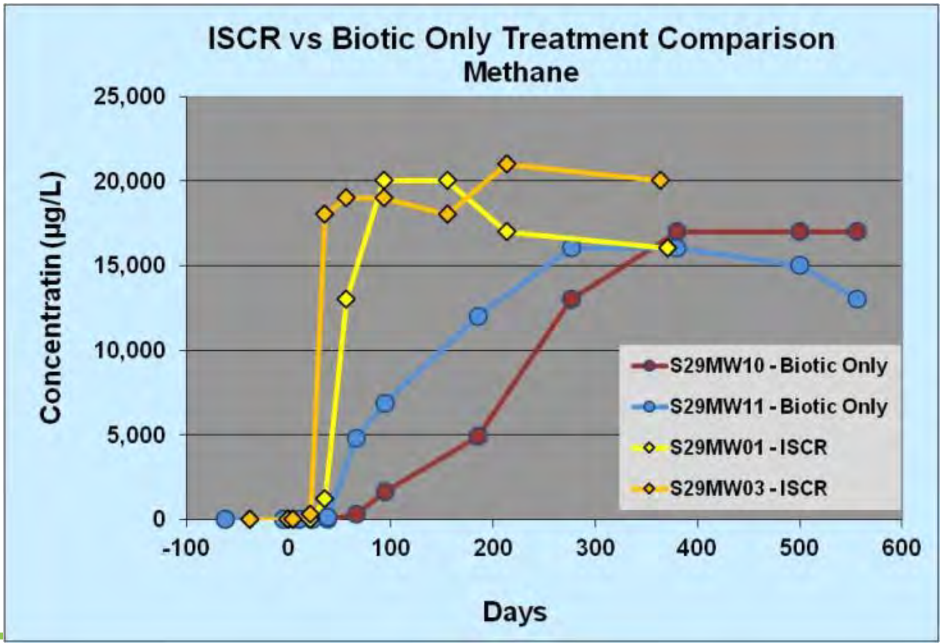
- Maintain pH in range favorable for biological degradation
- Bypass generation of toxic daughter products
- Reduction of daughter products more rapidly achieves goals
- Provide long term process for continued dechlorination.

Analytical Results

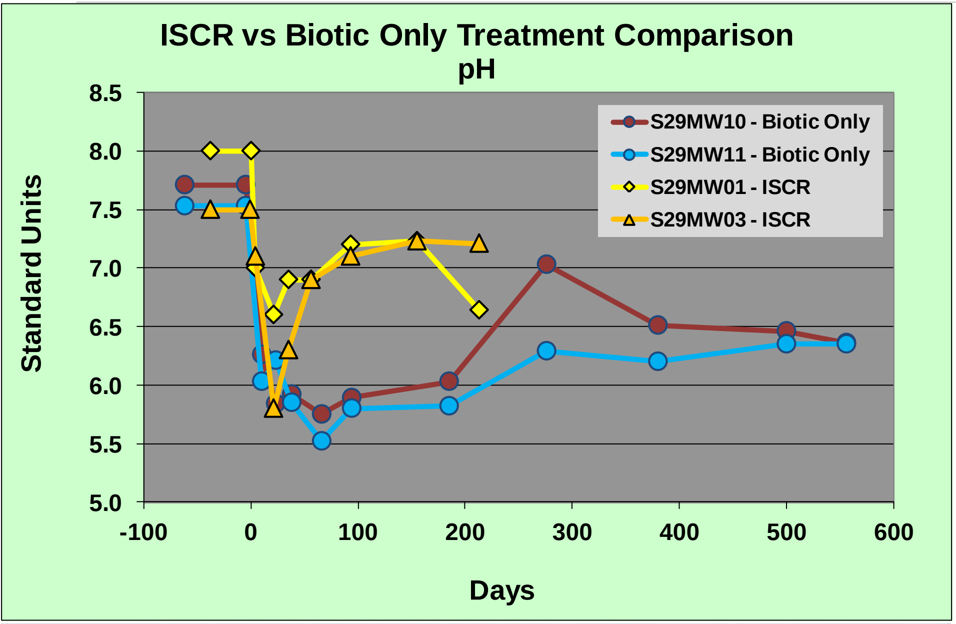


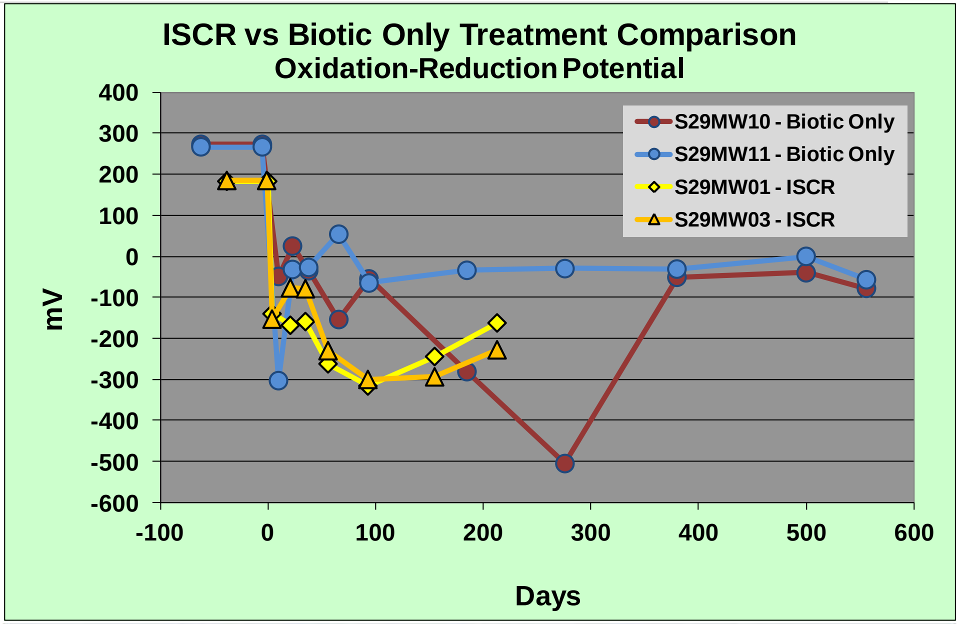


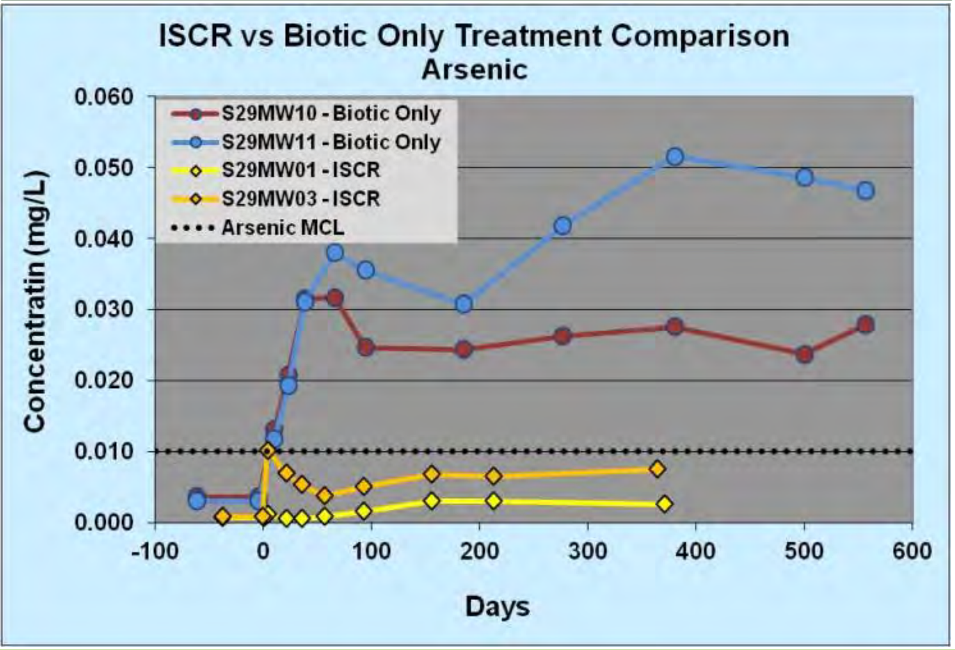


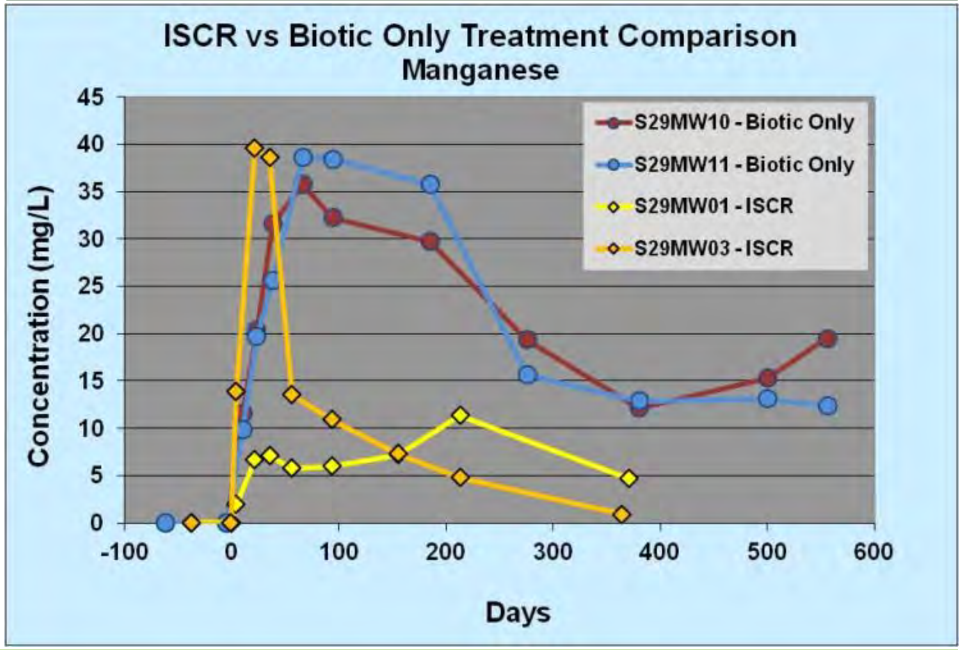


Analytical Results

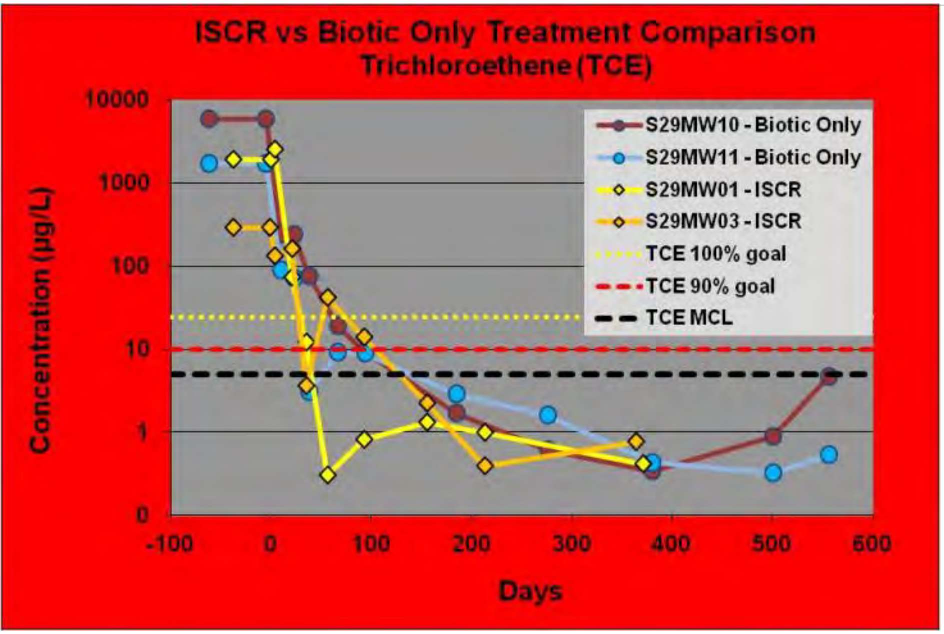


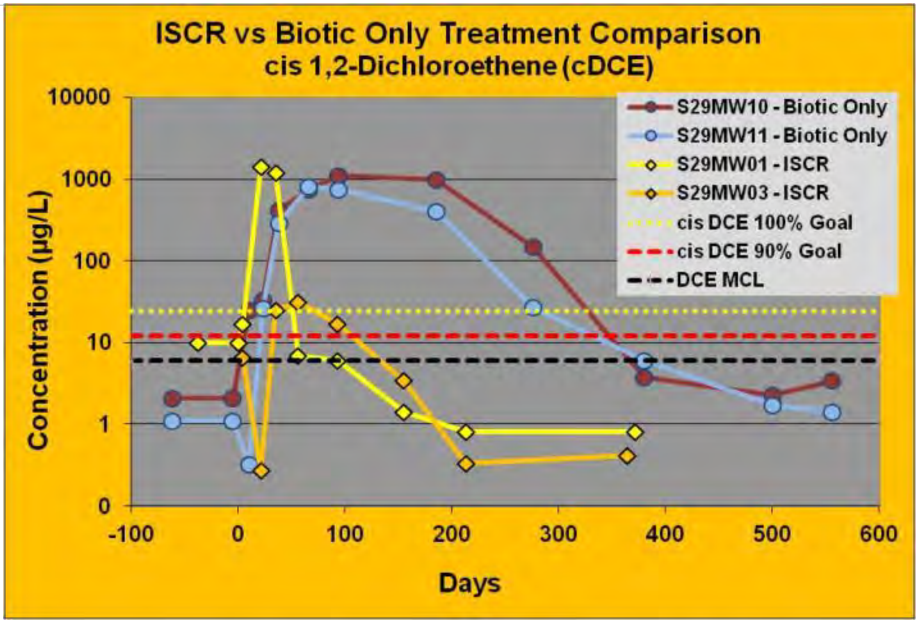


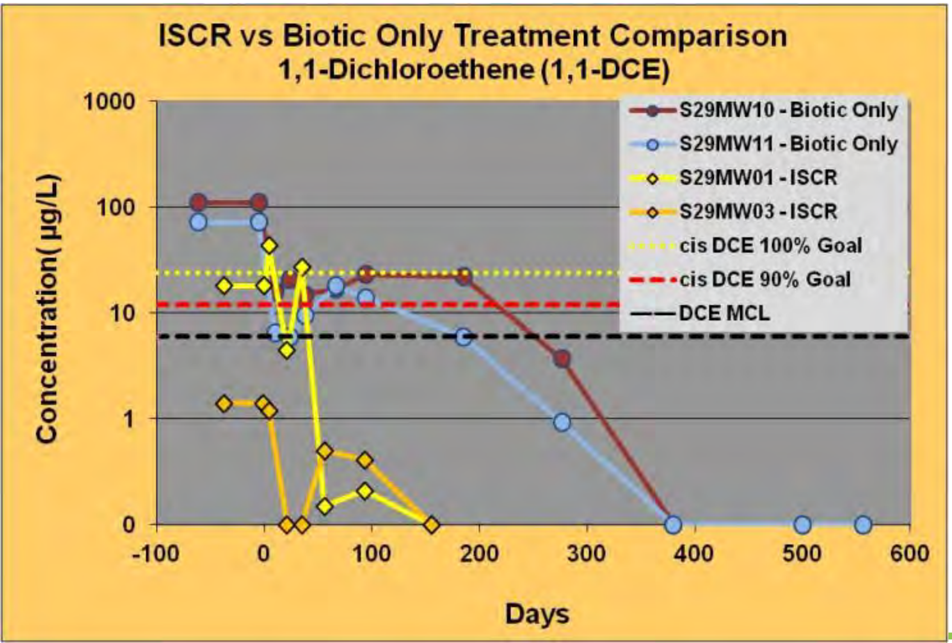


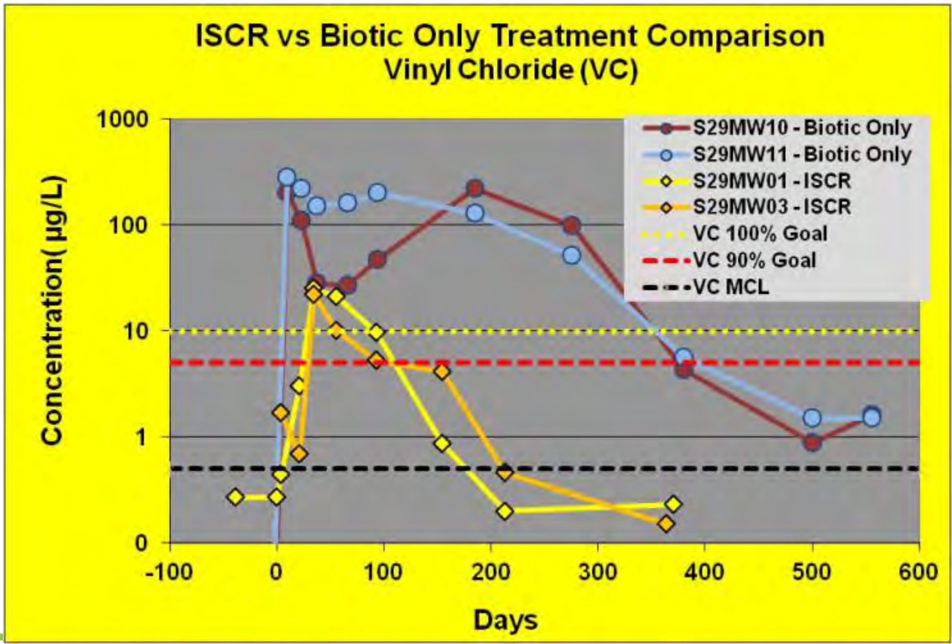


Analytical Results









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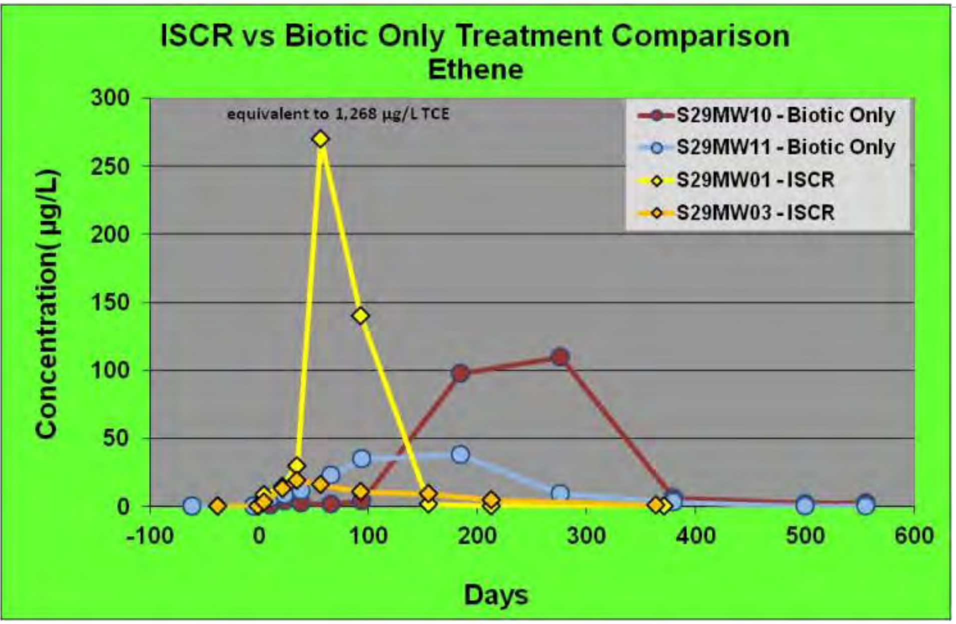

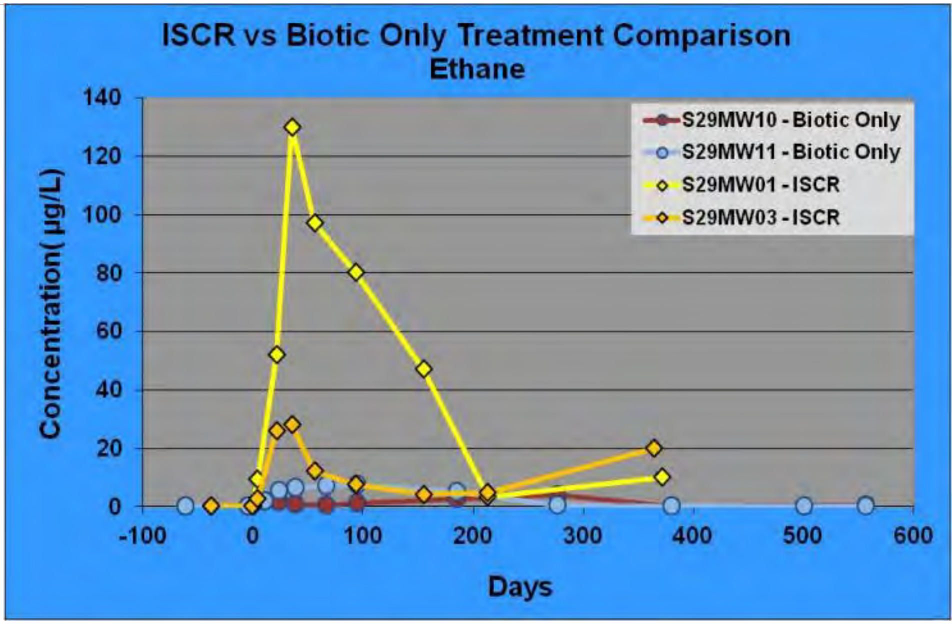

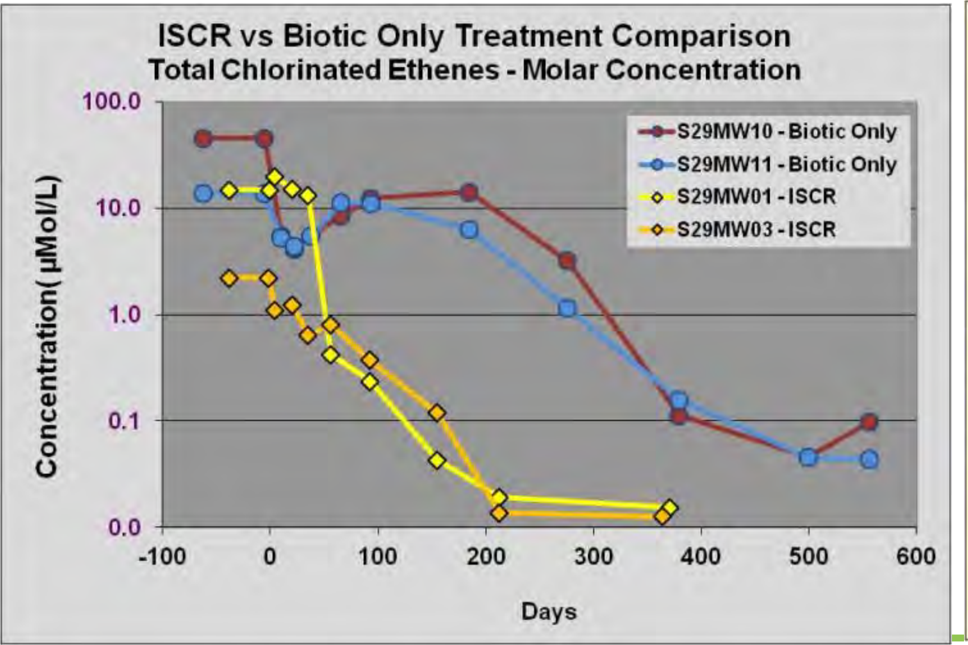

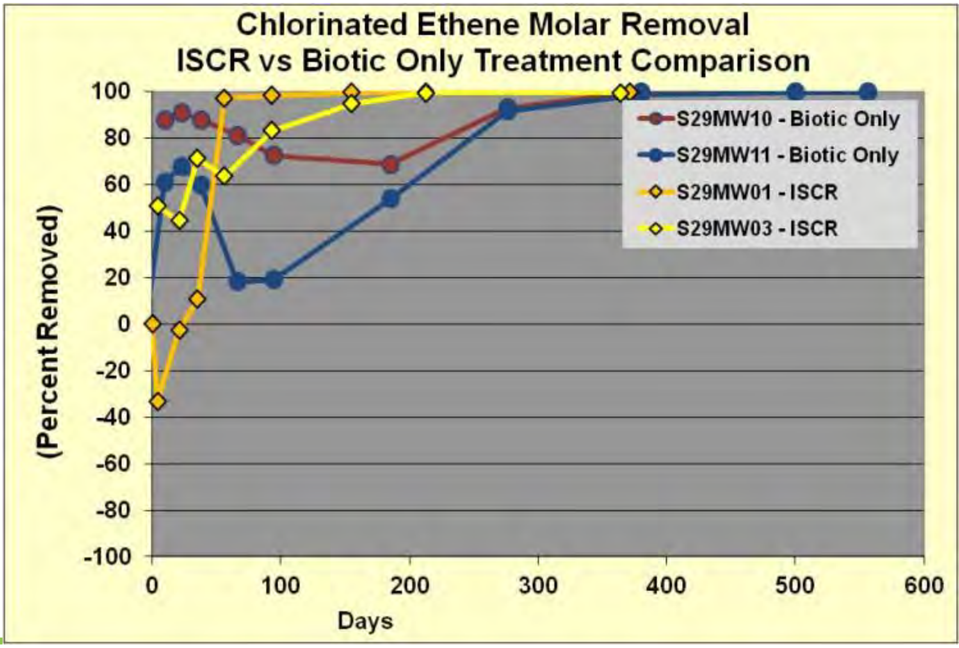

Considerations when applying biotic and abiotic reductive processes.

- 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 to 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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