Considerations for the Assessment of Chlorinated Solvents

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for

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Characterizing Chlorinated Solvents

September 11, 2007

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Questions

- **During Talk Is OK!**
- **Also Time for Questions at End of Talk**
- **Questions Before Break As I have to Go Back to UNH at 11:00am**

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Topics Covered

- **Properties of Chlorinated Solvents**
- **Fate in Environment**
  - **Sorption, Dissolution**
  - **Transport**
  - **Reactions**
- **DNAPL Issues**

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Overarching Considerations and Questions

- **Porous (Unconsolidated) Media and Fractured Rock**

- **Why Do Chlorinated Solvents End Up Where They Are?**

- **Why Are Chlorinated Solvents So Persistent?**

- **No Vadose Zone or Vapor Issues Covered Today**

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Chlorinated Solvents

- **Course Focus = Chlorinated Aliphatic Hydrocarbons (CAHs)**
  - **PCE, TCE, DCE, VC, chloroform, methylene chloride**
  - **Most used as solvents**
  - **No aromatic ring structures**
  - **Rarely 100% pure solvent**
    - **e.g., PCE often has 5% TCE**
    - **Waste mixtures are not pure either**

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Exhibit 2-1: CAHs Commonly Identified as Environmental Contaminants

Name	Common Name(s)	Abbreviation[1]	Common Waste Sources
CHLORINATED ETHENES			
Tetrachloroethene(-ethylene)	*Perchloroethene*	PCE	Solvent waste
Trichloroethene(-ethylene)	None	TCE	Solvent waste, degradation product of PCE
cis-1,2-Dichloroethene(-ethylene)	Acetylene dichloride	cis-DCE	Solvent waste, degradation product of PCE and TCE
trans-1,2-Dichloroethene (-ethylene)	Acetylene dichloride	trans-DCE	Solvent waste, degradation product of PCE and TCE
1,1-Dichloroethene(-ethylene)	Vinylidene chloride	1,1-DCE	Solvent waste, degradation product of 1,1,1-TCA
Chloroethene(-ethylene)	*Vinyl chloride*	VC	Polyvinyl chloride production waste, degradation product of PCE and 1,1,1-TCA
CHLORINATED ETHANES			
1,1,1-Trichloroethane	Methyl chloroform	1,1,1-TCA	Solvent waste
1,1,2-Trichloroethane	Vinyl trichloride	1,1,2-TCA	Solvent waste
1,2-Dichloroethane	Ethylene chloride	1,2-DCA	Solvent waste, degradation product of 1,1,2-TCA
1,1-Dichloroethane	Ethylidene chloride	1,1-DCA	Degradation product of 1,1,1-TCA
Chloroethane	None	CA	Refrigerant waste, tetraethyl lead manufacturing waste, degradation product of 1,1,1-TCA and 1,1,2-TCA
CHLORINATED METHANES			
Tetrachloromethane	*Carbon tetrachloride*	CT	Solvent waste, fire extinguisher waste
Trichloromethane	*Chloroform*, methane trichloride	CF	Solvent waste, anesthetic waste, waste degradation product of CT
Dichloromethane	*Methylene chloride*, methylene dichloride	MC	Solvent waste, degradation product of CT
Chloromethane	Methyl chloride, monochloromethane	CM	Refrigerant waste, degradation product of CT

Notes:
[1]Abbreviations are based on the names in bold italic type.
Sources: Sawyer and others 1994; Merck 1989

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Exhibit 2-2: Molecular Structures of Common CAHs

Chlorinated Ethenes

Perchloroethene

Trichloroethene

cis-1,2-Dichloroethene

Trans-1,2-Dichloroethene

1,1-Dichloroethene

Vinyl Chloride

Chlorinated Ethanes

1,1,1-Trichloroethane

1,1,2-Trichloroethane

1,2-Dichloroethane

1,1-Dichloroethane

Chloroethane

Chlorinated Methanes

Carbon Tetrachloride

Chloroform

Methylene Chloride

Chloromethane
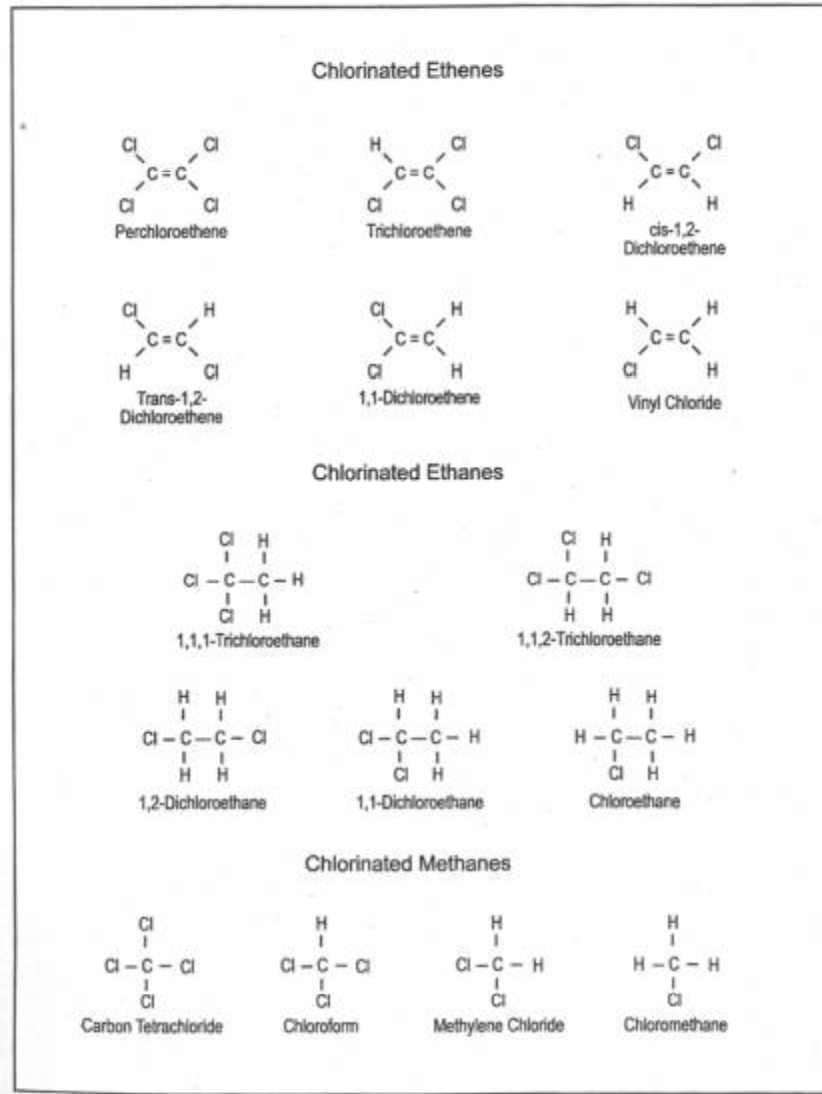
Source: Modified from Sawyer and others 1994

EPA 542 p. 2-3 Ex. 2-2

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Effects of Chlorine Substitution Into Aliphatic Structure

- **MW $\uparrow$, Density $\uparrow$**
  - **CAHs are sinkers (Dense NonAqueous Phase Liquids, DNAPLS)**
- **Vapor Pressure $\downarrow$, Aqueous Solubility $\downarrow$**
  - **High ug/L to low mg/L range**
- **Chlorines Are Electrophillic**
  - **CAHs rarely donate e$^-$ and H$^+$**
  - **Key difference vs. petroleum hydrocarbons**
- **CAHs Tend to End Up in the Lower Regions of Saturated Zone**
  - **Often in bedrock zone**
  - **At bottom of permeable media (pooling of DNAPL)**

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Fate and Transport of Chlorinated Solvents

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DNAPLs

- **Hard to Access if in a Pool of Immiscible Fluid**
- **Surfactants May Not Help Biodegradation as They Often Do Not Cause Dissolution of Compound**
  - **Only mobilize them as colloidal, non-aqueous phases**
- **DNAPL Issues Have Been Subject of Recent ITRC Committees**
  - **Last talk today**
  - **e.g., Bioremediation of DNAPLs**

Availability

- **To Be Degraded, Contaminant Must Be Available for Remediation**
  - **Microbes**
  - **Chemical/Physical oxidizing agent**
- **Less Available If:**
  - **Sorbed (adhered) to surfaces**
  - **In non-aqueous phase (DNAPL pool)**
- **For CAHs Low Concentration (ug/L to mg/L) in Aqueous Phase as Dissolved Species**
- **Less Dissolved = Harder to Remediate**
  - **Many remediation agents tend work best on dissolved species**

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Sorption

- **Function of Contaminant and the Type of Medium**
  - **Clay vs. sand**
  - **THF vs. TCE**
- **Rate of Desorption May Control Degradation Rate**
- **Sorption Has Positive Effect Because Movement to Downgradient Receptors Is Slower**
  - **Limits amount of contaminant in solution and being transported with groundwater**
  - **Contrast of CAHs vs. MtBE which is very soluble and moves rapidly with groundwater**

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Implications of Sorption and Low Solubility: Minimum Substrate Concentration (S_{min}) for Bioremediation

- **Concentration of Energy-Generating Substrate Below Which Microbe Gets Insufficient Energy for Growth**

- **Implications – If Contaminant Concentration *In Situ* < S_{min} → No Biodegradation**

- **Problem Can Be Avoided If:**

  - **Another energy-generating compound (e.g., glucose) is available in concentration > S_{min}**

  - **Multiple substrates all at low concentrations, but aggregate > S_{min}**

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Mass Transfer

- **Movement of Needed Substances (Substrates) to Cells**

- **Movement of Wastes Away From Cells**

- **Cells Can Be on Surfaces (Biofilm) or Floating in Groundwater**
  - **Normally pristine conditions sorbed to surfaces**
    - **Expend little energy swimming**
    - **Substrates flow to them and wastes flow away**
  - **When contamination increases, floating cells increase**
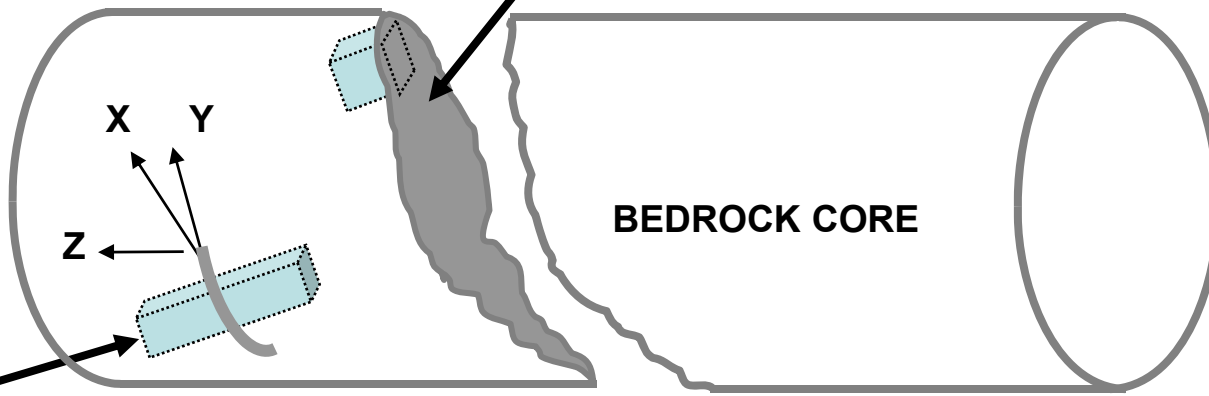   - **Less advantage to being attached**

Today's "Classification"

- **Open (macro) fractures/pores**
    - **mm to cm apertures**
    - **Minimal sealing**
    - **Higher (preferential) flows**
- **Microfractures/pores**
    - **μm to mm apertures**
    - **Partially sealed with minerals and clays**
    - **Diffusion dominates movement of contaminants, etc.**

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Macrofracture (mm to cm)

BEDROCK CORE

X   Y

Z

Microfracture (≤ mm)

Classification for Bedrock

Classification

- **Rock matrix (bulk or host rock) or porous media grain**
- **Weathering rind**
- **Stagnant boundary layer of fluid**
  - **Interface between rock/media surface and fluid**
- **Bulk fluid (porewater)**

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Subsurface Conceptual Model

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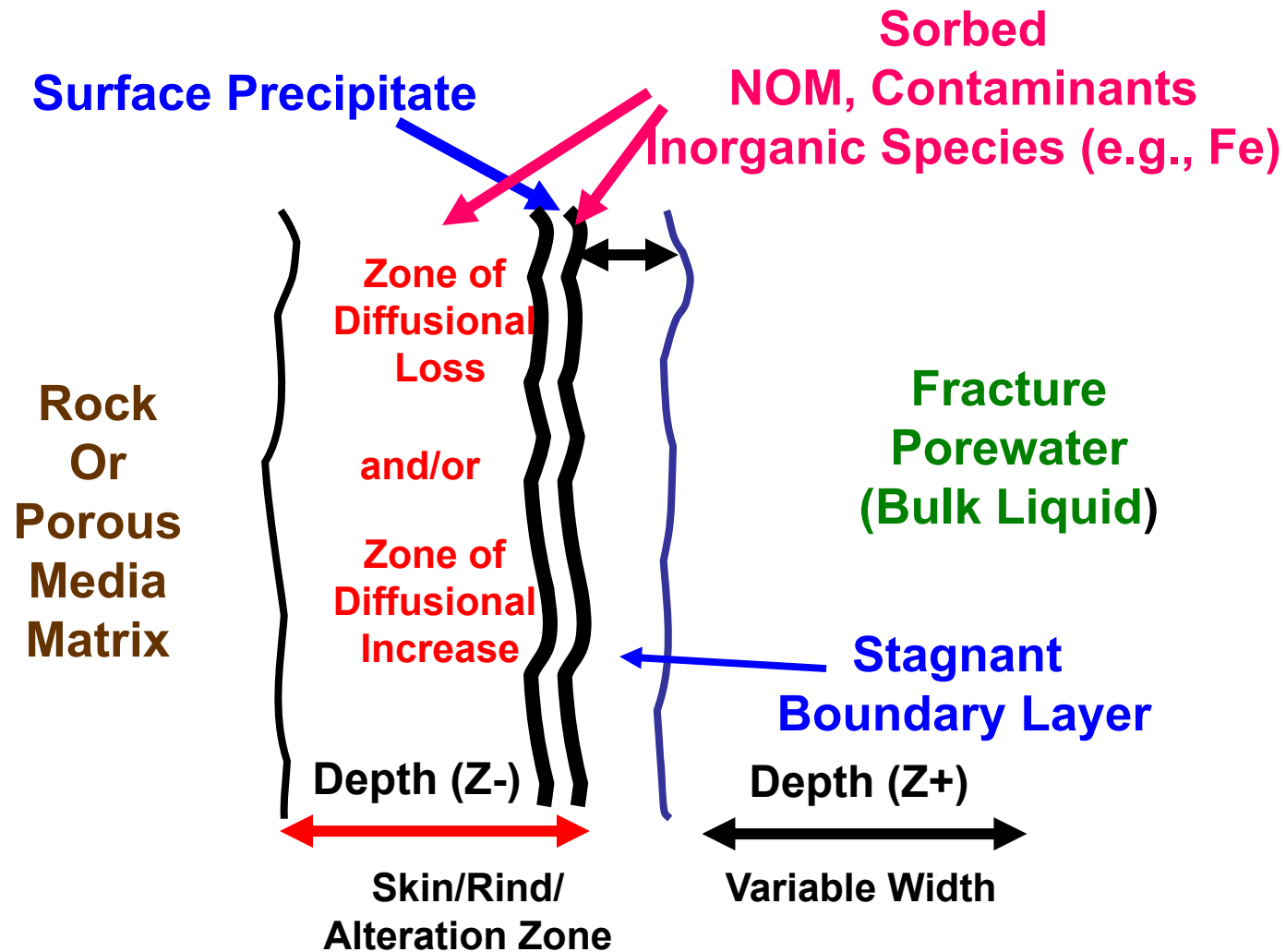
Microfractures/Pores vs. Open Fractures/Pores

- **Microfractures/pores often hydraulically isolated vs. open fractures/pores**

- **More reducing than groundwater pumped from open fractures/pores**

- **All fractures/pores can differ over small distances**

  - **Function of heterogeneity of mineralogy and flow regime**

Movements of Solutes Within Fractures/Pores

- **Flux (mass transfer) across interface**
  - **Stagnant boundary layer**
  - **By molecular diffusion only**
  - N_s **= Flux**
  - $N_s = \dfrac{K (S_o - S_i)}{L}$
  - N_s **= Flux = mass transferred / unit surface area * time (μg/cm^2 * d)**
  - **K = Mass transfer coefficient**
    - **f (temperature, solute diffusion coefficient, fluid types)**
    - **Surface area / time (cm^2/time)**

Movements of Solutes Within Fractures/Pores

$$N_s = \frac{K}{L} (S_o - S_i)$$

- **L = thickness of stagnant boundary layer across which diffusion occurs (cm)**
- **S_b = concentration of diffusing substance in bulk liquid (mass/volume) (μ g/L)**
- **S_i = concentration of diffusing substance on other "side" of stagnant boundary layer (mass/volume) (μ g/L)**

Factors Controlling Mass Flux

- **K = type of substance, environmental conditions, fluid characteristics**
  - **Molecular size, temperature, fluid viscosity**
- **Flow regime – L – thickness of stagnant layer (Flow ↑, L ↓), surface roughness**
- **Concentration gradient of (S_b – S_i)**
  - **High S_b = highly contaminated zone**
  - **Low S_i usually = biodegradation**

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Why Do Chlorinated Solvents End Up Where They Are?

- **At the bottom of aquifers**
  - **They are more dense than water, so they sink**
- **Sorbed to surfaces of porous media/fractures**
  - **They can penetrate into the weathering rind (i.e., the matrix)**

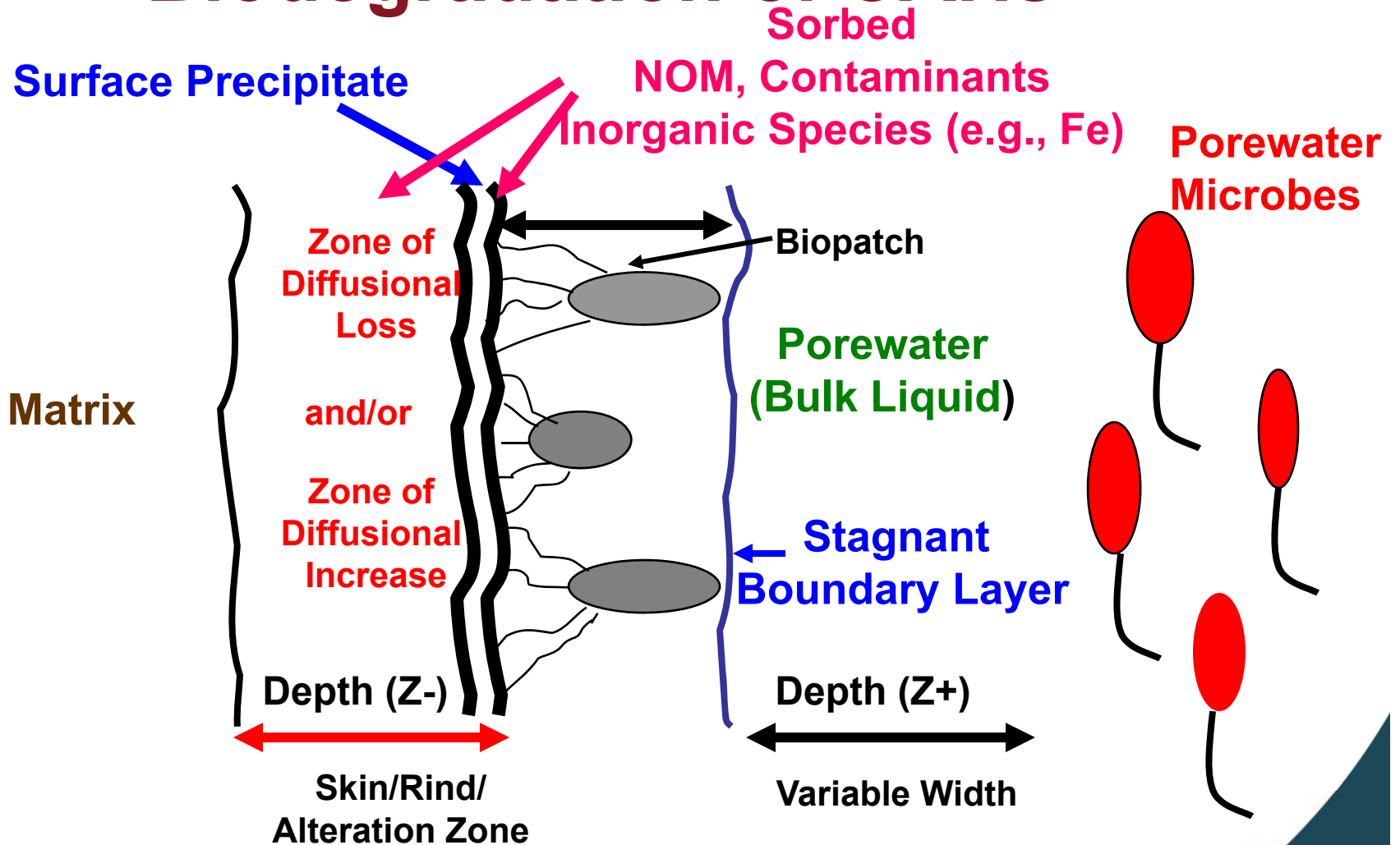# Why Are Chlorinated Solvents So Persistent?

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Abiotic Degradation of CAHs

- **Hydrolysis, Elimination, Abiotic Reductive Dechlorination**
- **Rates Slow vs. Biodegradation**
    - **Only applicable if plume moves very slowly**

Microbial Conceptual Model: Biodegradation of CAHs

CAH Biodegradation Processes

- **Aerobic Degradation**
  - **Direct aerobic oxidation of CAH**
  - **Co-metabolic oxidation of CAH under aerobic conditions**
- **Anaerobic Reductive Dechlorination**
  - **Direct anaerobic reductive dechlorination of CAH (Halorespiration)**
  - **Co-metabolic oxidation of CAH under anaerobic conditions**
- **Anaerobic Oxidation of VC and DCE**
- **Many Complex Processes that Will Not Be Considered Today**

CAH vs. Petroleum Hydrocarbon Biodegradation

- **CAH Is Much More Confusing**
    - **CAH often acts as an <u>electron acceptor</u>**
- **Biological Reactions May Not Convert CAH to CO_2**
    - **Reactions may stop at intermediates (e.g., VC) which can be worse than original CAH present**

CAH Biodegradation Generalizations

- **More Chlorines Per Molecule, Biodegradation More Likely to be Anaerobic Reductive Dechlorination**
  - **Carbon atoms in these molecules are highly oxidized because of chlorines**
  - **So molecules are easily reduced**
- **Less Chlorines Per Molecules = Aerobic Degradation**
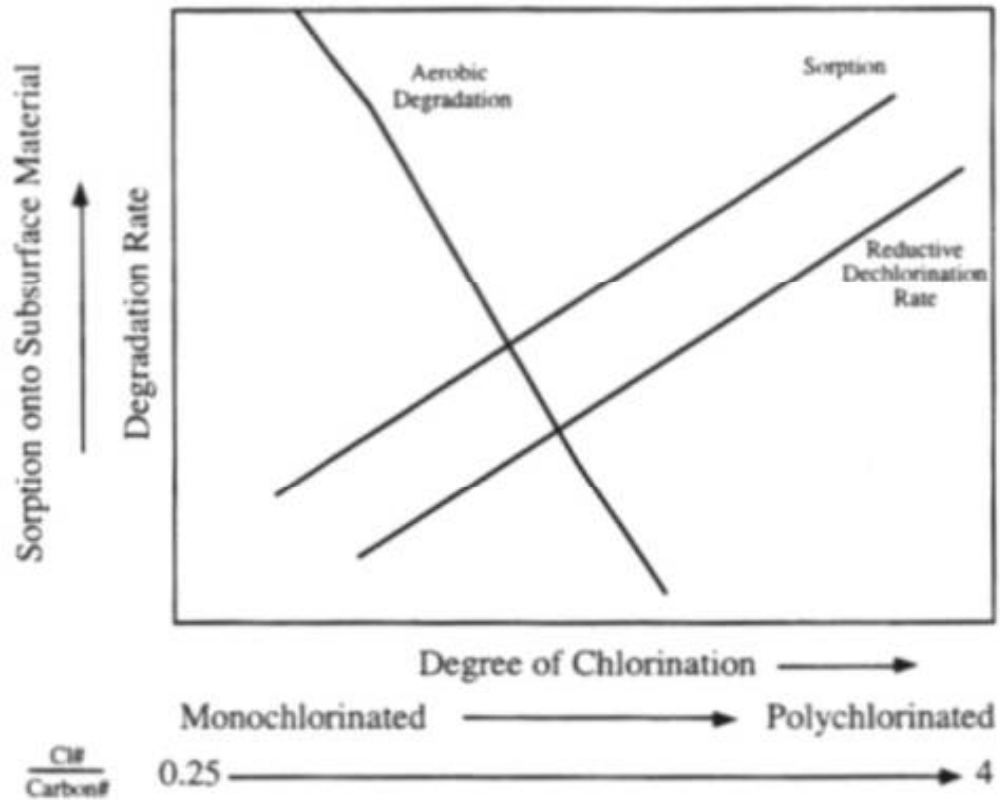- **More Chlorines = More Sorption**

Figure 10.9. Relationships between degree of chlorination and anaerobic reductive dechlorination, aerobic degradation and sorption onto subsurface material.

# Anaerobic Reductive Dechlorination

- **Direct Anaerobic Dechlorination**
    - **Also called halorespiration or dehalorespiration**
- **Co-metabolic Anaerobic Dechlorination**
- **Results of Both Processes Look the Same**
- **Different Bacteria Perform Them**
- **Need H_2**
    - **Source = fermentation**

Anaerobic Reductive Dechlorination

- **Chlorinated Solvents are Electron Acceptors (Oxidizing Agents)**
- **Reduction Reaction**
- **Hydrogens Replace Chlorines in Molecule**
- **Need More Reducing Conditions for VC to Replace Chlorine Than PCE or TCE**

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Figure 2.2
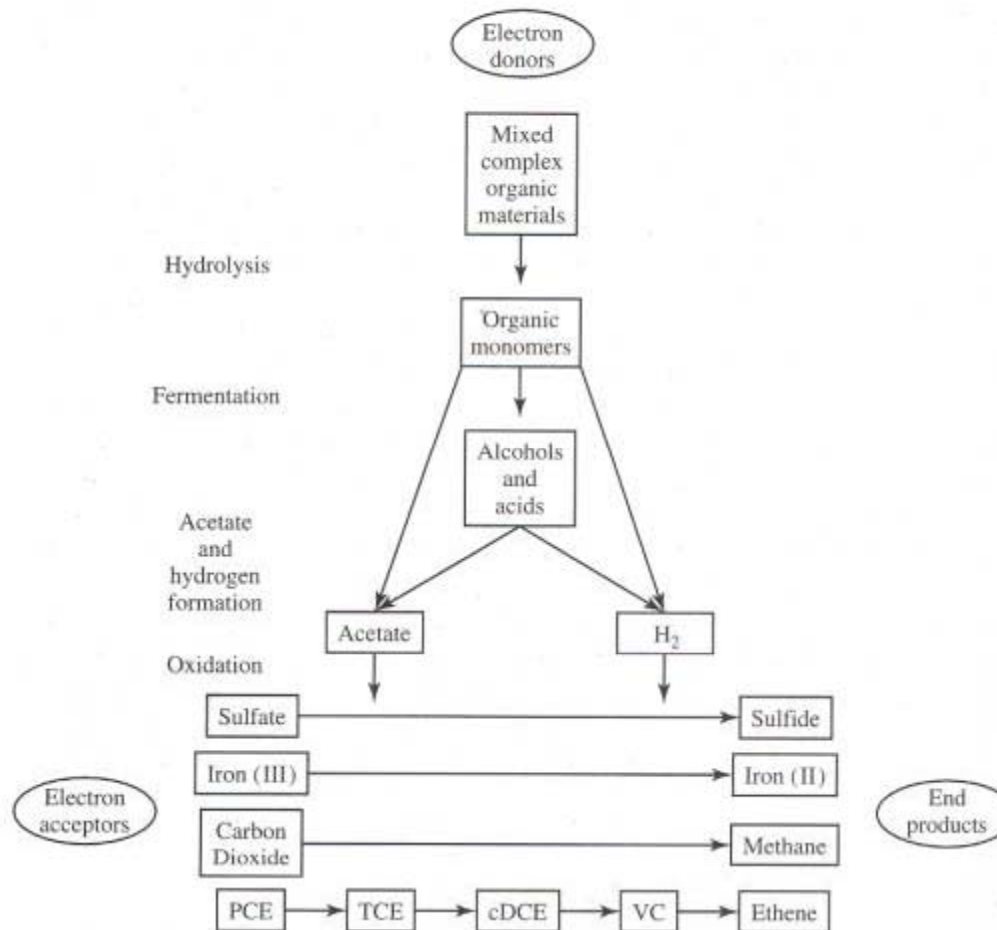Reductive Dehalogenation of Chlorinated Ethenes
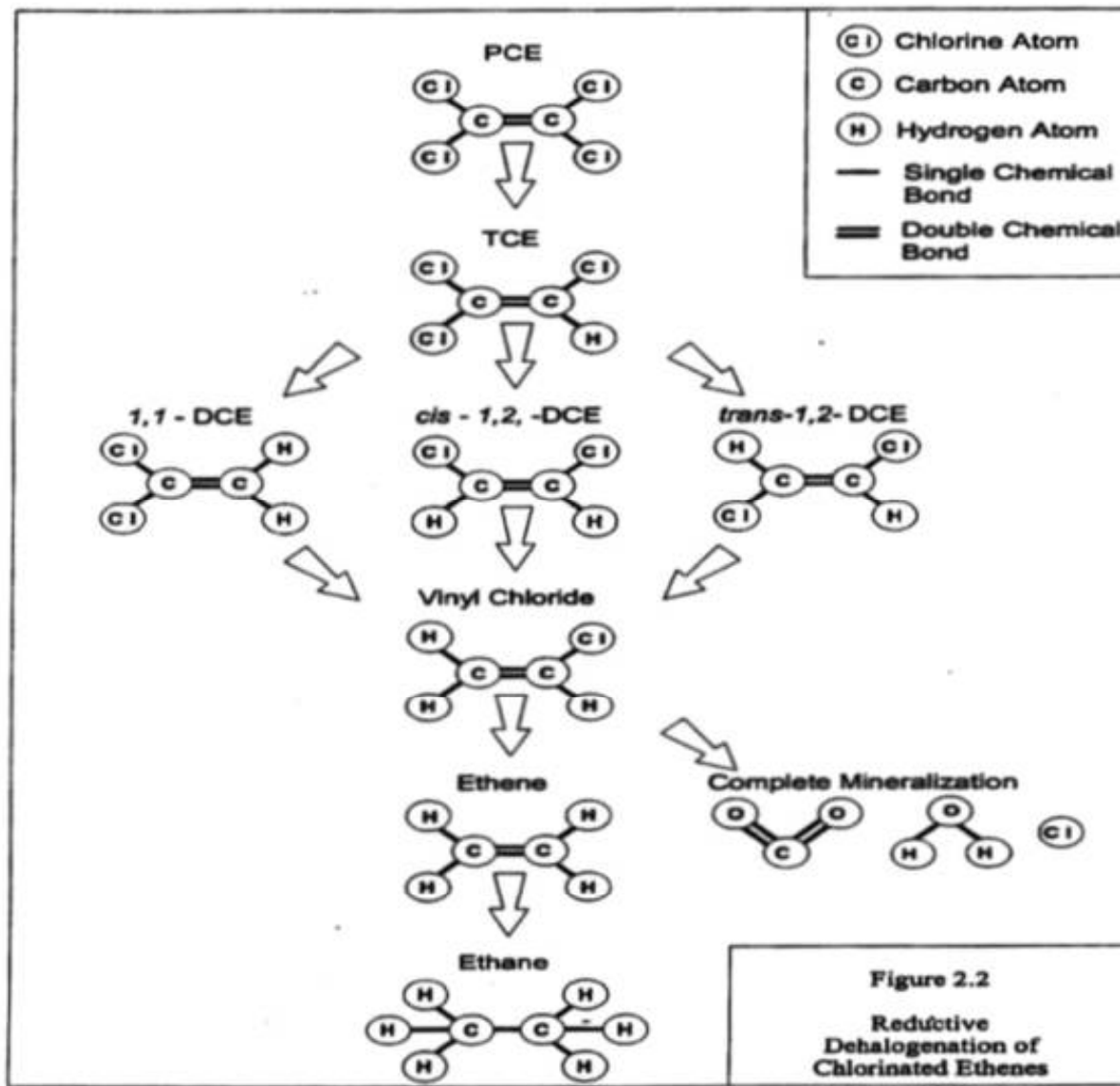
Figure 14.4 Electron flow from electron donors to electron acceptors in the anaerobic oxidation of mixed and complex organic materials. Microorganisms that can use chlorinated compounds (PCE, TCE, cDCE, and VC) as electron acceptors in *dehalorespiration* compete for the electrons in the acetate and hydrogen intermediates with microorganisms that can use sulfate, iron (III), and carbon dioxide. SOURCE: P. L. McCarty, 1997b.
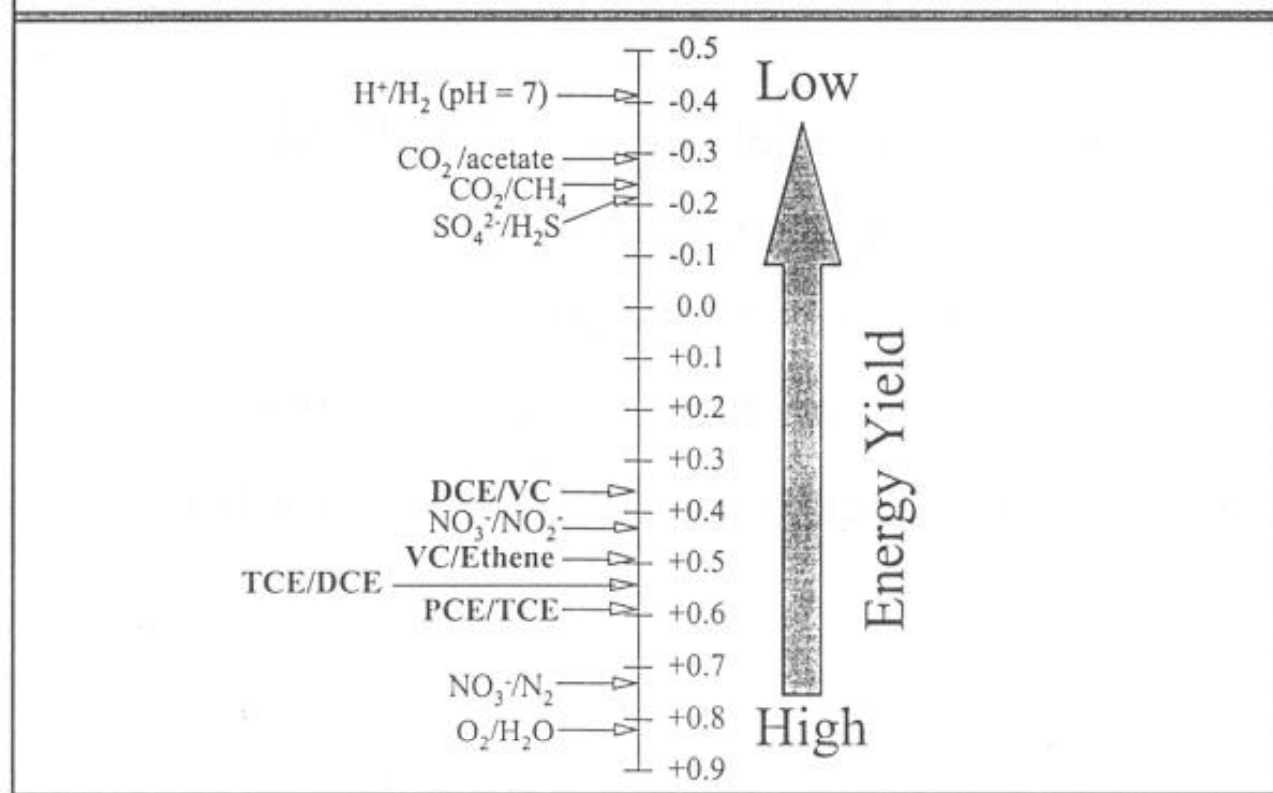
McCarty Figure 3-8

Reduction Hierarchy

PCE	4 Cl	Strongest Oxidizing Agent
TCE	3 Cl	
DCE	2 Cl	
VC	1 Cl	Weakest Oxidizing Agent

Energetics

Energy Generating Processes

- **Energy Generated by Transfer of Electrons (Redox Rxn)**

- **Stored in ATP (Cell's Energy Source)**

- **Need Electron Donor**
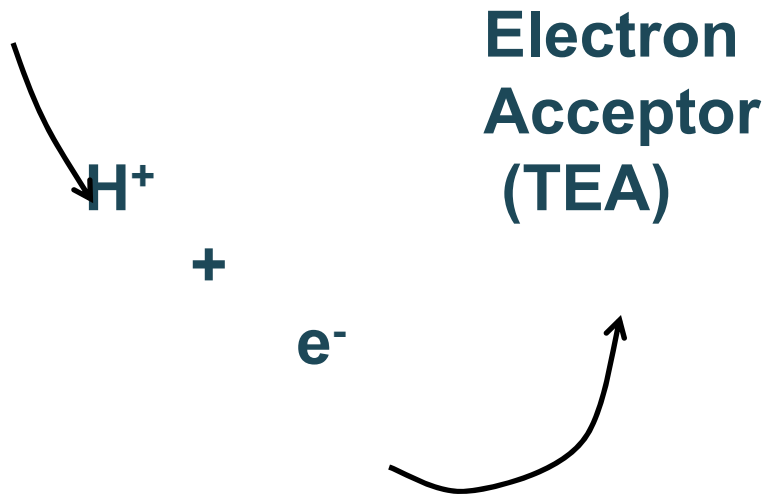 - **Loses e$^-$**

- **Need Electron Acceptor**
  - **Gains e$^-$**

Catabolism / Energy Generation

- **Based on:**
  - **Energy source**
  - **Electron donor (redox rxn)**
  - **Carbon requirement**

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Basic Respiration:
Heterotrophic Bacteria

Organic Carbon + Terminal $\rightarrow$ CO_2 + H_2O + Energy
Electron
Acceptor
(TEA)

H^+

+

e^-

Electron Transport System (ETS)

- **No Organic Molecule Involved**
- **Pass H$^+$ and e$^-$ Removed from Organic Molecule Down a Chain (ETS)**
  - **Series of oxidation / reduction reactions that generate energy**
- **Need Electron Acceptor at End of Chain (ETS)**
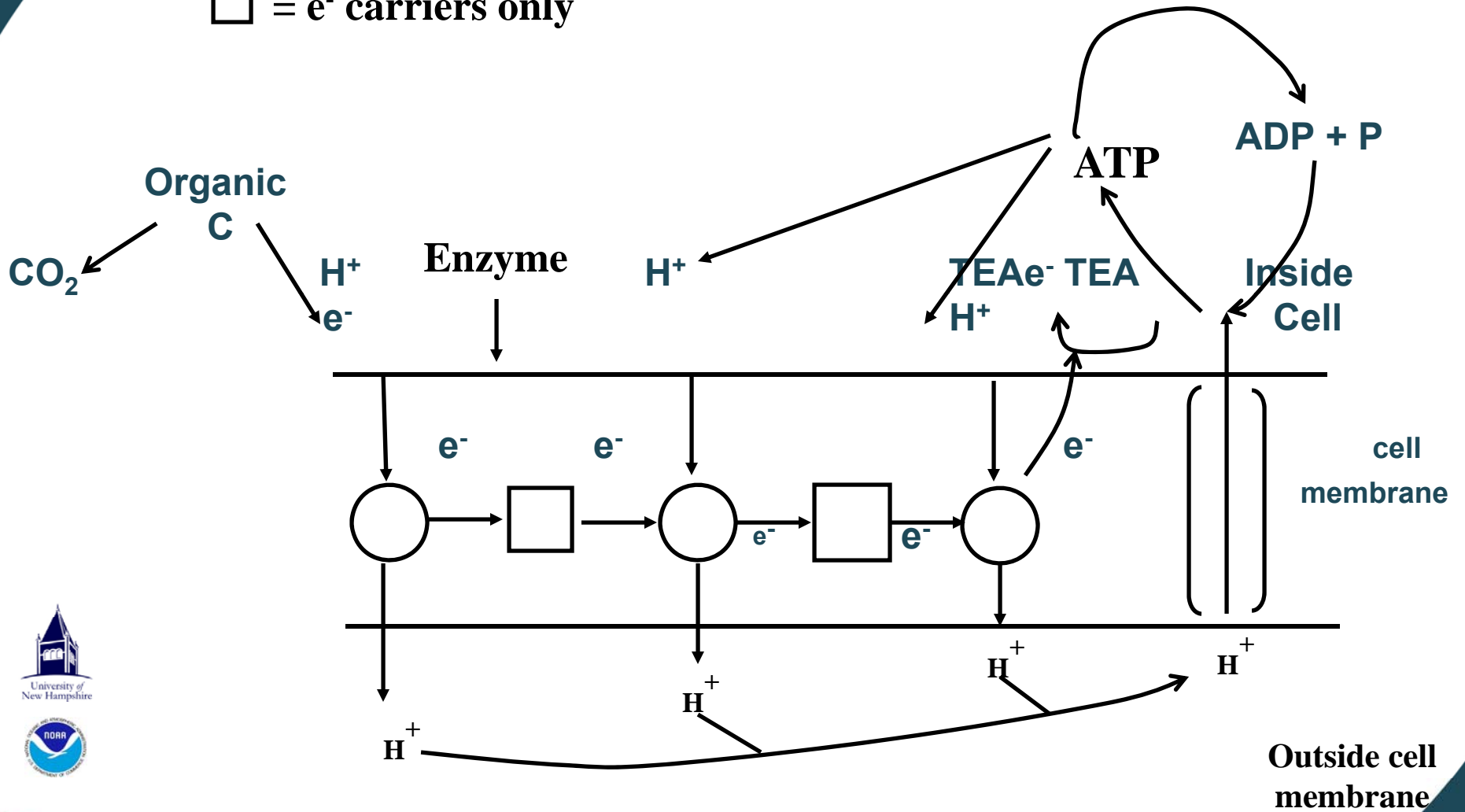 - **Terminal electron acceptor (TEA)**

Terminal Electron Acceptor (TEA)

- **Brought Into Cell**
- **At End of Electron Transport System**
- **Accepts Electrons**
- **Leaves Cells with Electrons**

○ = e⁻ and H⁺ carriers

□ = e⁻ carriers only

ADP + P

ATP

Organic C

CO₂

Enzyme

H⁺
e⁻

H⁺

TEAe⁻ TEA
H⁺

Inside Cell

e⁻   e⁻   e⁻

e⁻   e⁻

cell membrane

H⁺   H⁺

H⁺

H⁺
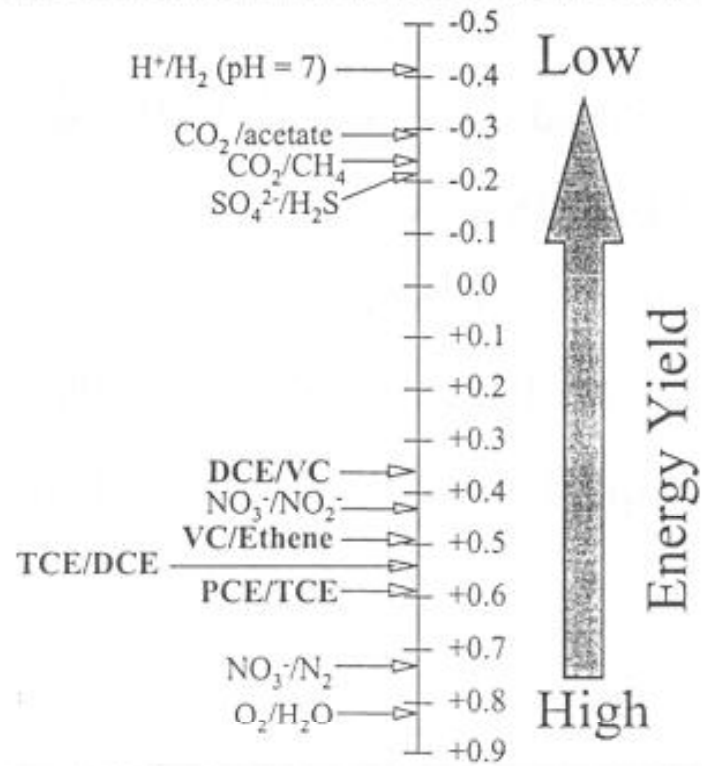
Outside cell membrane

Energy Generation / Storage

- **When H^+ Is Pushed Outside Cell Membrane Get Gradient**
  - **pH (H^+)**
  - **Electrical (+)**
- **Gradients = Potential Energy**
- **Bring H^+ Back Inside Cell**
  - **Conversion potential $\rightarrow$ kinetic energy**
- **Energy Stored in Higher Energy Phosphate Bonds**

Energy Generation / Storage (cont.)

- **ADP + P $\rightarrow$ AT ~ PH**

  + H$^+$
- **Release H$^+$ and Energy When ATP $\rightarrow$ ADP**
  - **Energy used to fuel cell processes**

How Far Down ETS Can e$^-$ Go?

- **e$^-$ Can Only be Transferred from One Compound to Another if Receiver Has Higher Affinity for e$^-$ Than Donor**

  - **Gibbs free energy ($\triangle G_0$' in kJ/e$^-$ equiv)**
  - **If $\triangle G_0$' is more + (larger) number than species can donate e$^-$ to more – (smaller) number**

$$\xrightarrow{\text{e}^-}$$

Glucose $\quad\Longrightarrow\quad$ **O_2^0**

+41.4 kJ/e$^-$ eq $\qquad\qquad$ **-78.7 kJ/e$^-$ eq**

Redox Potential (Eh°)
in Millivolts @ pH = 7
and T=25°C

Decreasing Amount of Energy Released During Electron Transfer

1000 — Aerobic — $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $(E_h^° = +820)$

$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$ $(E_h^° = +740)$

Anaerobic

500 — $MnO_x(s) + HCO_3^- + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_2O$ $(E_h^° = +520)$

Possible Range for Reductive Dechlorination

0 — $FeOOH(s) + HCO_3^- + 2H^+ + e^- \longrightarrow FeCO_3 + 2H_2O$ $(E_h^° = -50)$

Optimal Range for Reductive Dechlorination

$SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ $(E_h^° = -220)$
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$ $(E_h^° = -240)$

-500 —

Figure B.3.3

Oxidation-Reduction Potentials for Various Oxidation-Reduction Reactions

Modified From Bouwer (1994)

AFCEE, 1996.

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Other Factors Affecting Biodegradation

- **Other Substances Cells Need**
- **Abiotic Factors**
- **Interaction Between Substrates**
- **Effects of Other Biological Processes**
- **Bioavailability / Mass Transfer**
- **Recalcitrance**
- **Acclimation**

Interaction Between Substances

- **Little is Known About This**
- **If Multiple Organic Substances Present:**
  - **One may be preferred**
    - **Easier to degrade**
    - **More energy generated**
    - **Byproducts of one may inhibit other**
    - **Repression**
  - **First may enhance degradation of the second**
    - **Byproducts of first may be needed in degradation of second**
    - **First may induce enzymes needed for second**
    - **Synergism**
    - **Co-metabolism**

Synergism

- **Multiple Types of Microbes Accomplish Degradation That Neither Can Do Alone**

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Co-Metabolism

- **Microbial Transformation of Organic Compound Occurs, But <u>No</u> Energy Gained by Cell**
  - **Fortuitous oxidation / metabolism**
  - **Getting energy and N, P, S etc. elsewhere (from another transformation)**
  - **C Often Not Incorporated Into Cell Biomass Either**

Co-Metabolic Enzymes

- **Enzymes That Catalyze Other Reactions, Catalyze This Co-Metabolic Reaction**
  - **Mostly non-specific enzymes**
  - **e.g., methyl mono-oxygenases that bacteria use to co-metabolize TCE**

Effects of Other Biological Processes

- **Predation – One Organism Eats (Preys Upon) Another**
  - **Predators**
    - **Protists**
    - **Bacteriophage (viruses)**
  - **Latest data shows protists affect CAH biodegradation**

Direct Anaerobic Dechlorination (Dehalorespiration)

- **Bacteria Present in Many Environments, But Not Ubiquitous**
  - **e.g., <u>Dehalococcus ethenogenes</u>; <u>Dehalospirillum multivorans</u>**

Electron Donor + Electron Acceptor → R-H + Cl$^-$ + H$^+$ + Energy
H$_2$ R-Cl

  - **R-H produced can be ethene, CH$_4$, CO$_2$, Less Chlorinated R-Cl**
  - **Need H$_2$ and Depletion of Competitive Electron Acceptors (e.g., NO$_3^-$, SO$_4^{-2}$)**

Dehalorespiration

- **Bacteria Gain Energy from this Reduction**
- **Source of H_2 = Fermentation of Organics Occurring in the Environment**
- **Can Sequentially Degrade PCE → TCE → DCE → VC → Ethene**
  - **Most readily for PCE and TCE**
  - **DCE and VC can accumulate**
  - **Presence of PCE can inhibit dehaloresporation of VC**

Impediments to Dehalorespiration

- **Competition for H_2**
    - **Methanogenic bacteria vs. dehalorespirers**
    - **Dehalorespirers can survive at much lower partial pressures of H_2 (i.e., if H_2 production is at slow rate)**
- **If NO_3^- or Sulfate Reduction Occurring May Limit Dehalorespiration**

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Enhancement to Dehalorespiration

- **Add Simple Organic Substrates to Spark Fermentation → H$_2$ Produced**
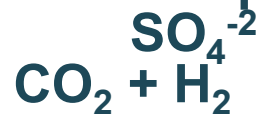 - **(e.g., amendments = methanol, lactate, benzoate, molasses, vegetable oil, HRC)**

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Co-Metabolic Reductive Dechlorination

- **Methanogens and Sulfate Reducing Bacteria**

Main Rxn:

Electron Donor + Electron Acceptor $\rightarrow$ CH$_4$ + CO$_2$ + Energy

Dissolved   SO$_4^{-2}$ or

Organic   CO$_2$ + H$_2$ H$_2$S

Matter

(DOM)

Co-Metabolic Rxn

       R-Cl   **Co-metabolic**

       PCE   **Rxn**   **R-H + Cl$^-$ (No Energy Generated)**

       &   **may stop here**

       TCE

       DCE

   VC, DCA, CT

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Anaerobic Reductive Dechlorination Co-Metabolism

- **Review Earlier Slides on Co-Metabolism**
- **Microbial Transformation of Organic Compound Occurs, But <u>No</u> Energy Gained by Cell**
- **Enzymes That Catalyze Other Reactions, Catalyze This Co-Metabolic Reaction**
  - **Mostly non-specific enzymes**
- **Why Does Co-Metabolism Occur?**
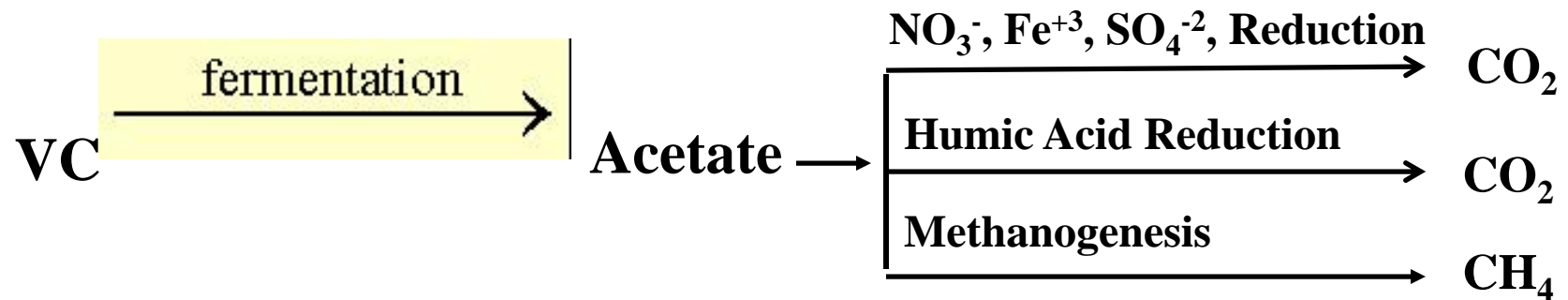 - **Non-specific enzyme in the microbe converts A→B, but other specific enzymes in cell cannot degrade B**

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Anaerobic <u>Oxidation</u> of DCE and VC

- **Anaerobic Oxidation of VC and Some DCE $\rightarrow$ CO_2 Under Fe^{+3} Reducing Conditions**
- **Anaerobic Oxidation of DCE $\rightarrow$ VC $\rightarrow$ CO_2 Under Humic Acid Reducing Conditions**
- **Also Under SO_4^{-2} Reducing and Methanogenic Conditions**
- **Recent Work by Bradley and Chapelle (USGS-SC)**
- **Different Pathway**
  - **Fermentative acetogenic bacteria**
  - **Generate acetate**

$$VC \xrightarrow{\text{fermentation}} Acetate \longrightarrow \begin{cases} \xrightarrow{NO_3^-, Fe^{+3}, SO_4^{-2}, \text{Reduction}} CO_2 \\ \xrightarrow{\text{Humic Acid Reduction}} CO_2 \\ \xrightarrow{\text{Methanogenesis}} CH_4 \end{cases}$$

- **Still Unknown How DCE Degradation Works**

Anaerobic Biodegradation

- **PCE → TCE → DCE**
  - **PCE and TCE strongest oxidizing agents**
  - **Occurs under less reducing conditions**
  - **e.g., nitrate and iron reduction**
  - **Best under more reducing conditions**
- **DCE → VC → Ethene**
  - **DCE and VC less strong oxidizing agents**
  - **Definitely need more reducing conditions (sulfate reducing or best if, methanogenic conditions)**
  - **Need more hydrogen present**

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Aerobic Degradation

- **Direct Oxidation of CAHs**
- **Co-Metabolic Oxidiations of CAH's Under Aerobic Conditions**

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Direct Aerobic Oxidation

- **CAH Serves as Carbon and Energy Source (i.e., Electron Donor)**

Electron Donor   + Electron Acceptor → Cl⁻ + CO₂

$$\text{Electron Donor} + \text{Electron Acceptor} \rightarrow Cl^- + CO_2$$

e.g., VC   e.g., O₂ Aerobic   +Reduced TEA

- **Done by Wide Variety of Bacteria (Ubiquitious)**
- **More Prevalent for Less Chlorinated VOCs**
  - **1 to 2 Chlorines**
  - **VC, DCE, DCA, Chloromethane, Methylene Chloride**

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Aerobic Oxidation Co-Metabolism

- **Fortuitous Oxidation of CAHs by Bacteria Using Simple Electron Donors**
  - **CH_4, Propane, Ethene, Butane, Ammonia, Toluene, Phenol**
  - **No energy gained**

Main Rxn Electron Donor + Electron Acceptor $\rightarrow$ CO_2 + H_2O + Energy
      e.g., CH_4 Ethene O_2

Co-metabolic
Rxn   Aerobic   Epoxide Formed
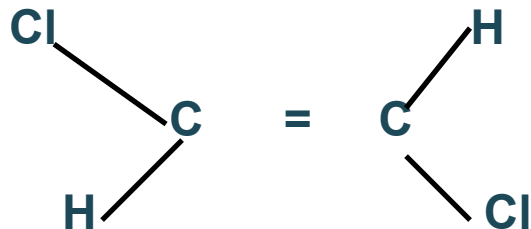   co-metabolism

            R-Cl

Aerobic Oxidation Co-Metabolism (cont.)

- **Enzyme is a Mono-oxygenase**
- **TCE, DCE, VC, TCA, DCA, Chloroform, Methylene Chloride**
- **Epoxide Is Unstable**
  - **Degrades to alcohols and fatty acids**
  - **Alcohols and fatty acids biodegraded to CO_2 + H_2O**

Cl   O   H

C —— C   epoxide

H   Cl

formed from DCE

Cl   H

C = C

H   Cl
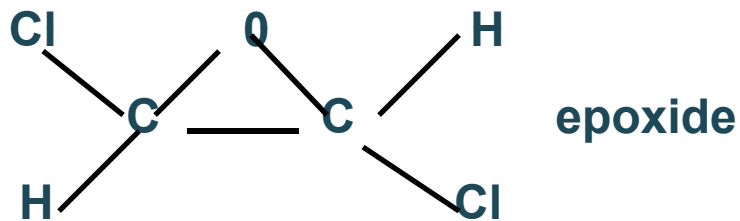
Aerobic Oxidation Co-Metabolism (cont.)

- **Nitrification (Autotrophic Process)**

Electron Donor + Electron Acceptor $\longrightarrow$ NO_3^- + Energy

NH_4^+ + O_2

Co-metabolic Rxn   Aerobic co-metabolism   Epoxide

R-Cl CO_2 + H_2O + Cl^-

- **Aerobic Co-Metabolism Done by Wide Variety of Bacteria**
  - **Ubiquitious**
- **Competition Between Primary Substrate (e.g., CH_4) and Co-metabolite for Enzyme**
  - **>1,000:1 Primary Substrate: Chlorinated Solvent**

         Consumed   Metabolized

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NOAA

Aerobic Oxidation Co-Metabolism (cont.)

- **Process Can Be Stimulated by Adding CH_4 and O_2**
  - **Alternately, microbes can use toluene or phenol in plume**

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Combination Anaerobic / Aerobic Processes

- **Anaerobic Reductive Dechlorination Zone (Upgradient)**

    PCE → TCE → DCE → VC

- **Direct Aerobic Oxidation Zone (Downgradient)**

    VC → Ethene / Ethane → CO_2

Why Are Chlorinated Solvents So Persistent?

They Are Tough to Degradation Biologically ("All Stars Must Be Aligned) and They Are Tough to Degrade Physio-Chemically (Abiotic Natural Processes Very Slow; Hard to Get Engineered Agents Distributed *In Situ*)

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Final Note on CAHs

CAH Monitoring – Units

- **Monitor Parent COC and Progeny**
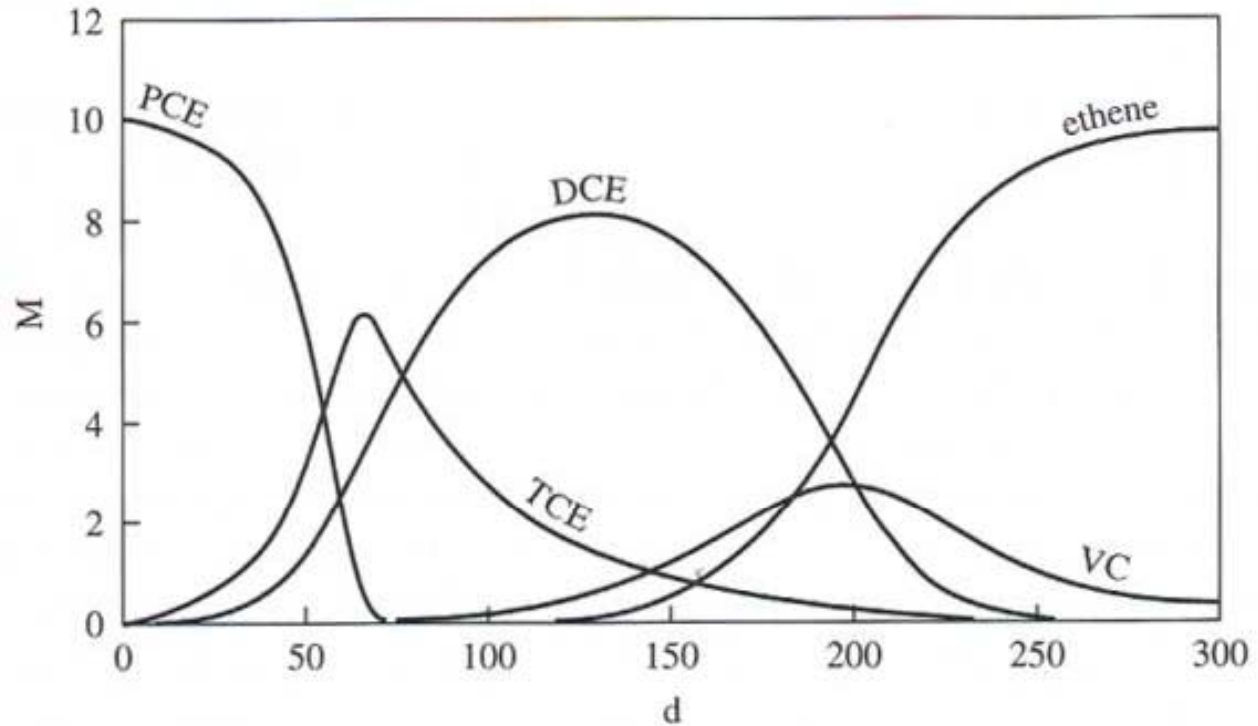 - **Not as mg/L**
  - **Use M = moles/L**

Figure 14.13   Transformation of PCE to ethene by reductive dehalogenation in a batch reactor and assuming two separate microbial populations, one that converts PCE into DCE, and the other, DCE to ethene. The starting concentration of each population is taken as 0.0001 mg/l.
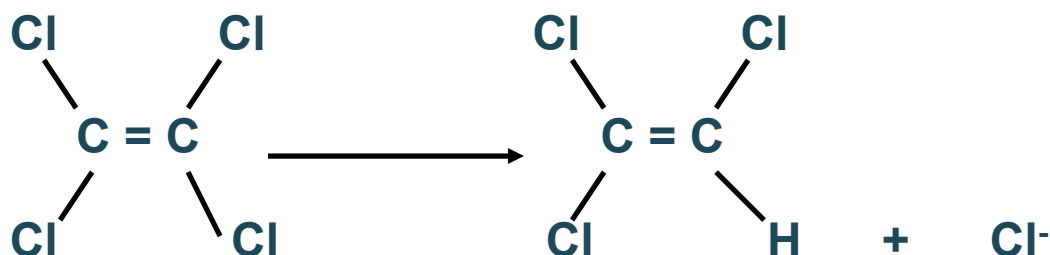
Ritmann and McCarty Fig. 14.13

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CAH Stoichiometric Relationships

- **For Mass Balance**

  1 mole PCE → 1 mole TCE → 1 mole DCE → 1 mole VC → 1 mole ethene

1 mole TCE $=$ 132 g   or 1 μ mole TCE $=$ 132 x 10^{-6} g = 132 μg
1 mole DCE $=$ 97 g   or 1 μ mole DCE $=$ 97 x 10^{-6} g = 97 μg
1 mole VC $=$ 62.5 g   or 1 μ mole VC $=$ 62.5 μg VC
1 mole Ethene $=$ 28 g or 1 μ mole Ethene $=$ 28 μg VC

Conversion of Molar to Concentration

$$1\,\mu M = 1\frac{\mu mole}{L}\,TCE\,x\,\frac{132\,\mu g\,TCE}{1\mu mole\,TCE} = 132\frac{\mu g}{L}\,TCE$$

$$1\,\frac{\mu mole}{L\,DCE}\,x\,\frac{97\,\mu g\,DCE}{1\,\mu mole\,DCE} = 97\frac{\mu g}{L}\,DCE$$

So $1\,\dfrac{\mu mole}{L}$ **TCE** $\longrightarrow$ $\dfrac{1\,\mu mole}{L}$ **DCE**

But $132\,\dfrac{\mu g}{L}$ TCE $\neq$ $\dfrac{132\mu g}{L}$ DCE $\longleftarrow$ Not $1\,\dfrac{\mu mole}{L}$ of DCE

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Conversion of Concentration (μg/L) to nM

$$\frac{5\ \mu g}{L}\ TCE\ x\ \frac{nanomole}{0.132\ \mu g\ TCE} = 38\ nM = \frac{38\,nMoles}{L}$$

nanomole = 1 x 10^{-9} moles

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My Deepest Thanks to Steve Druschel for Covering Today's Talk for Me. I am Sorry I Could Not Be With You.

Contact Info for Further Questions or Comments:

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