Enhanced In-Situ Bioremediation: How to Assess if It Can Work at Your Site

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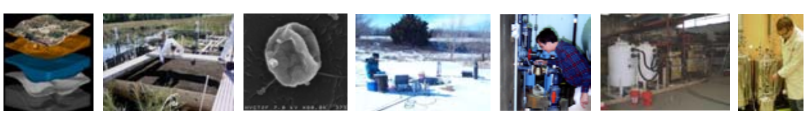
Geosyntec Consultants

October 5-6, 2010

Introduction

- Overview of key microbiological processes
- Applicable contaminants
- Implementation strategies for EISB
- Hydrogeology
- Typical remediation timeframes



Important Microorganisms

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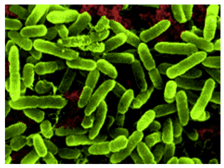
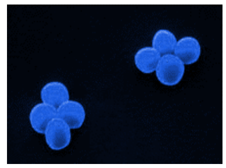
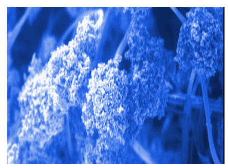
- Bacteria are the most important

- Fungi may play a role in soil but are less important in ground water

What do Microbes Need to Grow?

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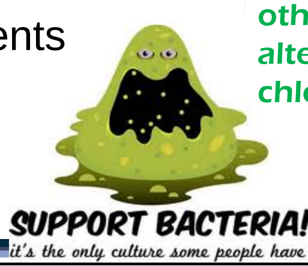
Like all living things microorganisms need:

- Food
  - To supply carbon
  - To supply energy

→ Usually from the same source

- Respiratory substrate
  - Something to "breathe" → Some use oxygen as the "electron acceptor", others can use alternatives, including chlorinated solvents
- Mineral nutrients
- Water



Terminology and Definitions

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Electron donor

- A compound that donates electrons during its oxidation
- Simple organic compounds such as sugars, alcohols, or methane can be oxidized to carbon dioxide (CO_2)

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Terminology and Definitions

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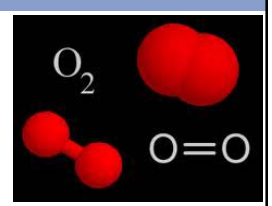

Electron acceptor

- A compound that accepts electrons during its reduction
- Inorganic compounds like oxygen, nitrate, sulfate, oxidized metals, or CO_2 can be reduced to water, dinitrogen gas, hydrogen sulfide, dissolved metals, or methane, respectively

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Overview of Microbial Metabolism

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Electron Donor or Substrate (Reduced)

Sugars, Proteins, Fats
Toluene; H_2; Fe(II)

Electron Acceptor (Oxidized)

Oxygen
Nitrate (NO_3)
Sulfate (SO_4)
Fe(III), CO_2

Enzymes in a microbe

Electron Donor or Substrate (Oxidized)

CO_2, H_2O, Fe(III)

Electron Acceptor (Reduced)

Water
N_2, H_2S
Fe(II), CH_4

Chlorinateds as Electron Acceptors

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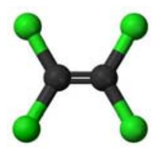
Electron Donor or Substrate (Reduced)

H_2; Acetate

Electron Acceptor (Oxidized)

PCE, TCE, cDCE, VC

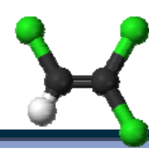


Enzymes in a microbe

Electron Donor or Substrate (Oxidized)

CO_2, H_2O

Electron Acceptor (Reduced)



TCE, cDCE, VC, ethene

Key Microbiological Processes

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- Oxidation
  - Bacteria use the contaminant as a food source (electron donor)
  - Need an electron acceptor (e.g., oxygen)
- Reduction
  - Bacteria use the contaminant as an electron acceptor
  - Need a food source (electron donor)
- Co-metabolism
  - Bacteria fortuitously break down contaminant (e.g., by enzyme secretion)

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Example Biodegradation Pathways

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- Direct oxidation: Contaminant as food
  - Aerobic oxidation
  - Anaerobic oxidation
- Aerobic co-metabolic biodegradation
- Anaerobic reductive dechlorination

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Aerobic Oxidation

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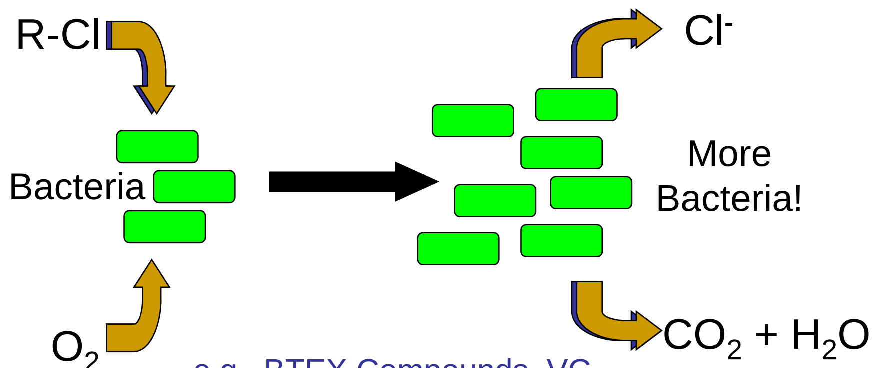

e.g., BTEX Compounds, VC
SVE/Bioventing
Airsparging/Biosparging
ORC

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Anaerobic Oxidation

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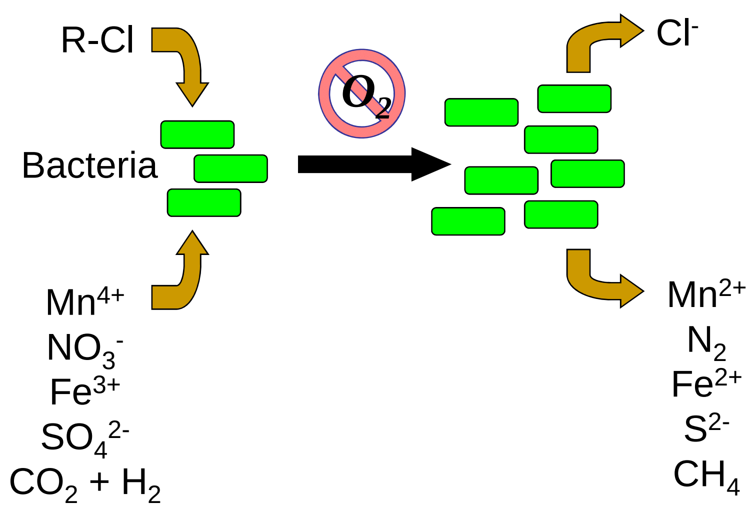

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Aerobic Co-metabolism

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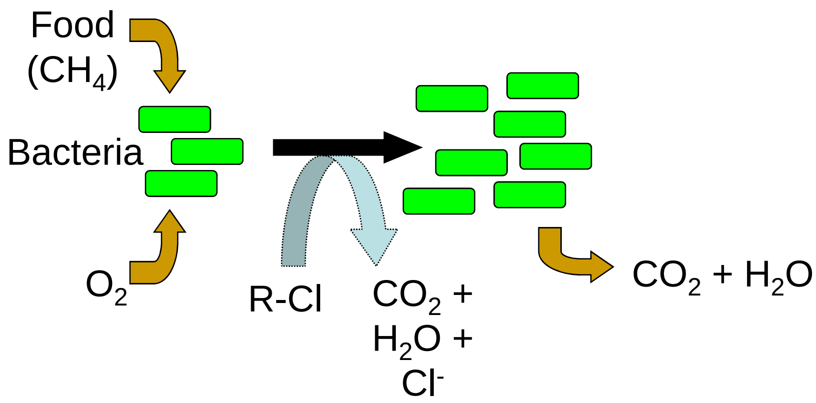

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Contaminant Types

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- Volatile Organic Compounds (VOCs)
  - Aromatic and aliphatic compounds
  - Chlorinated compounds
- Semi-volatile Organic Compounds (SVOCs)
  - Polynuclear aromatic hydrocarbons (PAHs)
  - Phthalates
  - Explosives (HMX, RDX, TNT)
- Polychlorinated biphenyls (PCBs)
- Pesticides
- Metals and Other Inorganics (e.g., As, rad, CN, ClO_4)

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Oxidation-Reduction Potential

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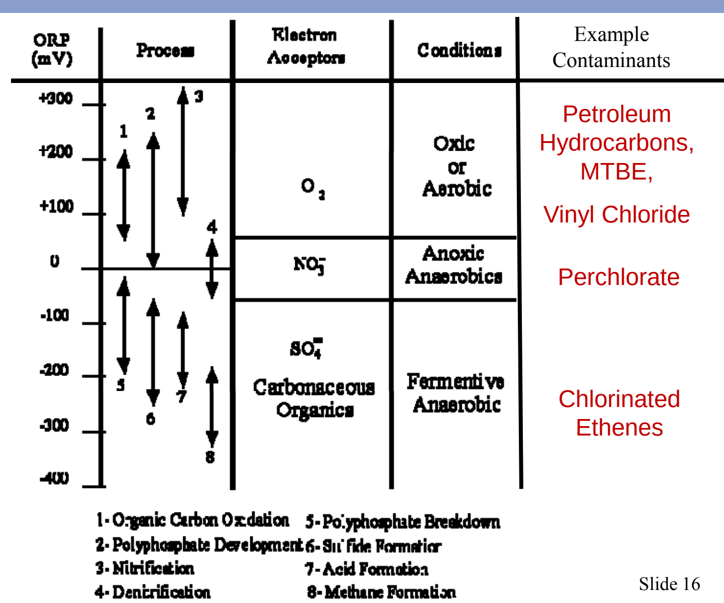

ORP Probe

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Biodegradable Contaminants

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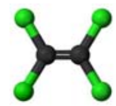
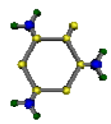
- Volatile Organic Compounds (VOCs)
  - Aromatic and aliphatic compounds
  - Chlorinated compounds



- Semi-volatile Organic Compounds (SVOCs)
  - Polynuclear aromatic hydrocarbons (PAHs)
  - Phthalates
  - Explosives (HMX, RDX, TNT)



- Polychlorinated biphenyls (PCBs)
- Pesticides (in some cases; e.g., dieldrin)
- Metals and Other Inorganics (e.g., As, rad, CN, ClO_4)

Chlorinated Solvent Concerns

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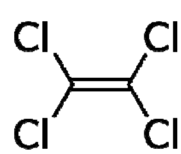
- Most common contaminants other than petroleum hydrocarbons
- Carcinogenic at very low concentrations in drinking water
- Volatile: can pose significant vapor intrusion risk
- Persistent: they usually don't biodegrade on their own



Rules of Thumb for Degradation of Chlorinated VOCs

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- Fully-chlorinated VOCs (PCE, CT) cannot be oxidized biotically
- Highly chlorinated VOCs (PCE, TCE) are more susceptible to reductive dechlorination
- Less chlorinated VOCs are more susceptible to oxidation (aerobic or anaerobic)

Biological Reductive Dechlorination

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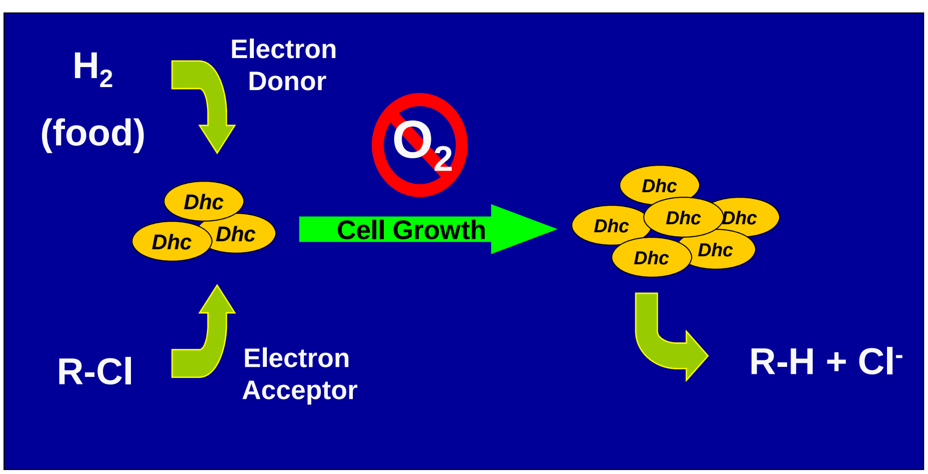

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Reductive Dechlorination

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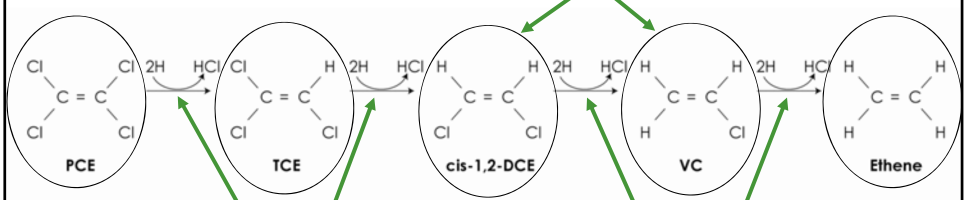
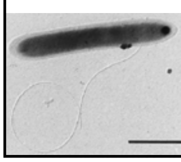
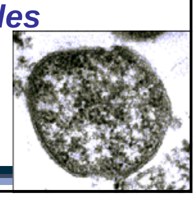
Can accumulate if requisite bacteria are absent



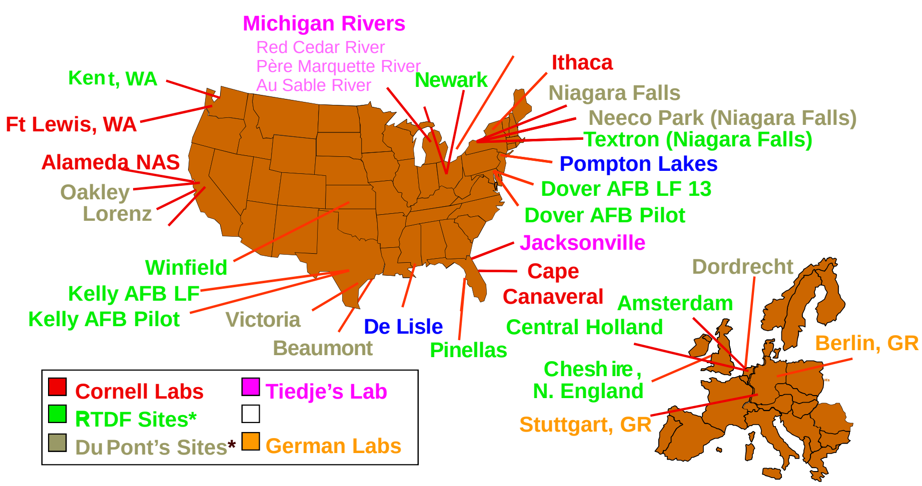
Dehalobacter
Dehalospirillum
Desulfitobacterium
Desulfuromonas
Dehalococcoides

some strains of *Dehalococcoides* *(Dhc)*





Dehalococcoides are Ecologically Widely Distributed



Compiled by Edwin R. Hendrickson, DuPont Company,CRD/CCER & CRG

Detection by 16S rDNA

You Need the Right Bugs

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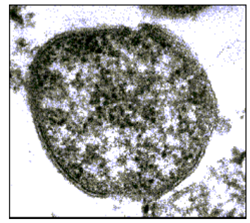
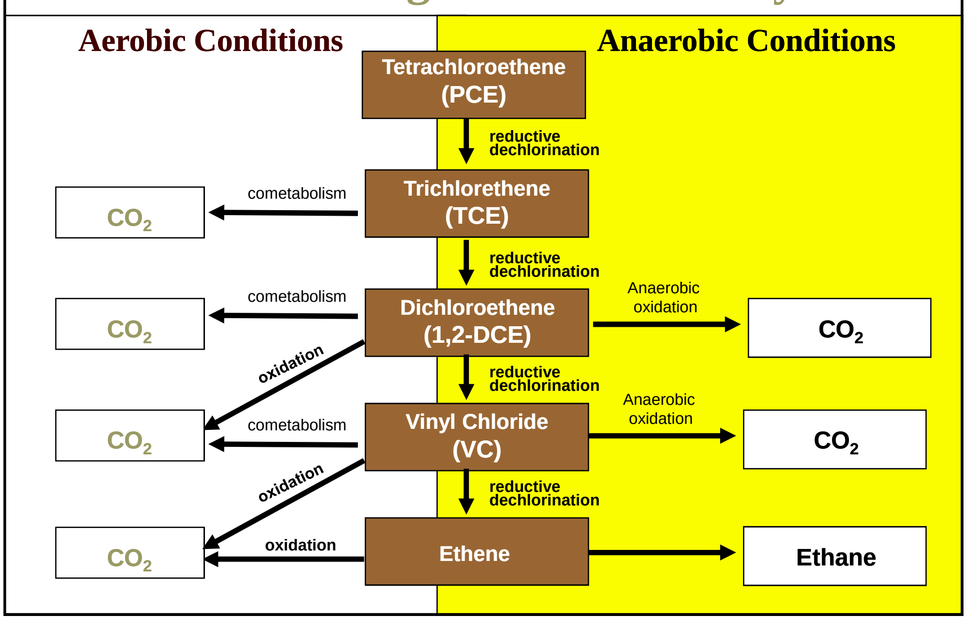
- *Dehaloccoides* (the Queen) has to be present for complete dechlorination to ethene
- Fermentative Bacteria
  - Worker bees help the Queen
  - Provide trace nutrients
  - Ferment compounds, provide hydrogen
  - Poise Eh, redox, buffer against other compounds

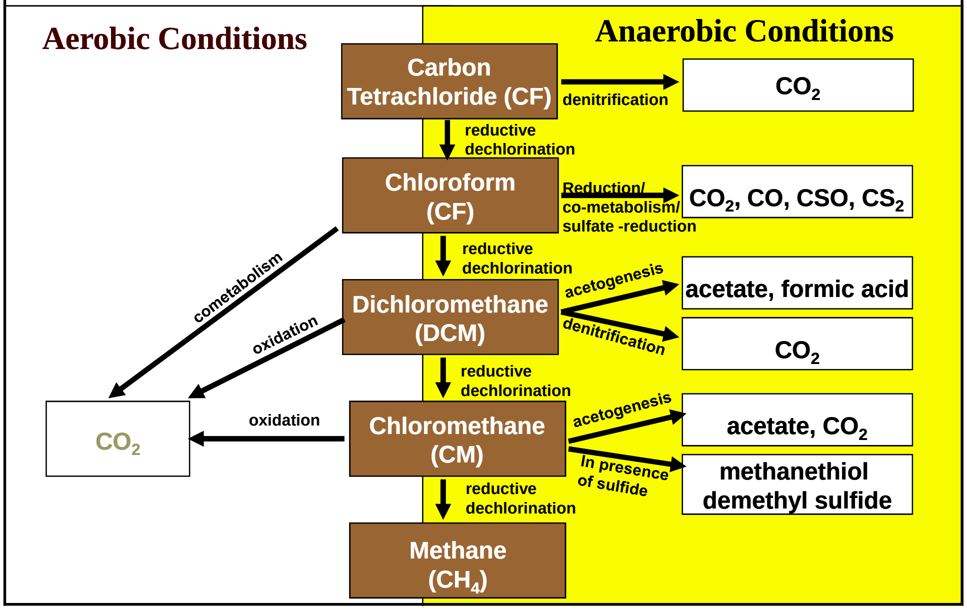


Thin-section electron micrographs showing coccoid DHC cells

PCE/TCE Degradation Pathways

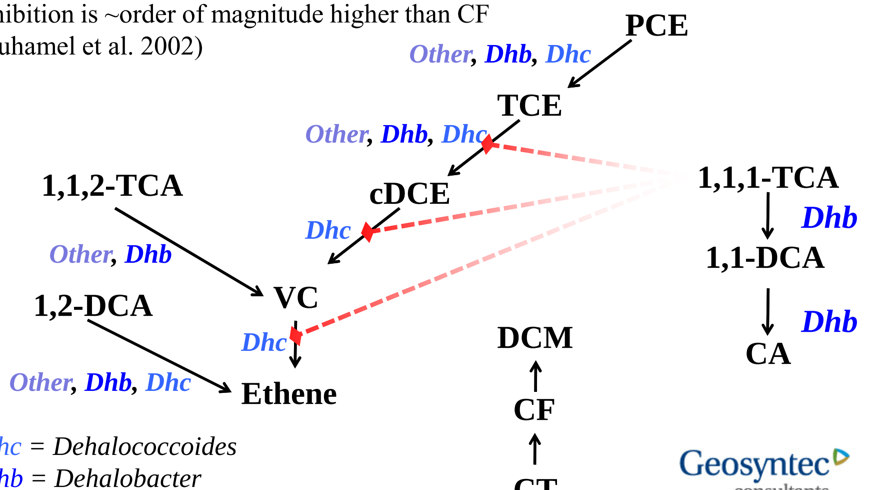


CT/CF/Degradation Pathways



Inhibition of Dechlorination - TCA

Inhibition TCE/cDCE starts ~1.5 mg/L
Inhibition of VC to Ethene starts ~0.07 mg/L
Inhibition is ~order of magnitude higher than CF
(Duhamel et al. 2002)



Dhc = *Dehalococcoides*
Dhb = *Dehalobacter*
Other = *Desulflitobacterium, Sulfurosprillium, Clostridium*
Inhibition = ♦- - - - - -

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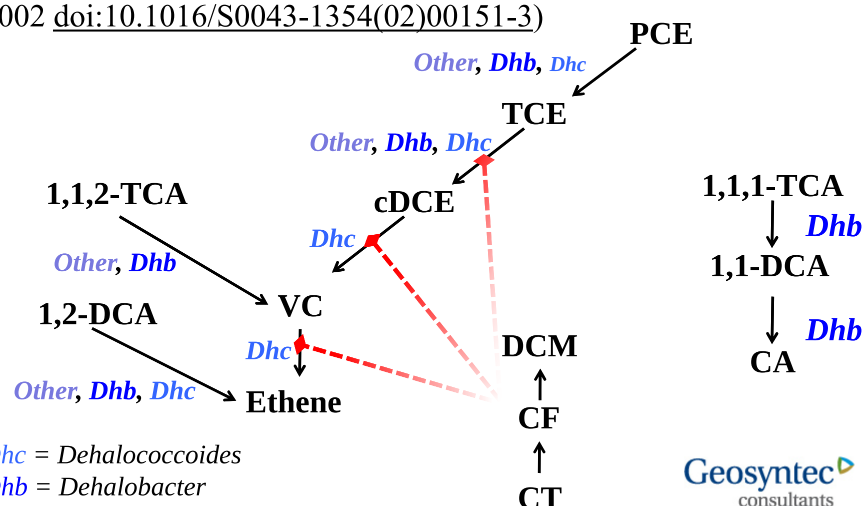
Inhibition of Dechlorination - CF

Inhibition starts ~ >0.07 mg/L (Duhamel et al, 2002 doi:10.1016/S0043-1354(02)00151-3)



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Inhibition =

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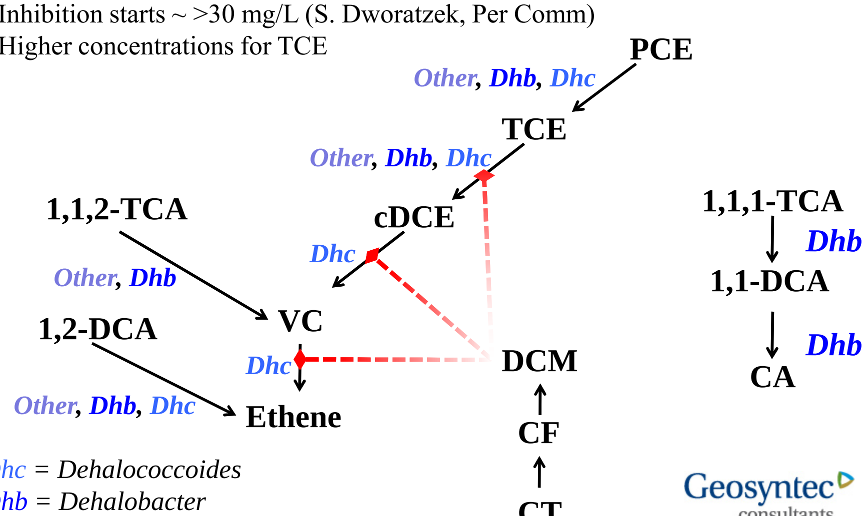
Inhibition of Dechlorination - DCM

Inhibition starts ~ >30 mg/L (S. Dworatzek, Per Comm)
Higher concentrations for TCE



Dhc = *Dehalococcoides*
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Inhibition =

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In Situ Bioremediation

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- Natural Attenuation - biodegradation via natural processes
- Biostimulation – addition of electron donor or acceptor to enhance natural processes
- Bioaugmentation – increasing the activity of bacteria (sometimes through the addition of specific bacteria) that break down pollutants, a technique used in bioremediation. (www.dictionary.com)

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Oxygen Delivery (Air Sparging)

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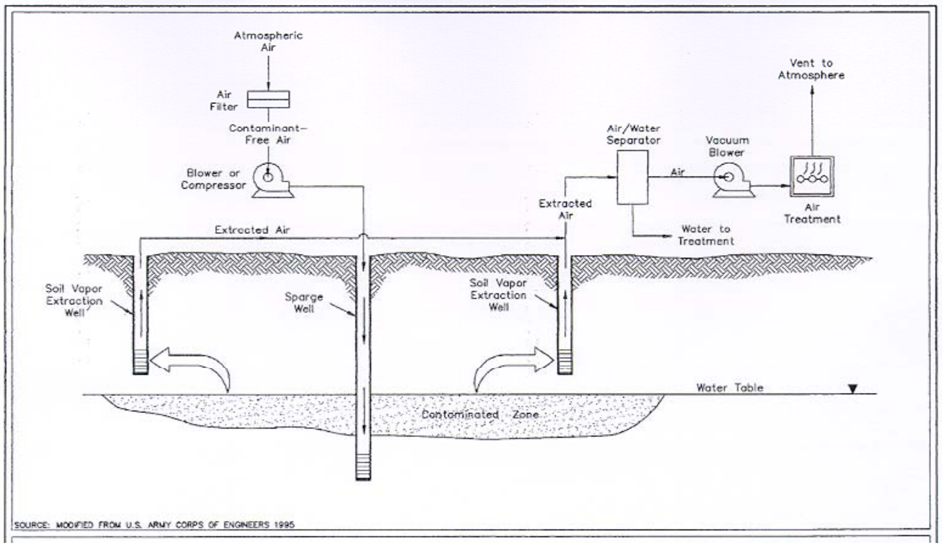

Electron Donors for Chlorinateds

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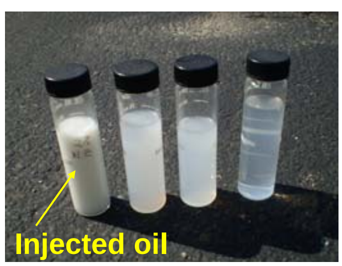
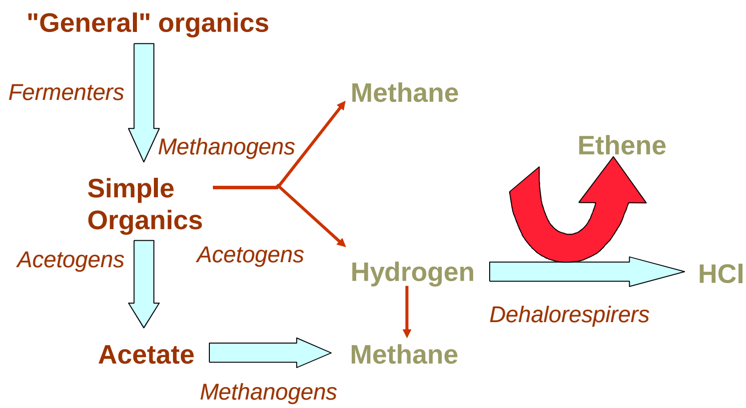
- Groups are developing/demonstrating various electron donors
  - HRC
  - Vegetable oils
  - Molasses
  - Chitin
  - Etc., etc., etc.



- Differ on how they ferment and encourage “worker bee” activities; all produce hydrogen for the “Queen”
- Choice is based on cost-effectiveness, ease of use/installation, objectives
- None will work if *Dehaloccoides* are absent

Reductive Dechlorination Involves A Complex Microbial Community



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Electron Donor Delivery Strategies

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- Common methods for delivering electron donor
  - Active Recirculation
  - Semi-Passive Delivery
  - Jet-Injection
  - Pull-Push
  - Biobarrier

- Selection depends in part on hydrogeology

Example Biobarrier Application

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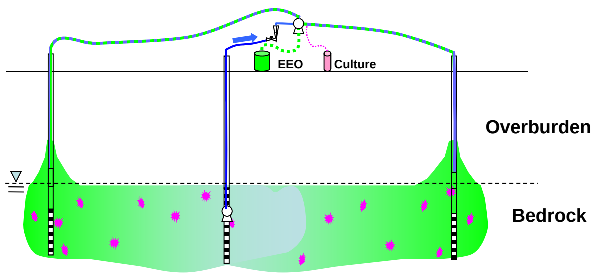
- Pump between wells at least until breakthrough of emulsified vegetable oil (EVO)
- Add bacterial culture during EVO injection
- In one week, a 300’ biobarrier was constructed using 290 gallons of EVO and 40 liters of bacterial culture



Full-Scale Biobarrier

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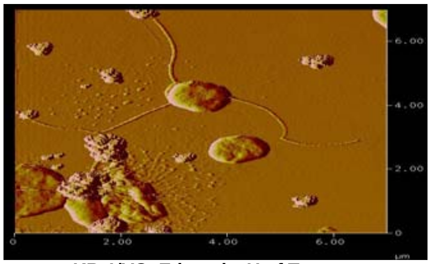
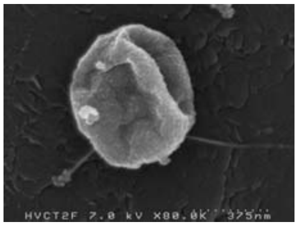
When to Bioaugment?

- At PCE and TCE sites that "stall" at cis-DCE or VC during biostimulation
- To assure success and accelerate enhanced *in situ* bioremediation (EISB)
- To increase bioactivity and shorten remediation time frames
- At mixed chlorinated solvent sites
- At sites with DNAPL concentrations of chlorinated solvents



KB-1/VC: Edwards, U of Toronto



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Important Design Factors

Some Factors That Impact Doubling Time of Dhc and Observed Ranges for Successful Bioaugmentation

- Temperature 8-28ºC (20-30ºC probably ideal)
- Chloroethene concentrations (> 40 µg/L – saturation)
- pH (6.0- 8.5)
- Co-contaminants (CF <50 µg/L/ 1,1,1-TCA 200 µg/L)*
- ORP -90 mV… and lower
- Sulfate up to 400 mg/L
- Chloride up to 5500 mg/L

*may be corrected with new cultures

Bioaugmentation Cultures

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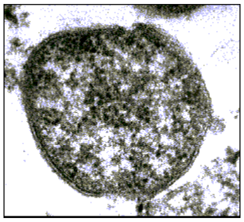
- Bioaugmentation cultures are now available for the following types of compounds:
  - Chlorinated ethenes (PCE, TCE, DCEs and VC)
  - Chlorinated ethanes (TeCA, 1,1,2-TCA, 1,1,1-TCA and 1,2-DCA)
  - Chlorinated methanes (carbon tetrachloride, chloroform)

  and mixtures of the above
- New molecular tests are available to better monitor new cultures in situ, and more are under development
- Not all DHC bacteria can dehalogenate completely – vcrA gene analysis



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Example Bioaugmentation Cultures

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- KB-1® and SDC-9™ culture
  - chlorinated ethenes
- BCI Labs
  - chlorinated ethenes and ethanes
- KB-1® Plus = KB-1® + ACT-3™
  - chlorinated ethenes and ethanes
- WBC-2
  - chlorinated ethenes, ethanes and methanes (e.g., carbon tetrachloride, 1,1,2,2-TECA)

KB-1® Bioaugmentation Culture

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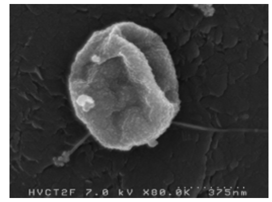
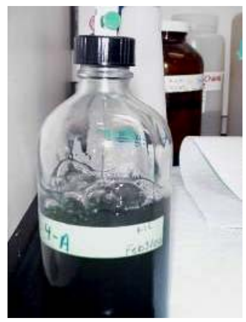
- Anaerobic bioaugmentation culture enriched from TCE site in Ontario
- Used to introduce Dhc to sites – Contains ~100 billion Dhc/Liter
- Not genetically engineered/pathogen free
- Added at ~1/35,000 dilution in groundwater



Dehalococcoides KB-1/VC (SEM)



SiREM Bioaugmentation Kit

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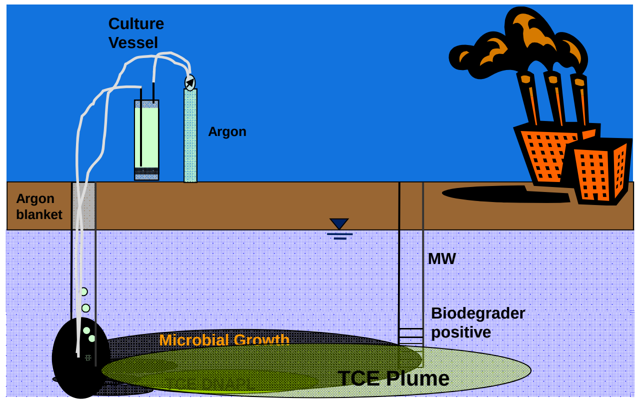
Field Application of Bioaugmentation Cultures



DHC spread rates of ~ 0.1 to 0.2 feet per day typical

Groundwater Flow

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Technology Limitations

- Typically requires nutrient delivery and mixing
- Potential for system fouling and associated operation and maintenance (O&M)
- Potential to form undesirable degradation intermediates
  - Methane, hydrogen sulfide, daughter products, etc.

Technology Limitations (cont'd)

- May not be feasible for large, dilute plumes
- Potential for undesirable geochemical changes (e.g., metals mobilization)

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Heterogeneity

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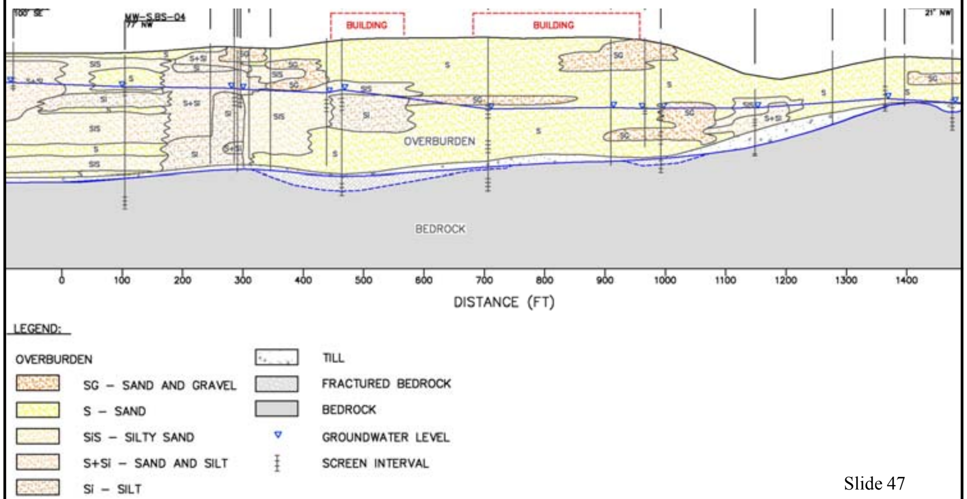

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Impacts of Stratigraphy

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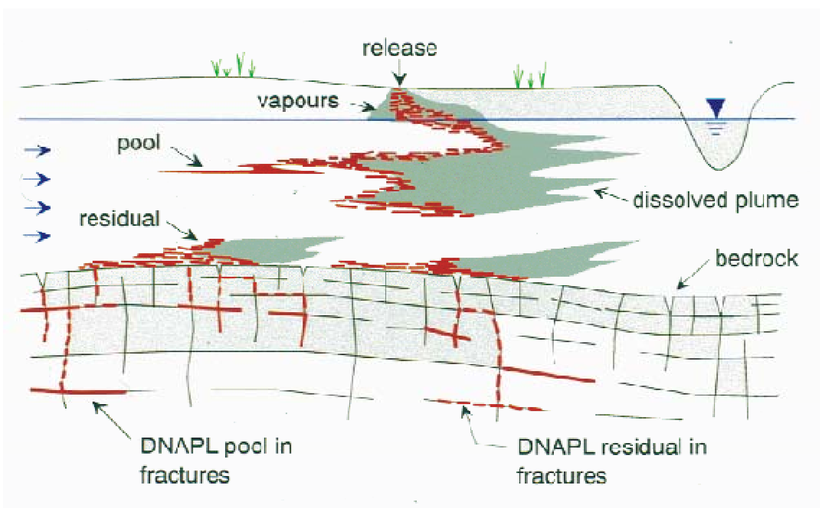

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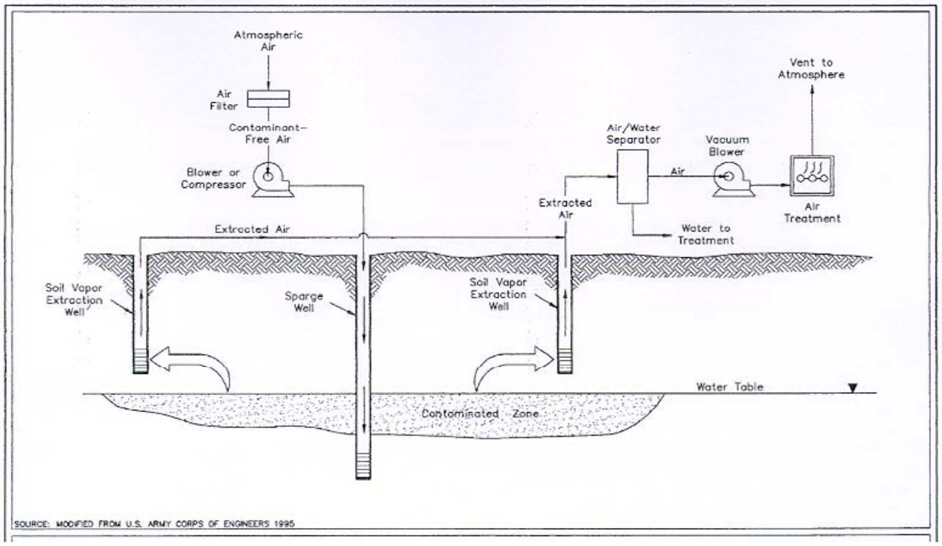
Oxygen Delivery (Air Sparging)



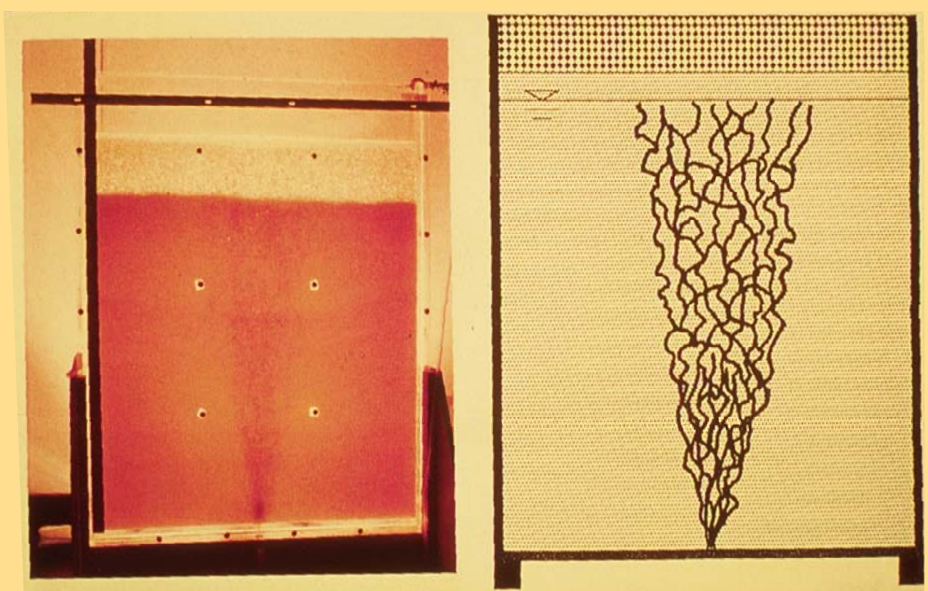


Figure 7. Air channel pattern at moderate air injection rate in 0.75 mm uniform bead medium: (a) photograph; (b) drawing.

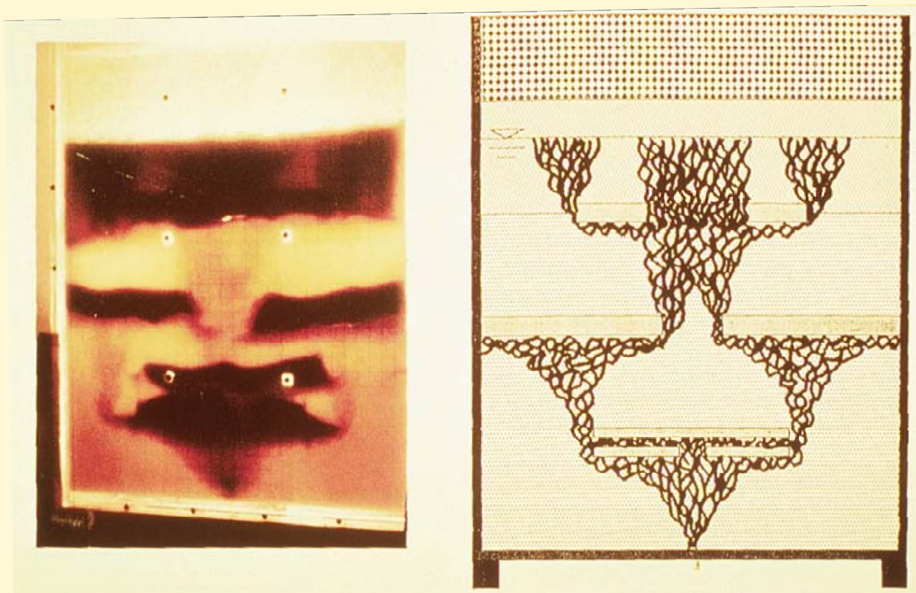


Figure 15. Air channel pattern in a stratified medium at lower air injection rates: (a) photograph; (b) drawing.

Hydraulic Conductivity

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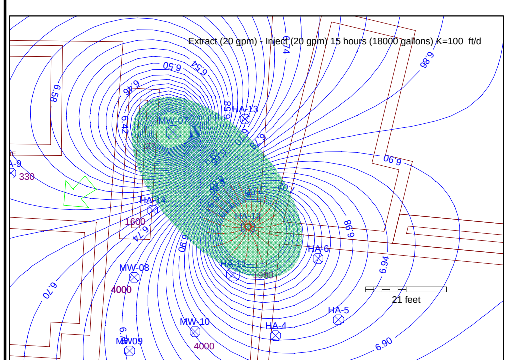
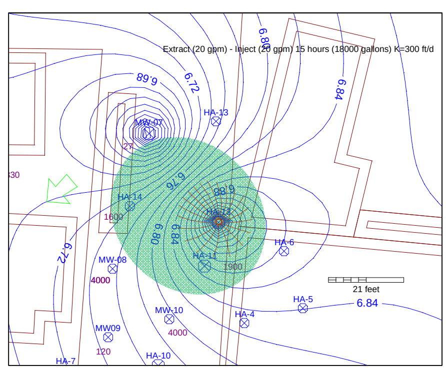
Both Scenarios: Extract and Reinject @ 20 gpm for 15 hours

Contour interval on both maps = 0.2 ft.



K = 100 ft/d



K = 300 ft/d

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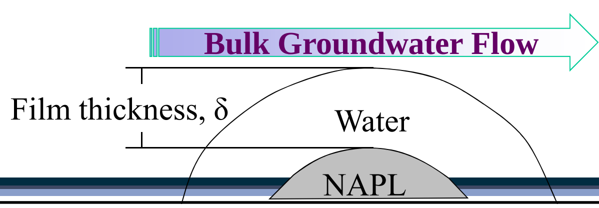
Some Factors Affecting Remediation Timeframe

- Contaminant type
  - Complex molecules
  - Simpler molecules

  ↓ Faster

- Contaminant concentrations
  - Lower concentrations can sometimes lead to slower degradation rates
  - Free product (LNAPL, DNAPL): Mass transfer limitations affect dissolution rates



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Some Factors Affecting Remediation Timeframe (cont'd)

Geosyntec consultants

- Aggressiveness of approach
  - MNA
  - Biostimulation
  - Bioaugmentation

  Faster (↓)
- Geochemistry
  - Aerobic processes generally faster
  - Generally slower reactions as you move down the RedOx scale

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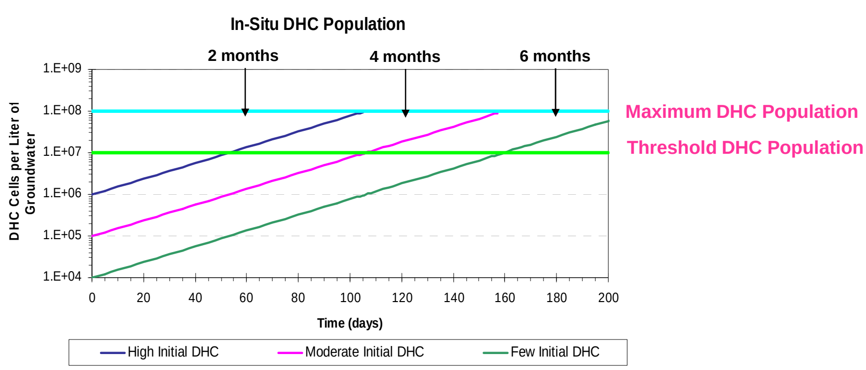
Critical Cell Count

Geosyntec consultants

- 1x10^7 DHC/L is the target concentration for effective biodegradation
- The in-situ doubling rate for DHC is ~16 days



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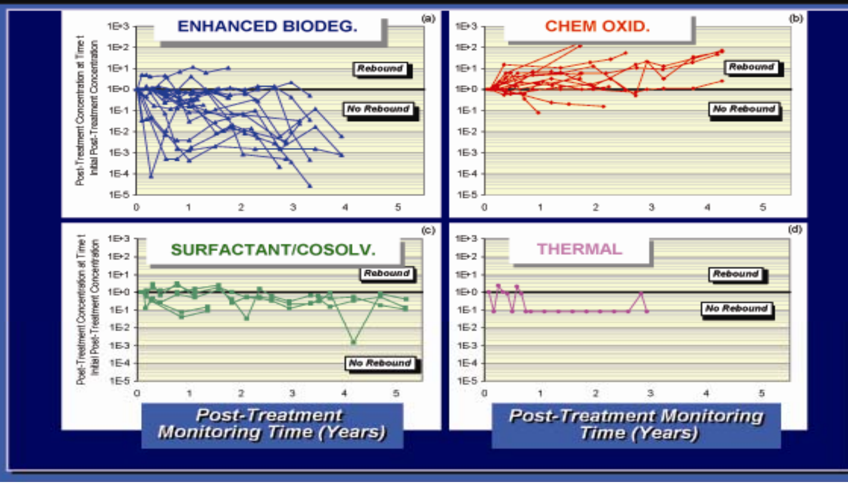
Long Term Impact of Source Technologies

WHAT ABOUT *REBOUND?* (Parent Compounds)



From C.J. Newell et al., 2004 SERDP Poster, *Temporal changes in chlorinated solvent concentrations at 59 source depletion sites.*

Some Factors Affecting Remediation Timeframe (cont'd)

Geosyntec consultants

- Hydrogeology
  - Ability to distribute electron donor or acceptor throughout treatment area
  - Diffusion limitations (e.g., at clay interfaces)

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Questions?

- Overview of key microbiological processes
- Applicable contaminants
- Implementation strategies for EISB
- Hydrogeology
- Typical remediation timeframes

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