Biodegradation of Chlorinated Solvents

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Biodegradation Reaction

Biodegradation = Redox Reactions

E-donor + E-acceptor → Oxidized E-donor + Reduced E-acceptor

Reduction

Oxidation
Example: vinyl chloride as electron donor

\[
\begin{align*}
\text{CH}_3\text{Cl} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \\
\text{oxydation} & \rightarrow \\
\text{reduction} & \\
\text{CH}_3\text{Cl} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O}
\end{align*}
\]

Example: perchloroethylene as electron acceptor

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{Cl}^- & \rightarrow \text{CO}_2 + \text{Cl}^- + 4\text{Cl}^- \\
\text{oxydation} & \rightarrow \\
\text{reduction} & \\
\text{CH}_3\text{OH} + \text{Cl}^- & \rightarrow \text{CO}_2 + \text{Cl}^- + 4\text{Cl}^-
\end{align*}
\]
**Definitions Biodegradation**

- **Biodegradation**: biologically catalyzed transformation of chemical resulting in simpler forms

- **Mineralization**: Conversion of organics to mineral products

- **Biotransformation**: Transformation of pollutant by a biological process

\[ \text{CO}_2 + \text{Cl}^- \]
**Definitions Biodegradation**

- **Growth Substrate, Primary Metabolism:** Pollutant (substrate) used as the primary energy and carbon source for microbial growth. As pollutant is degraded, biocatalyst concentration increases.

- **Cometabolism:** Accidental conversion of pollutant by enzymes and cofactors used for the metabolism of a primary substrate.

![Chemical Reaction Diagram]

\[
\text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CO}_2
\]
Definitions Biodegradation

- **Reductive Dehalogenation**: Microbially catalyzed replacement of a halogen atom on an organic compound with a hydrogen atom

  \[ R-\text{Cl} + 2e^- + 2H^+ \rightarrow R-\text{H} + \text{HCl} \]

- **Halorespiration**: An organohalogen is used as an electron acceptor in an energy yielding metabolism as pollutant is degraded biocatalyst concentration increases

  \[
  \begin{align*}
  \text{CH}_3\text{OH} & \quad \text{CO}_2 \\
  \text{Cl} & \quad \text{H} \quad \text{H} \\
  \text{Cl} & \quad \text{H} \quad \text{H} \\
  \text{Cl} & \quad \text{Cl} \\
  \end{align*}
  \]

  \[ + 4\text{HCl} \]
Mechanisms of Dechlorination

**Oxygenolytic:**

\[
\text{HCl} + \text{O}_2 \xrightarrow{\text{spontaneous}} \text{H}_2\text{O} + \text{Cl}^{-} + \text{organic acids}
\]

**Hydrolytic:**

\[
\text{RC-Cl} + \text{H}_2\text{O} \xrightarrow{\text{spontaneous}} \text{RC-OH} + \text{HCl}
\]
Mechanisms of Dechlorination

**Reductive Hydrogenolysis:**
\[
egin{align*}
2e^- + 2H^+ & \rightarrow 2H^2 \\
R - C - Cl & \rightarrow R - C - H + HCl
\end{align*}
\]

**Hydrolytic Reduction:**
\[
egin{align*}
2e^- + 2H^+ & \rightarrow 2H^2 \\
R - C - Cl & \rightarrow 2HCl + R - C^\cdot - Cl
\end{align*}
\]

\[
\begin{align*}
H_2O & \rightarrow CO + 2HCl \\
H_2O & \rightarrow COOH + 2HCl
\end{align*}
\]
Mechanisms of Dechlorination

Reactive Dichloroelimination:

\[
\text{R-Cl-Cl} \quad \xrightarrow{2e^-, 2H^+} \quad \text{R-H} + 2\text{HCl}
\]
Important Trends

Aerobic Degradation

Chlorine # increases  ↑  Biodegradation decreases  ↓

Elimination of PCB's in Aerobic Activated Sludge as a function of chlorine content

Important Trends

Anaerobic Degradation

Chlorine # increases ↑  Biotransformation increases ↑

Cometabolism of chlorinated solvents by anaerobic sludge

- ■ chloroethanes
- ▲ chloromethanes
- ✗ chloroethenes

## Five Physiological Roles

<table>
<thead>
<tr>
<th>Role</th>
<th>Description</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>aerobic carbon and energy source</td>
<td>ED-A</td>
</tr>
<tr>
<td>2nd</td>
<td>aerobic cometabolism (cooxidation)</td>
<td>CoM-A</td>
</tr>
<tr>
<td>3rd</td>
<td>anaerobic carbon and energy source</td>
<td>ED-AN</td>
</tr>
<tr>
<td>4th</td>
<td>anaerobic electron acceptor (halorespiration)</td>
<td>EA-AN</td>
</tr>
<tr>
<td>5th</td>
<td>anaerobic cometabolism (reduced cofactors)</td>
<td>CoM-AN</td>
</tr>
</tbody>
</table>
Strategies of Bioremediation

1. Bioaugmentation
   - adding microorganisms

2. Substrate (Pollutant)

3. Surfactants, cosolvents, chelators

4. Microorganisms

5. Environment

(Physiological Requirements)

Env. Factors
- H₂O, T, pH

Nutrients
- N, P, vit.

E-acceptors
- O₂, NO₃⁻

E-donor/Cosubstrate
- H₂/CH₄

Abbreviations Chloroethenes

- Perchloroethylene (PCE)
- Trichloroethene (TCE)
- cis Dichloroethene (cDCE)
- Vinyl chloride (VC)
- Ethene (E)
### Biodegradation Chloroethenes

<table>
<thead>
<tr>
<th>VC; cDCE</th>
<th>faster</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED-A</td>
<td>VC; cDCE; TCE</td>
</tr>
<tr>
<td>CoM-A</td>
<td>VC; cDCE; TCE</td>
</tr>
<tr>
<td>ED-AN</td>
<td>VC (?), cDCE (?)</td>
</tr>
<tr>
<td>EA-AN</td>
<td>VC; cDCE; TCE; PCE</td>
</tr>
<tr>
<td>CoM-AN</td>
<td>VC; cDCE; TCE; PCE</td>
</tr>
</tbody>
</table>
Chloroethenes ED-A

**Microorganisms Involved:** *Mycobacterium*, *Nocardioides*, *Pseudomonas*

**Pathway**

monooxygenase → epoxyalkane:CoM transferase → Coenzyme M

**Kinetics**

Growth rates 0.05 to 0.96 d^{-1}
Activity 226 to 4950 mg g^{-1} dwt d^{-1}
\( K_m \) or \( K_s \) 0.07 to 0.70 mg l^{-1}

Coleman & Spain 2003 JB 185:5536
**Microorganisms Involved:** *Methylosinus, Peudomonas, Burkholderia, Nitrosomonas, Mycobacterium, Rhodococcus, Alcaligenes*

**Pathway**

Chloroethenes CoM-A (cooxidation)

- **Primary Substrates Supporting Cooxidation:**
  methane, toluene, phenol, ammonium, ethane, ethene, propane etc
  Substrates for which monooxygenases are utilized for biodegradation

- **Kinetics**
  - Activity: 57 to 55,000 mg g\(^{-1}\) dwt d\(^{-1}\)
  - Transformation Capacity: 86 to 150 mg TCE g\(^{-1}\) dwt
  - \(K_m\): 0.4 to 29.6 mg l\(^{-1}\)
Chloroethenes EA-AN (Halorespiration)

Pathway

Successive Steps of Reductive Hydrogenolysis

\[ \text{PCE} \xrightarrow{2e^-, 2H^+} \text{TCE} \xrightarrow{2e^-, 2H^+} \text{cDCE} \xrightarrow{2e^-, 2H^+} \text{VC} \xrightarrow{2e^-, 2H^+} E \]

High Biodiversity
7 genera from 4 major bacterial phyla

Low Biodiversity
1 genus
## Chloroethenes EA-AN (Halorespiration)

### Microorganisms Involved: PCE to cDCE

<table>
<thead>
<tr>
<th>Group</th>
<th>Species</th>
<th>Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low G+C gram +</td>
<td><em>Desulfitobacterium</em></td>
<td>H₂, lactate, formate, etoh</td>
</tr>
<tr>
<td></td>
<td><em>Clostridium</em></td>
<td>YE, glucose</td>
</tr>
<tr>
<td>δ Proteobacteria</td>
<td><em>Dehalobacter</em></td>
<td>H₂</td>
</tr>
<tr>
<td>ε Proteobacteria</td>
<td><em>Desulfuromonas</em></td>
<td>acetate, pyruvate</td>
</tr>
<tr>
<td></td>
<td><em>Dehalospirillum</em></td>
<td>H₂, lactate, formate, etoh</td>
</tr>
<tr>
<td></td>
<td><em>Sulfurospirillum</em></td>
<td>lactate</td>
</tr>
<tr>
<td>Green non-sulfur</td>
<td><em>Dehalococcoides</em></td>
<td>H₂</td>
</tr>
</tbody>
</table>

### Microorganisms Involved: cDCE to E

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</table>
Chloroethenes EA-AN (Halorespiration)

Biochemistry
- Reactions catalyzed by specific reductive dehalogenases
  - All contain vitamin B12
  - Most are membrane bound enzymes

Kinetics: PCE to TCE and/or cDCE
- Growth rates: 0.23 to 6.65 d\(^{-1}\)
- Activity: 856 to 37,312 mg g\(^{-1}\) dwt d\(^{-1}\)

Kinetics: VC to E
- Growth rates: 0.32 to 0.40 d\(^{-1}\)
- Activity: 3047 to 6030 mg g\(^{-1}\) dwt d\(^{-1}\)
- \(K_m\) or \(K_s\): 0.16 to 0.31 mg l\(^{-1}\)
Chloroethenes EA-AN (Halorespiration)

Hypothetical Example

Assumptions:  
- $t_0 = 1$ bacterium per $m^3$  
- 1 bacterium = $1 \times 10^{-12}$ g  

Ideal conditions for growth

Kinetic data:  

<table>
<thead>
<tr>
<th></th>
<th>Dehalosprillum multivorans</th>
<th>Dehalococcoides strain VS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate (d$^{-1}$)</td>
<td>6.65</td>
<td>0.40</td>
</tr>
<tr>
<td>Activity (mg g$^{-1}$ dwt d$^{-1}$)</td>
<td>5970</td>
<td>3047</td>
</tr>
</tbody>
</table>

Growth Equation:  

$C_{xt} = C_{x0}e^{\mu t}$

$C_{x0}$ & $C_{xt}$ = cell biomass conc. at time 0 & t (g dwt l$^{-1}$)  
$\mu$ = growth rate (d$^{-1}$), t = time (d)
Hypothetical Example (continued)

Question: How long will it take for a bioconversion rate of 10 mg l\(^{-1}\) chloroethenes per day?

Initial Biomass: \(1 \times 10^{-15}\) g dwt l\(^{-1}\)

Final Biomass: 
\[
\frac{10}{5970} = 1.675 \times 10^{-3} \text{ g dwt l}^{-1} \text{ Dehalosprillum} \\
\frac{10}{3047} = 3.282 \times 10^{-3} \text{ g dwt l}^{-1} \text{ Dehalococcoides}
\]

Time:
\[
t = \frac{\ln \left( \frac{C_x t}{C_{x0}} \right)}{\mu}
\]

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehalosprillum</td>
<td>4.2</td>
</tr>
<tr>
<td>Dehalococcoides</td>
<td>72.1</td>
</tr>
</tbody>
</table>
**Chloroethenes CoM-AN**

- **Microorganisms Involved:** Methanogens, Acetogens

- **Pathway**  
  Successive Steps of Reductive Hydrogenolysis  
  - Reactions catalyzed by reduced enzyme cofactors  
    - Cobalt containing vitamin B12; Nickel containing Factor 430

- **Kinetics:** PCE to TCE and/or cDCE  
  - Activity: 0.006 to 20 mg g\(^{-1}\) dwt d\(^{-1}\)

- **Kinetics:** cDCE or VC to E  
  - Activity: 0.001 to 0.366 mg g\(^{-1}\) dwt d\(^{-1}\)
**Chloroethenes Bioremediation**

- **Anaerobic - Aerobic**
  - First: Rapid reductive dehalogenation to TCE & cDCE
  - Second: Rapid cooxidation of TCE and cDCE to CO$_2$ & Cl$^-$

  \[
  \text{PCE} \xrightarrow{\text{anaerobic}} \text{cDCE} \xrightarrow{\text{aerobic}} \text{CO}_2, \text{Cl}^-
  \]
  + electron donor
  + primary substrate

- **Anaerobic with *Dehalococcoides***
  - Promote complete halorespiration to ethene

  \[
  \text{PCE} \xrightarrow{\text{anaerobic}} \text{E}
  \]
  + electron donor
  + *Dehalococcoides* (if absent)
Bioremediation Breda (Holland)
**Bioremediation Breda (Holland)**

**Facts about Full-Scale Bioremediation**

- 85% removal of PCE in situ within 6 months
- Inorganic chloride concentration in anaerobic zone increased from 1 to 6 mM
- In the aerobic zone all of the cDCE and VC as well as injected phenol was removed
- After one year the total mass of chloroethenes decreased from 1500 to 550 mol

Bioremediation (Bachman Rd, Mi)

Comparison Bioaugmentation vs Biostimulation

Bioremediation (Bachman Rd, Mi)

Control Experiment at Bachman Road Site (Michigan)

Bioremediation (Bachman Rd, Mi)

Biostimulation Plot: Day 0 = lactate addition

Bioremediation (Bachman Rd, Mi)

Bioaugmentation Plot: Day −29 = lactate addition; Day 0 = *Dehalococoides* addition

Bioenhancement DNAPL Dissolution

Dissolution equation

\[ r_{TA} = K_la(C_s - C_b) \]

- Dissolution rate (mg l\(^{-1}\) s\(^{-1}\))
- \(K_L\) = mass transfer coefficient m s\(^{-1}\)
- \(a\) = interfacial surface area m\(^2\) m\(^{-3}\)
- \(C_s\) = maximum aqueous solubility
- \(C_b\) = actual concentration

Biodegradation can increase \((C_s - C_b)\) and enhance dissolution

Reported enhancements

- PCE dehalogenation feasible at saturated concentrations
  *Yang and McCarty 2000. EST 34:2979*

- 16 × dissolution enhancement
  *Cope and Hughes 2001. EST 35:2014*

- 5 × based on model
  *Christ et al. 2005. EHP 113:465*
Bioenhancement DNAPL Dissolution

Combine Surfactant/Cosolvent Assisted Dissolution DNAPL with Biodegradation

- Biodegradable surfactants/cosolvents will be used as electron donors
  - Residual PCE remaining after flushing reductively dehalogenated
  - Residual surfactant biodegraded

Christ et al. 2005. EHP 113:465
## Abbreviations Chloromethanes

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chloromethane (CM)" /></td>
<td>Chloromethane (CM)</td>
</tr>
<tr>
<td><img src="image" alt="Dichloromethane (DCM)" /></td>
<td>Dichloromethane (DCM)</td>
</tr>
<tr>
<td><img src="image" alt="Chloroform (CF)" /></td>
<td>Chloroform (CF)</td>
</tr>
<tr>
<td><img src="image" alt="Carbon Tetrachloride (CT)" /></td>
<td>Carbon Tetrachloride (CT)</td>
</tr>
</tbody>
</table>
# Biodegradation Chloromethanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Biodegradation Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED-A</td>
<td>CM; DCM</td>
</tr>
<tr>
<td>CoM-A</td>
<td>CM, DCM; CF</td>
</tr>
<tr>
<td>ED-AN</td>
<td>CM, DCM</td>
</tr>
<tr>
<td>EA-AN</td>
<td>?</td>
</tr>
<tr>
<td>CoM-AN</td>
<td>DCM, CF, CT</td>
</tr>
</tbody>
</table>

- **Faster**
- **Slower**
Chloromethanes CoM-AN

Microorganisms Involved: Methanogens, acetogens, fermentative bacteria, sulfate reducing bacteria, iron reducing bacteria, denitrifiers

Pathway
- Reductive Hydrogenolysis
  - Hydrolytic Reduction
  - Reactions catalyzed by reduced enzyme cofactors, chelating agents, magnetite, quinones
    - Cobalt containing vitamin B12
    - Zinc containing porphorinogens
    - Pyridine-2,6-bis(thiocarboxylic acid)
    - Quinones, humus
    - Biogenic magnetite
Chloromethanes CoM-AN

- **Kinetics: CF dechlorination**
  - Activity: 0.3 to 36 mg g\(^{-1}\) dwt d\(^{-1}\)

- **Kinetics: CT dechlorination**
  - Activity: 3 to 1198 mg g\(^{-1}\) dwt d\(^{-1}\)
Chloromethanes CoM-AN

Pathway:

CT

Cl–C–Cl

2e–, H+ → Cl–C=Cl

CF

Cl–C–H

2e–, H+ → Cl–C–H

DCM

H–C–H

2e–, H+ → HCOOH

HCl

2H2O → 2HCl → CO2

formic acid

carbon monoxide
Chloromethanes CoM-AN

Effect Redox Mediators

Experimental

- Phosphate buffer pH 7.0
- mineral medium (Cl⁻ free)
- methanogenic sludge (0.5 g VSS/L)
- VFA mixture (0.25 g COD/L)
- CT or CF (100 uM)
- Redox Mediators (10 uM)

Chloromethanes CoM-AN

Effect Redox Mediators

Cobalamin (vitamin B12)

Riboflavin (RF)

Anthraquinone Disulfonate (AQDS)
**Chloromethanes CoM-AN**

**Effect Redox Mediators: CT Concentration**

![Graph showing the effect of redox mediators on CT concentration over time.](image-url)

- **no sludge control**
- **no redox mediators**
- **10 µM B12**
- **10 µM AQDS**
- **10 µM RF**

Carbon Tetrachloride Conc. (µM) vs Time (days)
Chloromethanes CoM-AN

Effect Redox Mediators: Chlorine Balance day 5

Chlorine Balance (% CT-Cl)

Treatment

- Contr CT
- Autl CT
- CT
- CT+AQDS
- CT+rib0
- CT+HOB'12
- CT+B'12
Chloromethanes CoM-AN

Role Redox Mediators:

Substrate \rightarrow \text{bacterium} \rightarrow \text{Oxidized Substrate}

\[
\begin{align*}
\text{Substrate} & : \quad \text{Cl} - \text{C} - \text{Cl} \\
\text{Oxidized Substrate} & : \quad \text{Cl} - \text{C}^\bullet - \text{Cl}
\end{align*}
\]
Chloromethanes CoM-AN

Evidence of Direct Dechlorination by Hydroquinone

\[
\begin{align*}
\text{AH}_2\text{QDS} & \quad \text{Cl} & \quad \text{CT} \\
\text{AQDS} & \quad \text{H} - \text{C} - \text{Cl} & \quad + & \quad ? + \text{Cl}^{-}
\end{align*}
\]

Curtis & Reinhard. 1994. EST 28:2393
Conclusions 1

**Biodegradation Chloroethenes**
- High biodiversity for rapid halorespiration PCE to cDCE; halorespiration cDCE to E restricted to one genus, *Dehalococcoides*
- Slow anaerobic cometabolism of PCE, TCE, cDCE and VC (dominant process reductive hydrogenolysis)
- Rapid aerobic cooxidation of VC, cDCE, TCE feasible
- Aerobic biodegradation of VC (and cDCE) as growth substrates feasible with newly discovered bacterial strains

**Bioremediation Chloroethenes**
- Anaerobic halorespiration (PCE → cDCE) followed by aerobic cooxidation (cDCE → CO₂, Cl⁻)
- Complete reductive dechlorination with *Dehalococcoides* (PCE → E)
Conclusions 2

Biodegradation Chloromethanes

- Rapid aerobic or anaerobic biodegradation of CM or DCM as growth substrates
- Aerobic cooxidation CM, DCM and CF feasible
- Slow Anaerobic cometabolism of DCM, CF and CT
  1) hydrolytic reduction to CO$_2$
  2) reductive hydrogenolysis to lower chlorinated methanes
- Redox mediators can greatly enhance anaerobic biotransformation CT, CF

Bioremediation

- Anaerobic cometabolism for CF and CT
What is Phytoremediation?
What is Phytoremediation?

A solar driven, biological system that is used to Contain, Sequester, Remove, or Degrade Organic and Inorganic Contaminants in Air, Soils, Sediments, Surface Water, and Groundwater
## Types of Phytoremediation

<table>
<thead>
<tr>
<th>Artificial Wetlands</th>
<th>Phytodegradation</th>
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</thead>
<tbody>
<tr>
<td>Phytostabilization</td>
<td>Air purification</td>
</tr>
<tr>
<td>Phytoextraction</td>
<td>Water and</td>
</tr>
<tr>
<td>Rhizofiltration</td>
<td>Wastewater</td>
</tr>
<tr>
<td>Rhizosphere</td>
<td>Management</td>
</tr>
<tr>
<td>enhancement</td>
<td></td>
</tr>
<tr>
<td>Phytovolatilization</td>
<td>Landfill caps</td>
</tr>
<tr>
<td></td>
<td>Green Roofs</td>
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<tr>
<td></td>
<td>Combination</td>
</tr>
<tr>
<td></td>
<td>technologies</td>
</tr>
</tbody>
</table>
## Wide Range of Contaminants

**Organic:** hydrocarbons, chlorinated solvents, phenols, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), agricultural wastes

**Inorganic:** metals, radionuclides, salinity, nitroaromatics, amines, excess fertilizers, pesticides, CCA (chromium copper arsenic)
Different Types of Impacted Media

**Solid phase:** soils, sediments, sludges

**Liquid phase:** run-off, stormwater, wastewater, groundwater, leachate

**Gaseous phase:** greenhouse gases, VOCs, NO\textsubscript{x}
Advantages

Safety
- Minimized emissions & effluent and low secondary waste volume
- Controls erosion, runoff, rain infiltration, and dust emissions

Ecological
- Habitat friendly, habitat creation, promotes biodiversity
- Sequesters greenhouse gases (carbon dioxide)

Public / Regulatory
- Acceptable brownfields applications
- Aesthetics, green technology
- Increasing regulatory approval and standardization
Limitations or Common Regulatory Issues

Depth
Only effective if within the relative rooting depth of the vegetation

Time
Requires longer periods to become effective (establishment)
May requires longer periods to reach clean up targets
Seasonal effects
Phytotoxicity
Generally considered applicable for low to moderate concentrations
In most cases, the vegetation must survive in order to operate

Media Transfer / Food Chain Impacts
Fate and transport often unclear
Air emissions, leaf litter
Harvesting, hazardous waste?
Toxicity of parent vs. by-products
Web Addresses

http://www.rtdf.org/public/phyto/phytodoc.htm
http://www.itrcweb.org/gd_Phyto.asp
http://www.dsa.unipr.it/phytonet/
http://plants.usda.gov/
http://clu-in.org/techdrct/
http://www.acap.dri.edu/
Books

Phytoremediation (Hardcover)
Tsao

Phytoremediation
McCutcheon and Schnoor

Phytoremediation of Contaminated Soil and Water (Hardcover)
Terry and Banuelos

Plants That Hyperaccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining (Hardcover)
Brooks
Companies

Edenspace – Metals
Applied Natural Sciences – Organics
Phytokinetics – Organics
Applied Phytogenetics – Genetically Engineered Plants
Thomas Engineering - Organics
Ecolotree – Landfill caps and riparian restoration
Phytoextraction Associates – Metals and phytomining
Journals

International Journal of Phytoremediation
Environmental Science and Technology
Environmental Pollution
Plant and Soil
Chemosphere
Journal of Environmental Quality
New Phytologist
Plant Physiology
Conferences

EPA International Applied Phytotechnologies Conference
Battelle
American Society for Agronomy
American Chemical Society
Association for Environmental Health and Sciences
Phytodegradation

Using plants to themselves take up and degrade organic contaminants.
Enzyme Systems

Green Liver Concept
P-450’s
Peroxidases
Dehalogenases
Reductases
Glutathionone-s-transferases
Conjugation enzymes
Anaerobic Degradation of TCE

Figure II-1. Reductive dechlorination of chlorinated ethylenes under anaerobic (methanogenic) conditions.
Mammalian Degradation

Figure 1. Metabolism of trichloroethylene
Greenhouse Studies
Diagram of a cell

Top view

Side view

Injection well with T-bar
Direction of water

Injection well
T-bar connection
Soil layer
Sand layer
Slopes for drainage

Extraction well

Extraction well
Micromoles of TCE and metabolites recovered 28 September through 4 December 1995

- 3 - trees
- 5 - trees
- 8 - no trees
Three Year Daily Additions and Recoveries of TCE and Metabolites

- added
- recovered - no trees
- recovered - trees
- recovered - trees
Variation of Chloride Ion Concentration with Soil Depth in the Test Bed Cells

- Control
- CCH & Poplar
- TCE & Poplar
- Control with poplar (exposed to recirculated water)

Background levels of chloride ion in unexposed soils
Three Year Daily Additions and Recoveries of TCE and Metabolites

- added
- recovered - no trees
- recovered - trees
- recovered - trees

Millimoles

Other Compounds

MtBE, Benzene, other gasoline additives
Pesticides; Ethylene dibromide, lindane
Explosives; TNT, RDX, perchlorate
Solvents; TCE, CT, PCE
Deicing agents; benzotriazoles
Regulatory Concerns

How to convince the regulators that this is a good idea.
Regulatory Issues

Regulator unfamiliarity with process
Not knowing all the answers to assure the regulator
Testing and Monitoring

How often
What needs to be tested
  Soil
  Air
  Water
  Plant tissues
How do you analyze these crazy samples???
Unusual Monitoring Parameters

Tree health or why are all my plants brown?
Water issues
Nutrient availability
Is the soil itself killing the plants
Fungus, bugs and other munching critters
Convincing the regulators that plant health is a measurable criteria for success
Where do those roots go?
Weather Impacts on Monitoring

Why doing transpiration measurements in the rain is not a good idea.
Temperature and light intensity have strong effects on plant metabolism and thus your test results.
What do you mean by success?

Do you need different standards for success?
What are actually testing?
  Plant survival
  Root depth
  Root penetration
  Transpiration
  Presence of metabolites
  Groundwater depression
  Soil analysis
  Transpiration rates
Security Issues

Securing a field can be more challenging than securing a building.

Squatters/Vagrants on the site.

Community member access on sites.

   Involving the community with site protection.

Problems with radical groups.
Do Contaminants Enter the Food Chain?
Food chain transfer

Insects munching
Animals munching on the plants or insects
Local people taking the plants
Trees and Deer Don’t Mix Well
And children want to play
Decision making

How to decide if phytoremediation is right for the site.
Site Evaluation

Evaluating a site as a potential phytoremediation site involves some different parameters.

Weather
Water availability
Soil fertility
Toxicity
Site Evaluation

Will phyto work with the contaminant I have on the site?
How will the plants and contaminants interact?
Is this acceptable to the regulators?
Site Evaluation

Is the site now, or could it be, applicable to plant growth?
- Blacktop and plants do not mix
- Shade/sun issues
- Soil toxicity that is not related to contaminant
Designing a site

How do we make this work?
Unique Site Prep Problems

Concrete is not dependent on soil nutrients, but your plants will be.

Soil compaction can be an issue for planting.

Shades from buildings or other plants can be a major issue.
Security Issues

Securing a field can be more challenging than securing a building.
Squatters/Vagrants on the site.
Problems with radical groups.
Weather

Why doing transpiration measurements in the rain is not a good idea.

Temperature and light intensity have strong effects on plant metabolism and thus your test results.
Working With Mother Nature

Construction can go on anytime of the year, but planting has to be in sync with the seasons.

When dealing with natural systems we have to deal with all of nature (ie. bugs and birds are now a fact of life).
Selecting Plants For Your Site

You need to research and find the plant type that can handle the contaminant you are dealing with on the site.
You need to find a plant that will SURVIVE on your site, or why brown trees don’t impress anyone…
Screening Trees
Before You Install, or Why Feasibility Testing is a Good Idea

Better to have a few plants die in the greenhouse, rather than have a field full of dead plants.....
Preparing the Site for Planting, or Why You Need to Learn to Think Like a Farmer

Weather plays an important role
Why plowing mud is a BAD idea...
Plants have their own time schedules, and you have to meet theirs, not the other way around
Sometimes That Extra Plowing is NOT a Good Idea…
Department of Energy – Ash Basin

Understanding how your preparations will affect the site
Know How Your Treatment Will Work

- Tilled, no compost
- No site prep
Consider Combination Technologies

- Pump and irrigate
- Water management behind a plume containment wall
- Reactive barriers and plants
- Combined bioremediation and phytoremediation
- Using plants to minimize recharge zones
Spray systems
Tritium Irrigation System
Timing of the installation can be critical
Timing the herbicide application to remove existing vegetation can be vital
Digging up irrigation lines does not help
Mud, Anyone?
Or how about rocks?
But when they grow, they grow!
Navy Base I

- Plowing and moving mud
- Meeting unrealistic time schedules
- Why a wood chip road is NOT a good idea
- Hydrologic problems
- Poplars don’t swim real well
Plowing and Moving Mud
Water Problems
Earth Day 1999
Wood Chips are Not Always a Good Idea
Start of third year
Saginaw Mill

Drainage problems
Trees and deer don’t mix well
The problems with weeds
Why community knowledge is a good thing
Lake Saginaw
Surviving the weeds, the deer, the fire…
And finally they grow
Portland

Why plowing mud is a bad idea or adobe is not a good growing medium
Plant selection can be crucial
Adobe, anyone?
Plant Selection + Poor Growing Conditions…

[Two images of plants in different growing conditions]
Navy Base II

- You need to know what is happening all around you, even if it is not related to what you are doing
A Little Asphalt, Anyone?
What do you mean there is too much fertilizer or when wood chips ARE a good idea
Didn’t you say the pesticides were burned?
Why more mixing is not always better
A Little of Everything…
Wood Chips Just Might be a Good Idea Here!
And Then There Were Pesticides…
Still Not a Good Idea…
Okay, the Plants are Finally in the Ground and Growing. What Can Go Wrong Now???

Mechanical breakdowns
Invaders of the four-legged kind
Don’t forget the “Save the Trees Society”
Nutrient needs
Droughts are Mother Nature’s way of saying “Gotcha!”
Poplars Can’t Swim!
Trees and Deer Don’t Mix Well
Plants are Growing, Everything is Looking Green and Healthy. Time to Start Testing.
Now What?

Weather can still be a big issue
Sample collection can pose some unique problems (getting liquid nitrogen into the field is NOT fun)
Where do I ship the samples for analysis?
Tell Me Again…….

WHY Do I Want to Put Myself Through This???

Less expensive
Citizens groups LIKE trees
Many regulatory agencies are looking favorable at groups that try innovative technologies
Because it is a great technology that will have you constantly learning as you go
Have faith in the trees!
Thank you!
Thank You

After viewing the links to additional resources, please complete our online feedback form.