United States
Environmental Protection
Agency

Off ce of Solid Waste and
Emergency Response
(5201G)

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Superfund

EPA

Environmental Remediation Technologies
Student Manual

ENVIRONMENTAL REMEDIATION TECHNOLOGIES

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ENVIRONMENTAL REMEDIATION TECHNOLOGIES

presented by
Tetra Tech NUS, Inc.

for the
U.S. Environmental Protection Agency's
Environmental Response Team

Environmental Response Training Program (ERTP)

U.S. EPA	United States Environmental Protection Agency
OSWER	Office of Solid Waste and Emergency Response (Superfund)
OSRTI	Office of Superfund Remediation and Technology Innovation
ERT	Environmental Response Team

ERTP Training Courses

- Are offered tuition-free for environmental and response personnel from federal, state, and local agencies
- Vary in length from one to five days
- Are conducted at EPA Training Centers the United States

ERTP Training Courses

Course Descriptions, Class Schedules, and Registration Information are available at:

- www.trainex.org
- www.ertpvu.org

Course Objectives

- Evaluate appropriate techniques to assess, stabilize, and screen for potential remedies for contaminated sites
- Identify the processes and explain the limitations of the most frequently-used treatment technologies
- Identify resources that describe innovative treatment technologies

Course Materials

- Student Registration Card
- Student Evaluation Form
- Course Agenda
- Student Manual
- Facility Information
- Student Handouts

SUCCESSFUL TREATMENT DESIGN

Student Performance Objectives

Upon completion of this unit, students will be able to:

1. Understand the general principles of the Triad approach
2. Describe the key components of the conceptual site model

SUCCESSFUL TREATMENT DESIGN

Successful Treatment Design

- A successful treatment design requires a clear understanding of specific site conditions.
- During many earlier environmental restoration projects, the collection of site-specific data proved to be a lengthy and expensive process.

Triad Approach

Clear project goals are established through the use of:

- Systematic Project Planning
- Dynamic Work Strategies
- Real-time Measurement Technologies

Surface Release Fisherville, MA

Potential Receptor
Blackstone River

Fisherville Site Investigation

Initial investigation for the source of the oil release discovered high Concentrations of a chlorinated solvent (TCE) north of the mill building

Image Courtesy of USGS

Conceptual Site Model

In developing a CSM, key elements include:

- General physical site description
- Regional environmental setting
- Land use
- Contaminant information and site activities
- Potential exposure pathways and risk estimation
- On-going data evaluation and data gap identification

Conceptual Site Model

In developing a CSM, key elements include:

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General Physical Site Description

- Facility description
  - Site address
  - General site operation
- Physical setting
  - Area topography
  - Area land use

Facility Description Example

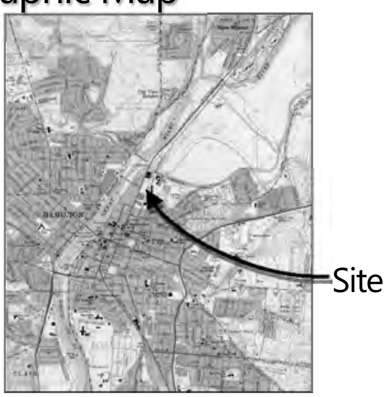
Chem-Dyne general site operations:

- Operated from 1974 to 1980 on a 10-acre site
- Stored, recycled, and disposed of many types of industrial chemical wastes
- Thousands of 55-gallon drums

General Physical Site Description

- Facility description
  - Site address
  - General site operation
- Physical setting
  - Area topography
  - Area land use

Topographic Map



Area Land Use Example

Conceptual Site Model

In developing a CSM, key elements include:

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Regional Environmental Setting Example

Geology

- Site is located on the Great Miami River alluvial deposits — glacial outwash materials consisting of poorly sorted, poorly bedded silt and sand.
- Depth of Ordovician limestone bedrock is greater than 100 feet below the surface.

Regional Environmental Setting Example

Hydrogeology

- Site is located on permeable sand and gravel deposits in ancestral drainage channels
- Deep aquifer groundwater wells yield 500–1000 gpm
- Site includes a shallow unconfined aquifer and a deep confined aquifer

Groundwater Resource Map

Groundwater Pollution Potential Map

Regional Environmental Setting

Ecological Profile

- Describes the physical relationship of the organisms on the developed and undeveloped portion of the site and adjacent off-site properties

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Land Use

Land use descriptions

- Land use history
- Current land use

The Triad approach works toward a viable end use of the land. Current use and proposed use are important.

Example Chem-Dyne site:

- Currently a remediation project operated by the Chem-Dyne Trust
- No future use has been proposed at this time

Land Use History

- Federal, state, and local operating permits
- Reported releases or spills
- Facility Records
- Public Records
  - Title history
  - City directories
  - Aerial photographs
  - Sanborn Fire Insurance Maps
  - Local agencies

Land Use History Example

Public records (title history & city directories):

1910 to 1960s	Ford Motor Co.
1960s to 1974	Nimrod Camping Trailer
1974 to 1980	Chem-Dyne Recycling Facility
1980 to present	Chem-Dyne Trust (remediation project)

Land Use History Example

Aerial photo
December, 1979

Land Use History Example

Sanborn Fire Insurance maps:

1927	Ford Motor Co. forge and manufacturing facility
1950	Ford Motor Co. metal stamping and wheel manufacturing facility
1969	Ward Manufacturing (Nimrod Camping Trailer Division)

Land Use History Example

Local agency reports (ChemDyne):

- Hamilton Fire Department reported numerous fire responses. Firemen became ill and fire hoses dissolved in standing puddles.
- Reports led to a health department and Ohio EPA investigation.
- Site operations were suspended in 1980.

Conceptual Site Model

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- Potential exposure pathways and risk estimation
- On-going data evaluation and data gap identification

Contaminant Information & Site Activities

This component of the CSM includes the following information:

- Previous site activities
- Contaminants of concern
- Potential contaminant source areas
- Contaminant fate and transport
- Contaminant susceptibility to treatment options

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Immediate Remedial Action

Immediate Remedial Action

General rule at many sites:

- 80% of the contamination removed during immediate remedial action often is completed for 20% of the total project cost

Immediate Remedial Action Example

Chem-Dyne:

- Removal of drums and standing liquid
- Excavation of grossly contaminated soil

Contaminant Information & Site Activities

This component of the CSM includes the following information:

- Previous site activities
- Contaminants of concern
- Potential contaminant source areas
- Contaminant fate and transport
- Contaminant susceptibility to treatment options

Contaminants of Concern

- Identification from records
  - Local Emergency Planning Committee
  - RCRA listing
  - Operator knowledge
- Identification by sample analysis
  - Field screening
  - Target Compound List (TCL) and Target Analyte List (TAL) analysis
  - Regulatory agency-specific list

Contaminants of Concern Example

At the Chem-dyne site, many TCL and TAL hazardous materials were detected, including:

- Volatile organic compounds (VOC)
- Semi-volatile organic compounds
- PCBs
- TAL (metals)

Contaminant Information & Site Activities

This component of the CSM includes the following information:

- Previous site activities
- Contaminants of concern
- Potential contaminant source areas
- Contaminant fate and transport
- Contaminant susceptibility to treatment options

Potential Contaminant Source Areas

- Areas where hazardous material is stored, used, or disposed, such as:
  - Drum pads
  - AST & USTs
  - Waste storage & Disposal areas
- Hazardous material usage areas:
  - Paint booths
  - Plating operations
  - Treating operations
  - Pipe runs

Chem-Dyne Loading Dock Filled With Liquid

Contaminant Information & Site Activities

This component of the CSM includes the following information:

- Previous site activities
- Contaminants of concern
- Potential contaminant source areas
- Contaminant fate and transport
- Contaminant susceptibility to treatment options

Contaminant Fate & Transport

- Relates how a contaminant reacts or travels through the environment to a receptor
- Based on the Contaminant characteristics:
  - Volatility
  - Solubility
- Characteristics of the medium, using soil as an example, could include:
  - Permeability
  - Organic carbon content
  - Grain size distribution

Contaminant Information & Site Activities

This component of the CSM includes the following information:

- Previous site activities
- Contaminants of concern
- Potential contaminant source areas
- Contaminant fate and transport
- Contaminant susceptibility to treatment options

Contaminant Susceptibility Example

Contaminants detected at the Chem-Dyne site included:

- Volatile organic compounds
- Semi-volatile organic compounds
- PCBs
- TAL (metals)

Conceptual Site Model

In developing a CSM, key elements include:

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- Potential exposure pathways and risk estimation
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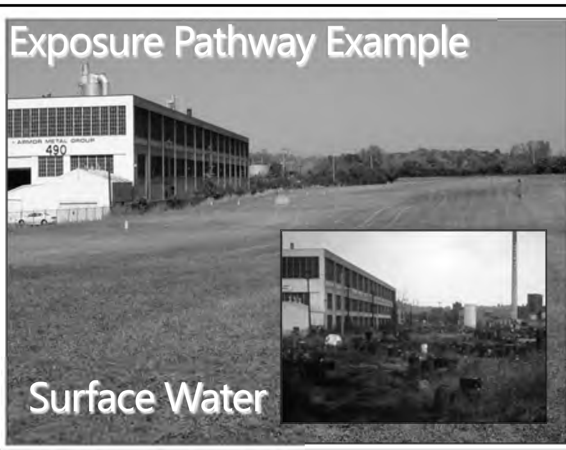
Exposure Pathway Example

Groundwater (Chem-Dyne site)	
Source	Onsite hazardous materials
Fate-and-transport mechanism	Through soil into shallow and deep Great Miami River Aquifers
Exposure route	Ingestion and/or dermal contact
Receptors	Residents using deep-aquifer groundwater

Exposure Pathway Example



Exposure Pathway Example

Surface Water *(Chem-Dyne site)*	
Source	Onsite hazardous materials
Fate-and-transport mechanism	Surface water runoff during heavy rains
Exposure route	Direct contact (e.g. burned feet)
Receptors	Employees of adjacent business

Exposure Pathway Example

Emissions *(Chem-Dyne site)*	
Source	Hazardous materials released by onsite activities
Fate-and-transport mechanism	Fugitive dust released into the air, migrating off site
Exposure route	Inhalation
Receptors	Neighbors

Exposure Pathway Example

Emissions

Exposure pathway: contaminated fugitive dust migrated offsite to neighboring habitats

Risk and Exposure Assessment

- Ensures that the selected remedial activities will protect human health and the environment.
- Examples:
  - Risk Based Corrective Action (RBCA)
  - Brownfield Program
  - Site Specific Risk Assessment

Conceptual Site Model

In developing a CSM, key elements include:

- General physical site description
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- Contaminant information and site activities
- Potential exposure pathways and risk estimation
- On-going data evaluation and data gap identification

Potential Data Gaps

As the CSM develops, data gaps may be identified and specific site information may need to be collected, such as:

- Soil Characteristics
- Hydrogeologic & geologic information
- Surface water & sediment information
- Additional information

Additional Information

- Meteorological
  - Annual rainfall
  - Average temperature
  - Evapotransporation
- Offsite information
  - Nearby population
  - Offsite land use
  - Zoning issues

Tale of Two Sites

Chem-Dyne Superfund Site
vs.
Pristine, Inc. Superfund Site

Chem-Dyne Superfund Site

Chem-Dyne Remediation

Remediation of Chem-Dyne included:

- Excavation of top 10 ft. of soil
  - Deeper contaminated soil remained
- Groundwater pump-and-treat system through 25 wells
- Treated groundwater through air stripper
- Treated air stripper emissions through granular activated carbon

Chem-Dyne Treatment Building With Air-Stripper Tower

Chem-Dyne Remediation

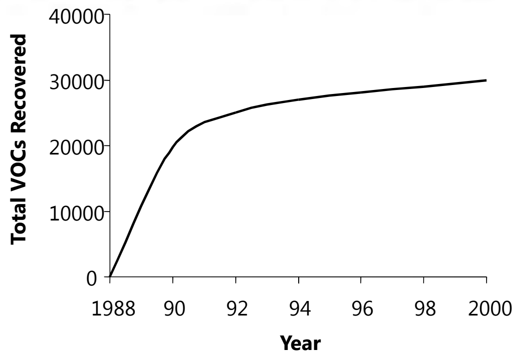
Remediation of Chem-Dyne included:

- Re-circulated half of the treated water into unsaturated zone to further leach remaining soil contamination
- Discharged remaining half of the treated water
- Constructed impermeable cap to prevent surface water infiltration

Cost

- $11.6 million construction
- Approx $18 million operation and maintenance (20 years)

Chem-Dyne Total VOC Recovery



Pristine Superfund Site

Very similar to Chem-Dyne site:

- Urban industrial waste recycling facility located in Reading, Ohio
- Operated from 1974 to 1981
- Stored, treated, and incinerated hazardous wastes: 10,000 drums & gallons of waste onsite
- Similar geology and hydrogeology

Pristine Treatment System

Remediation of Pristine

- Excavation of all visibly contaminated soil to 4′ bgs
- Onsite thermal desorption of contaminated soil
- SVE Treatment of unsaturated zone
- Groundwater pump-and-treat system w/ GAC & air stripping
- Cost
  - $13.5 million construction
  - $6 million operation & maintenance (20 years)
- On-track to reach cleanup goals

Successful Treatment Design Summary

Triad approach supports the project goal of a successful treatment design by combining:

- Site-specific information
- Contaminant-specific information
- Treatment options

FATE AND TRANSPORT OF CONTAMINANTS

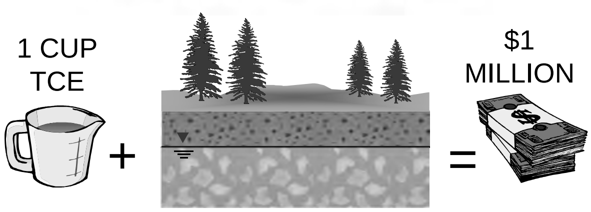
Student Performance Objectives

Upon completion of this module you will be able to:

1. Describe how chemicals travel through environmental media, such as rock or soil, air, and water.
2. Describe how chemicals can become associated with (stored by) various environmental media.
3. Describe chemical parameters which model (predict) the distribution of contaminants among media.
4. Describe environmental conditions which promote or retard the movement of chemicals in the subsurface.
5. Describe factors that affect organic chemical degradation.

FATE AND TRANSPORT OF CHEMICAL CONTAMINANTS

Million-Dollar Problem

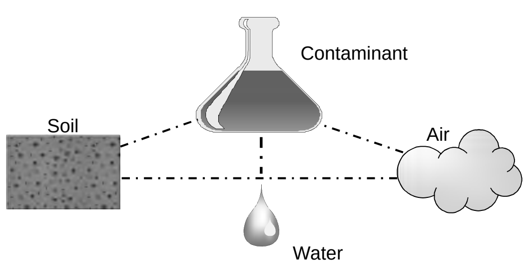


Pour one cup of TCE onto the ground, and it will cost you $1 million to get it out.

WHY?

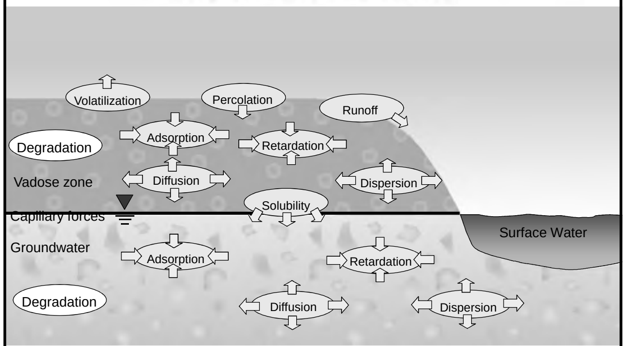
Million-Dollar Question

Why would it cost so much?



Contaminant behavior is a function of the properties of both the contaminant and the environmental media.

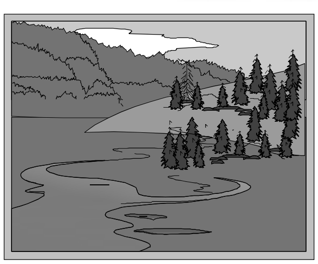
Fate and Transport Processes in the Environment



Fate and Transport

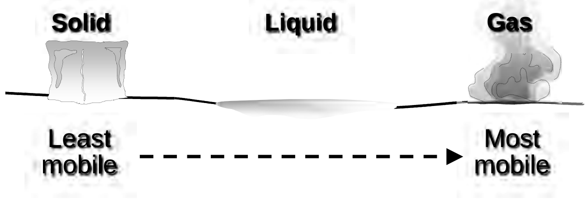
- Surface
- Subsurface
- Distribution
- Degradation

Contaminant Behavior on Surface



- Physical state
- Volatilization
- Runoff
- Solubility
- Percolation

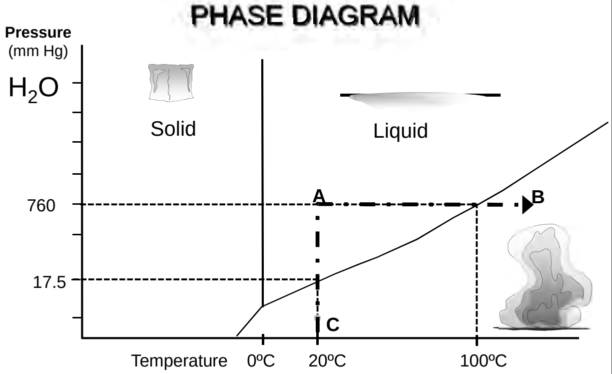
Physical State



- Organic vs. Inorganic
- Transition temperatures, e.g., melting point, boiling point

Physical State

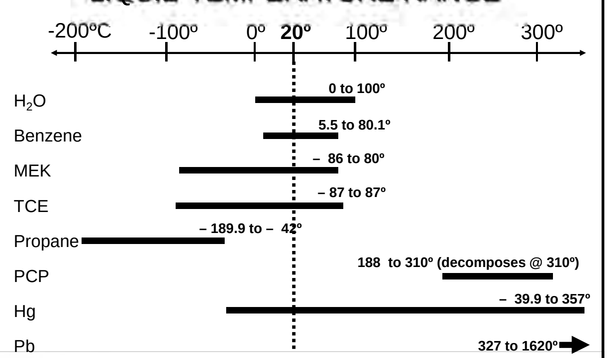
PHASE DIAGRAM



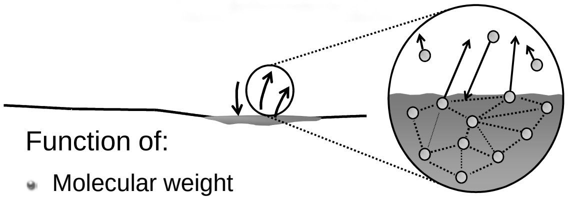
(Not to scale)

Quantifying Physical State

LIQUID TEMPERATURE RANGE



Volatilization



Function of:

- Molecular weight
- "Cohesive forces"
  - Van der Waals forces
  - Polarity
- Temperature

Quantifying Volatilization

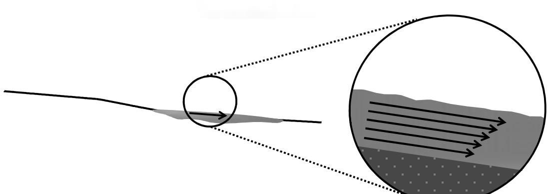
Vapor Pressure (VP): Pressure exerted above a compound in liquid or solid phase

Compound	VP (mmHg @ 20ºc)
Benzene	80.0
TCE	63.0
H_2O	17.5
PCP	.00011

↑ MORE VOLATILE

↓ LESS VOLATILE

Runoff



Function of:

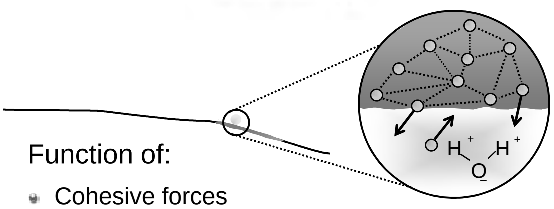
- Hydraulic gradient
- "Cohesive forces" (e.g., internal friction)

Quantifying Runoff

Dynamic viscosity (μ): Indicates degree of resistance to flow

Compound	μ (centipoise @ 20ºc)	
TCE	.57	↑ MOST MOBILE
Benzene	.65	
H_2O	1.0	
Kerosene	2.5	
Phenol	8.5	↓ LEAST MOBILE

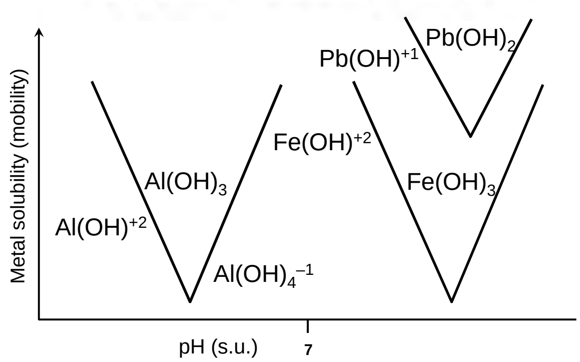
Solubility



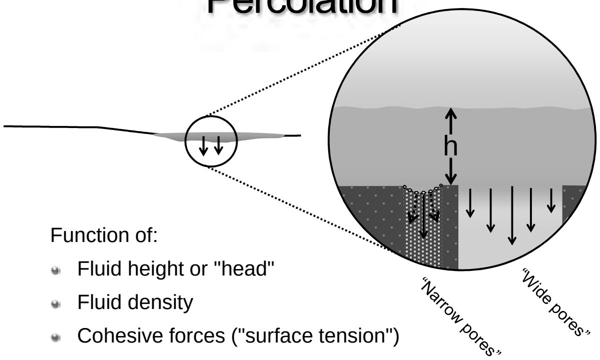
Function of:

- Cohesive forces
- Adhesive forces
  - Van der Waals
  - Polarity
  - Ionization

Inorganic Solubility vs. pH



Percolation



Function of:

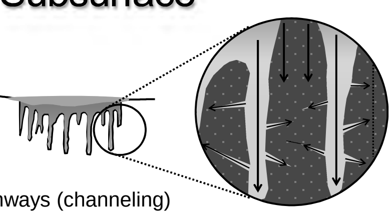
- Fluid height or "head"
- Fluid density
- Cohesive forces ("surface tension")
- Adhesive forces ("wetting")

Quantifying Percolation

Kinematic viscosity (ν): Indicates degree of resistance to downward flow (combines density with dynamic viscosity)

Compound	ν (centistokes @ 20ºc)	
TCE	.39	↑ MOST MOBILE
Benzene	.74	
H_2O	1.0	↓ LEAST MOBILE

Subsurface

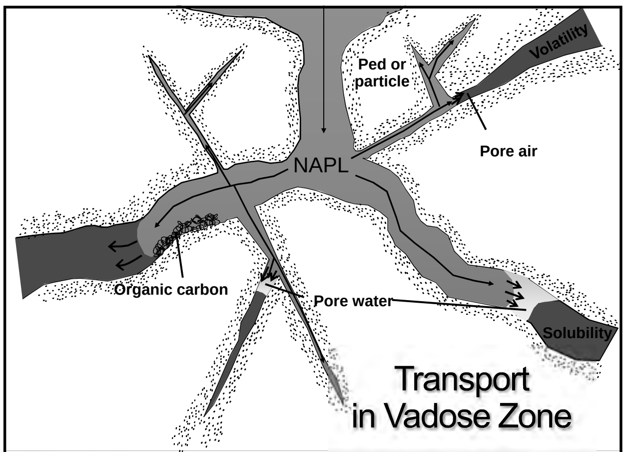


Function of:

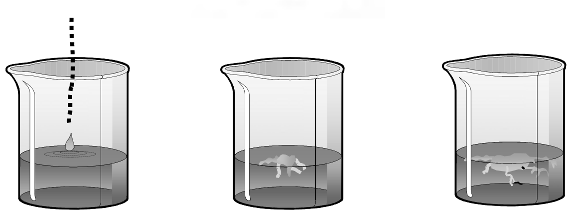
- Preferential pathways (channeling)
  - Macropores
  - Micropores
- Solubility
- Sorption
- Volatility

Subsurface Distribution

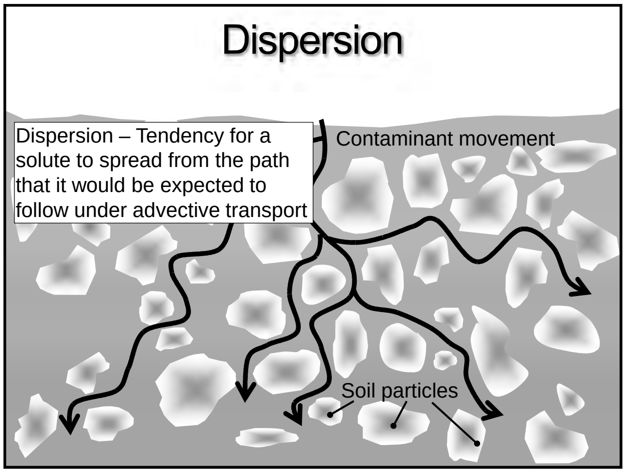
- Physical movement stops when matric potential and hydrodynamic head are balanced
- Molecular movement continues as long as relative concentration remains "unbalanced"

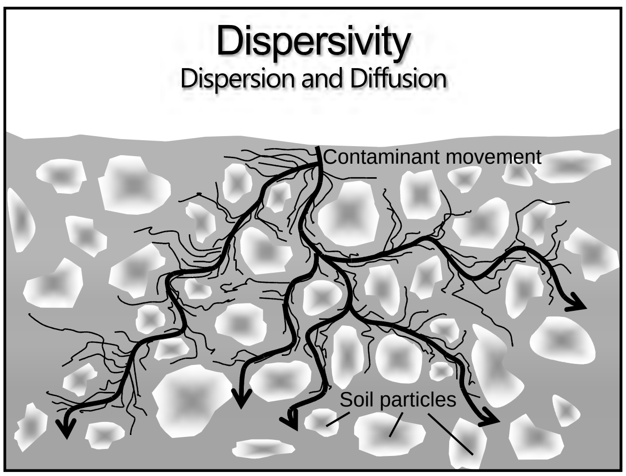


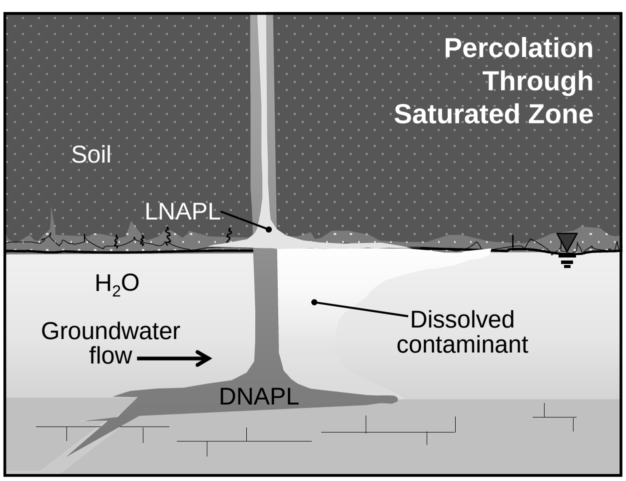
Diffusion



Diffusion – Process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion.


Dispersion
Dispersion – Tendency for a solute to spread from the path that it would be expected to follow under advective transport
Contaminant movement
Soil particles


Dispersivity
Dispersion and Diffusion
Contaminant movement
Soil particles


Percolation Through Saturated Zone
Soil
LNAPL
H2O
Groundwater flow
Dissolved contaminant
DNAPL

Quantifying Distribution

Air	Vapor pressure (VP)
Water	Solubility (Sol.)
Water/Air	Henry's Law (H_L)
Water/soil	Sorption (K_{OC}, CEC)

Henry's Law

$$HL = \frac{VP}{Solubility}$$

Compound	VP (mmHg)	Sol.(mg/L)	$H_L \frac{atm\text{-}m^3}{mol}$
VC	2,300	1,100	6.9×10^{-1}
Benzene	76	1,780	5.4×10^{-3}
TCE	58	1,100	8.9×10^{-3}
MEK	71.2	268,000	2.7×10^{-5}

Sorption

The degree of attraction between a non-polar chemical and the natural organic matter associated with an aquifer (retardation)

Function of:

- Contaminant
- Fraction of organic carbon in medium (fOC)
- Properties of soil, e.g., structure, texture (KOC)

Cation Exchange Capacity (CEC)

Total cations adsorbed on a unit mass of soil (centimoles/kg)

Function of:

- Soil texture (e.g., clay, silt, sand)
- Soil surface area (clay type, e.g., kaolinite)
- Organic matter content

Degradation of Contaminants

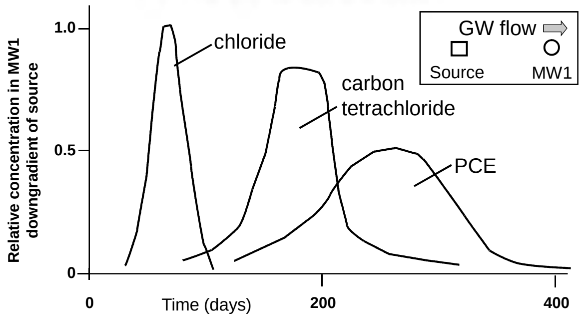
- Break down chemically (organics only)
- Examples of degradation processes:
  - Hydrolysis
  - Redox
  - Biodegradation

Degradation

Function of:

- pH
- Bond strengths of contaminant
- Properties of attacking agent
- Redox potential
- "Hospitable" environment (biodegradation)

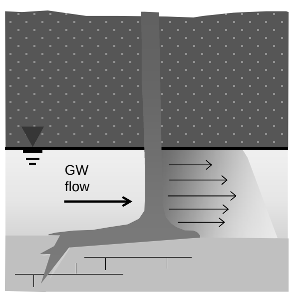
Fate and Transport of Contaminants



Million-Dollar Problem

What are you going to do?

Problem: Saturated soil contaminated with TCE (enough to contaminate groundwater to solubility limit for 15 years)



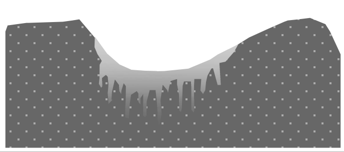
Another Million-Dollar Problem

What are you going to do?

Problem: Chrome plating bath solutions have been disposed into unlined lagoon (now dry).

Most of chromium has been adsorbed by underlying clay soils.

Groundwater contamination was not detected.



CAPPING AND CONTAINMENT

Student Performance Objectives

Upon completion of this module you will be able to:

1. State the application, limitations, working mechanisms, advantages and disadvantages of the following capping technologies:
   a. Clay caps
   b. Resource Conservation and Recovery Act (RCRA) multi-stage caps
2. State the application, limitations, working mechanisms, advantages and disadvantages of the following groundwater containment technologies:
   a. Slurry trench cutoff walls
   b. Grout curtain walls

CAPPING
AND
CONTAINMENT

EPA TETRA TECH

Capping

- Capping controls airborne contamination and surface water infiltration
- Containment controls groundwater movement

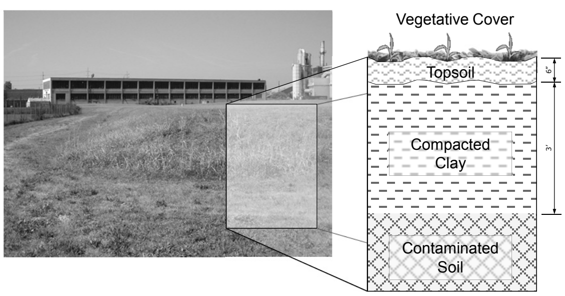
Capping

- Applications
  - Slows the movement of airborne or dustborne contaminants
  - Slows the movement of surface water into the ground
- Limitation
  - Does not directly remediate contaminants
  - Makes soil recovery and further treatment difficult

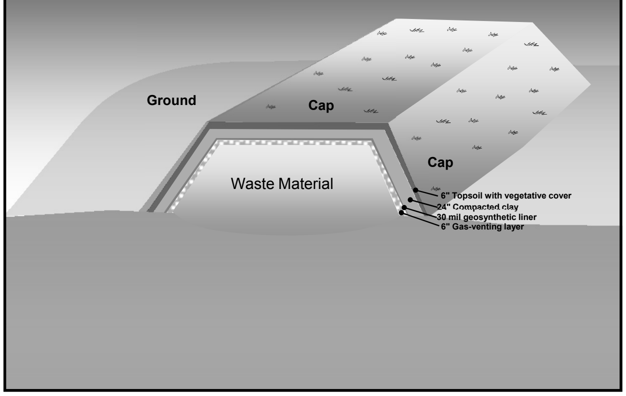
Capping

Capping materials may include natural or synthetic materials.

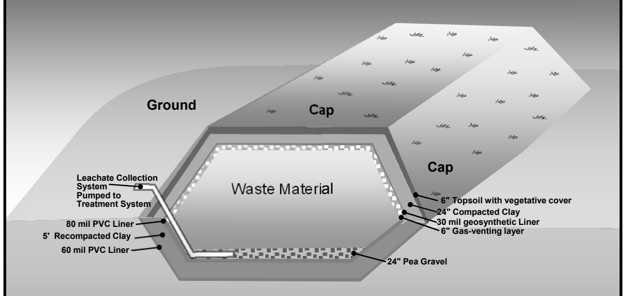
Compacted Clay Cap



Landfill Cap



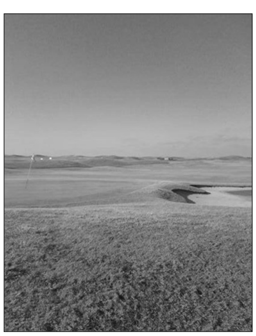
Landfill Cap with Bottom Liner



Landfill Cover with Solar Panels

Atlanta, GA
Hickory Ridge Landfill

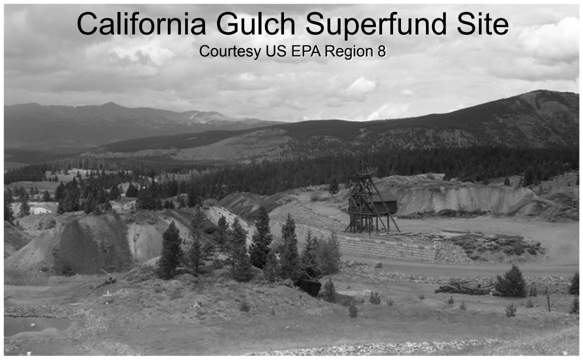
Landfill Cover, Columbus Ohio



Phoenix Golf Course

Gas collection and process system

Leadville, CO Case Study



The Denver City Pilot Study

Goals of Pilot Study

- Explore alternative and more aesthetically-pleasing ways to cover mine waste piles with materials that will help preserve the historic appearance of the mining landscape
- Water management strategy
  - Divert clean water
  - Enhance/ enlarge collection system for acid rock drainage
  - Gradually eliminate Leadville Mine Drainage Tunnel use, with exception of emergency

Surface Water Pond with Low pH

Earlier Cover "Wedding Cake"

Pilot Study Approach

- Alternative 1 – Natural Face with Partial Cap (preserve areas visible from Mineral Belt Trail/roads)
- Alternative 2 – Shotcrete with No Liner on Slope
- Alternative 2A – Shotcrete with Liner on Slope
- Alternative 3 – Inert Mine Waste Rock with Liner
- Alternative 4 – Inert Mine Waste Rock with Cribbing

Alt. 1: Natural Face With Partial Cap

Before capping

After capping

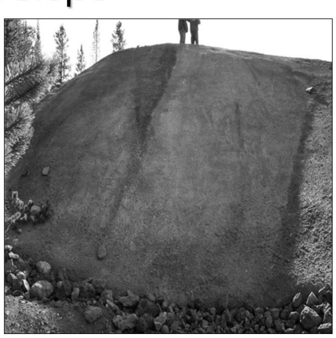
Alt. 2: Shotcrete Without Liner On Slope

Before capping

After capping

Alt. 2A: Shotcrete With Liner On Slope

After capping



Alt. 3: Inert Mine Waste And Liner

Before capping

After capping

Alt. 4: Inert Mine Waste With Cribbing

Before capping

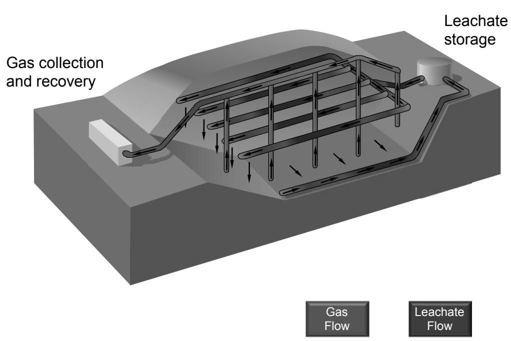
After capping

Drainage Trench On Top

On-line Information:

- Virtual Forum Web Address: **www.merid.org/leadville**
- EPA Web Address: **www.epa.gov/region8/superfund/co**

Bioreactor Landfills



Bioreactor Landfills

Bioreactor landfills are designed and operated by increasing the moisture content of the waste to enhance degradation and stabilization

Bioreactor Landfills

Primary advantages

- Efficient utilization of permitted landfill capacity
- Stabilization of waste in a shorter time
- Reduced leachate handling cost
- Reduced post closure care

Bioreactor Landfills

Secondary Advantages

- Potential for landfill gas can be a revenue stream
- Promotes more sustainable waste management
- Reduced air emissions containing VOC and hazardous air pollutants
- May possibly reduce long term costsReduced toxicity of leachate and waste material
- Consistency with sustainable landfill design

Bioreactor Landfills

Primary Disadvantages and Challenges

- Slope stability
- Higher capital costs
- Operator skills
- Temperature control in aerobic bioreactors
- Confusion over regulations to permit bioreactors
- Liner chemical compatibility
- Odor control
- Design & construction of liquid handling systems
- Waste heterogeneity

Containment

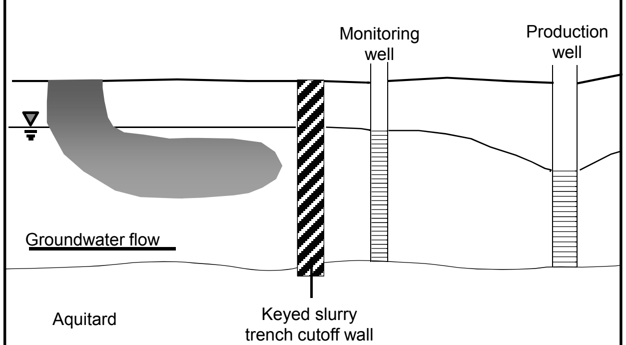
Subsurface walls to control groundwater movement

- Slurry trench cutoff wall
- Grout curtain
- Sheet piling

Containment

- Applications
  - Slows movement of groundwater-borne contaminants using subsurface walls
  - Can be used to dewater a site for remediation
- Limitations
  - Does not directly remediate contaminants

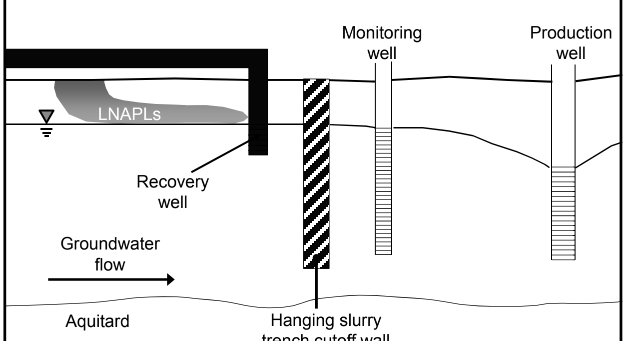
Slurry Trench Cutoff Wall



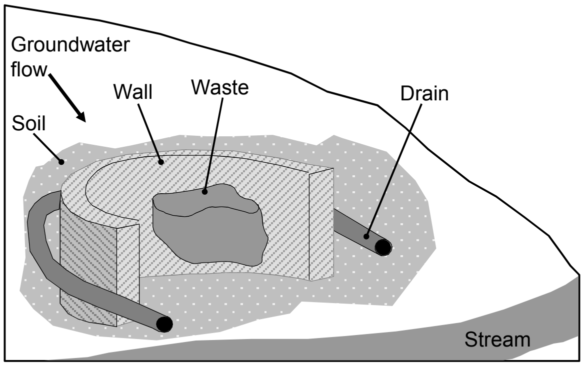
Slurry Trench Cutoff Wall

Slurry Trench Cutoff Wall

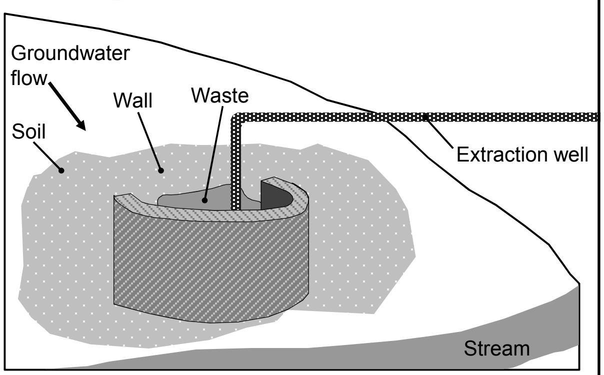
Hanging Wall



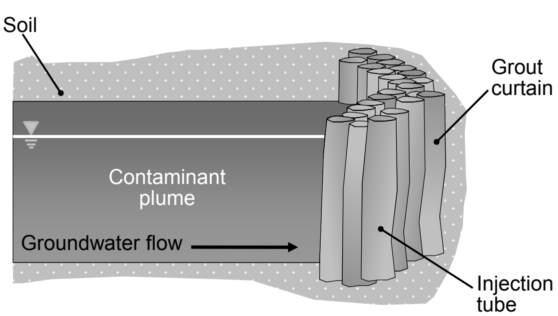
Upgradient Wall



Downgradient Wall



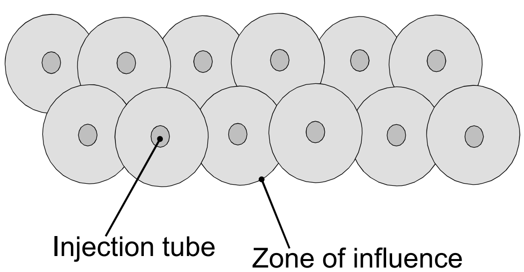
Grout Curtain



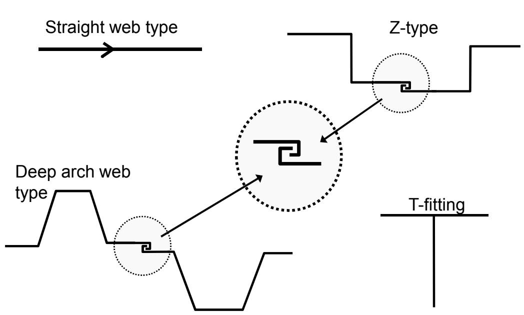
Grout Curtain

Photographs courtesy of Boart Longyear Drilling Services

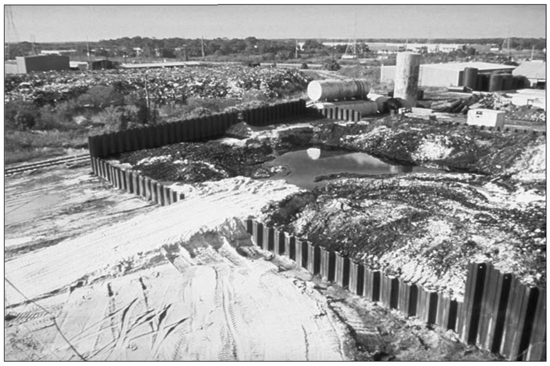
Grout Injection



Steel Piling Shapes and Interlocks



Sheet Piling



HDPE Sheet Piling

HDPE Sheet Piling

BASIC WATER TREATMENT

Student Performance Objectives

Upon completion of this module you will be able to:

1. State the advantages and disadvantages of basic water treatment systems.
2. State the working mechanisms of the following basic water treatment subsystems and/or components.
   - Oil/water separators
   - Iron removal systems
   - Filters
   - Clarifiers
   - Air strippers
   - Scale control systems
   - Carbon adsorption units

BASIC WATER TREATMENT

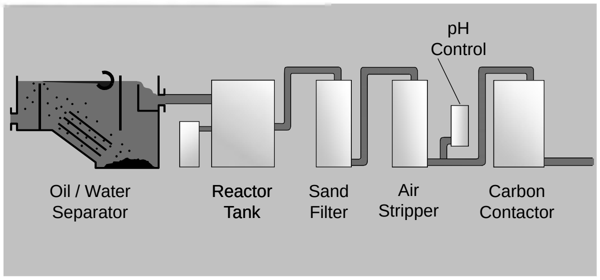
Advantages

- Treats most contaminants
- Highly flexible and reliable

Disadvantages

- Could be very expensive
- Energy- and labor-intensive
- Regulatory problems with discharge
- Fine-grained material a problem

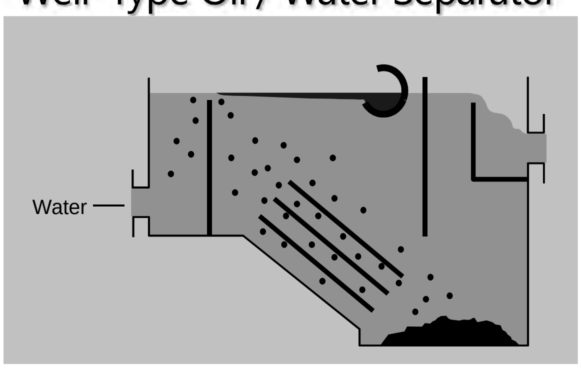
System Diagram



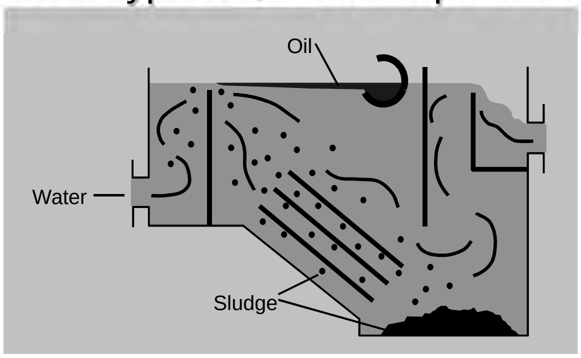
Oil / Water Separator

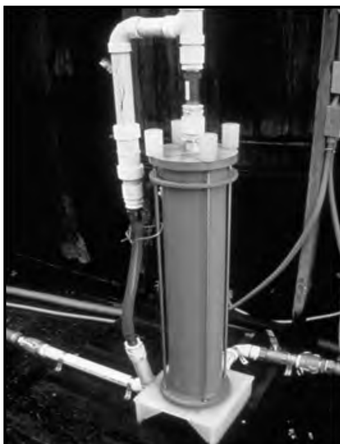
Courtesy State of Washington, Department of Ecology

Weir-Type Oil / Water Separator



Weir-Type Oil / Water Separator





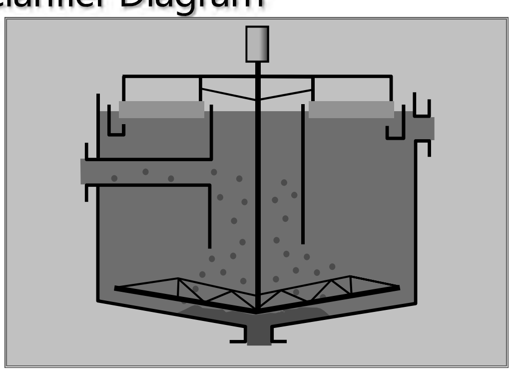
Oil Filter

Reaction Tank

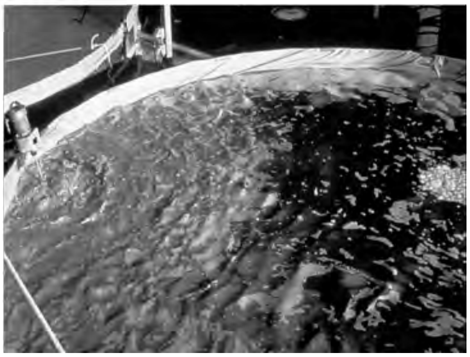
Sodium Hypochlorite Storage Tank

Sand Filter

Clarifier Diagram



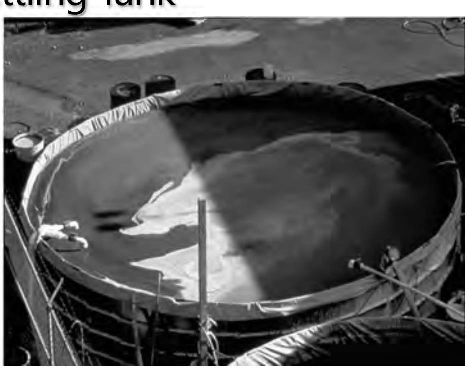
Clarifier



Settling Tanks

Courtesy State of Washington, Department of Ecology

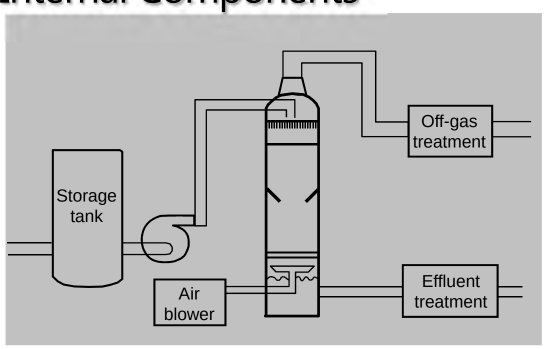
Settling Tank



Air Stripper

- Physically separates volatile or semi-volatile contaminants, usually organics, from water
- Process applies to volatile and semi-volatile organics with a Henry's Law Constant of >0.003 atm/mol/m3

Air Stripper Diagram Internal Components

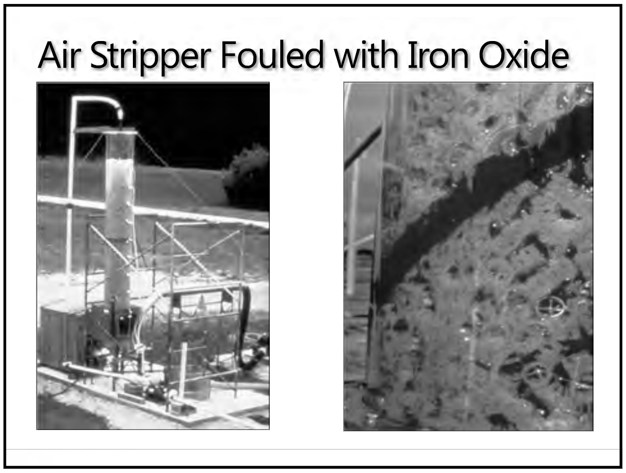


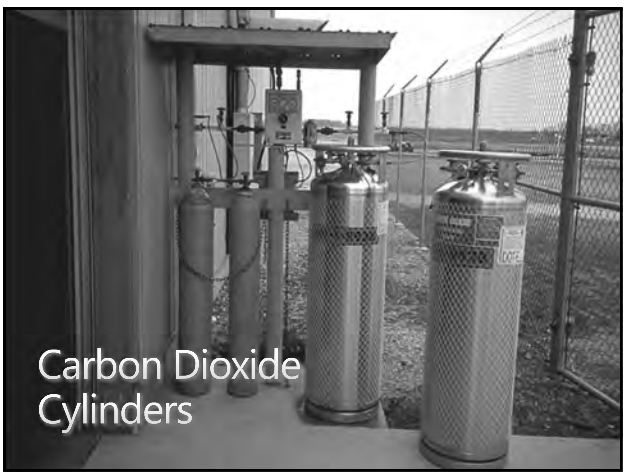
Common Air Stripper Packing Materials

Air Stripper

Air Stripper with Carbon Units

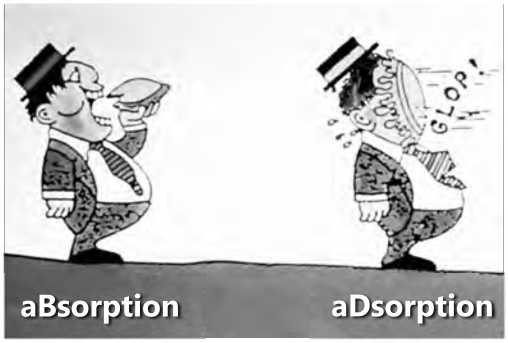
Low Profile Air Stripper


Air Stripper Fouled with Iron Oxide


Carbon Dioxide
Cylinders


Carbon
Adsorpton
Unit

Carbon Adsorption



Carbon Adsorpton Unit

Carbon Units

CHEMICAL REACTIONS AND SEPARATIONS

Student Performance Objectives

Upon completion of this module you will be able to:

1. State the advantages and disadvantages and describe the working mechanisms of the following chemical reaction systems:
   - Neutralization systems
   - Precipitation systems
   - Reduction and oxidation systems
2. State the advantages and disadvantages and describe the working mechanisms of the following separation systems:
   - Microfiltration systems
   - Reverse osmosis systems
   - Ion exchange systems

CHEMICAL REACTIONS AND SEPARATIONS

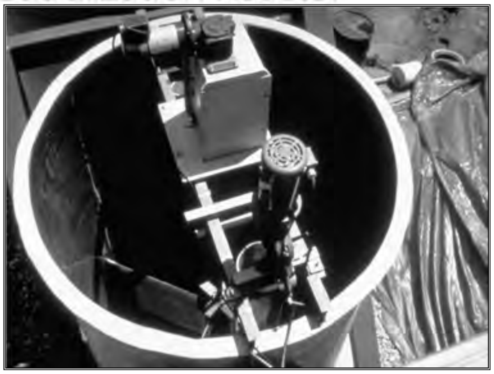
Chemical Reaction Systems

- Neutralization
- Precipitation
- Reduction
- Oxidation

Neutralization

- Advantage
  - Eliminates corrosives
- Disadvantages
  - Process chemicals are hazardous
  - Generates a lot of heat
  - Heavy-duty process equipment may be needed

Neutralization Reactor

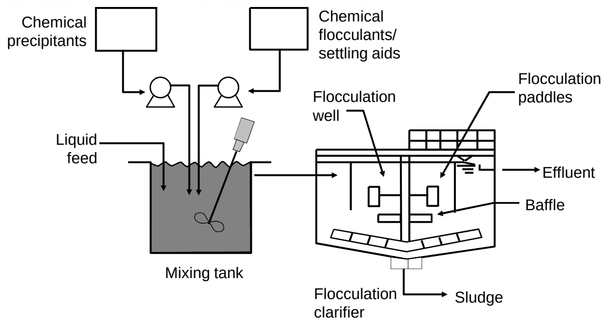


Neutralization Reactor

Precipitation

- Advantages
  - Removes dissolved heavy metals
- Disadvantages
  - Produces metal sludge
  - Often produces high pH wastewater
  - Doesn't always work on highly soluble metals

Sample Precipitation System



Source: U.S. EPA 1991

Simple Precipitation System

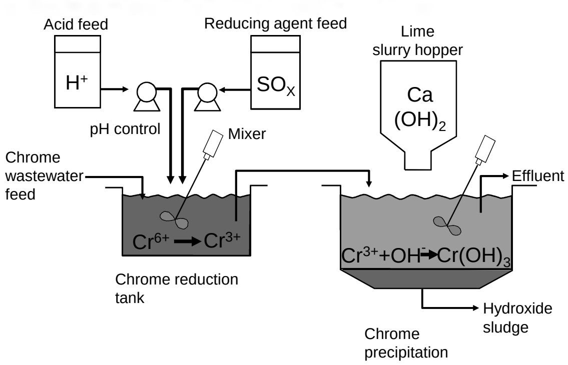
Simple Precipitation System

Simple Precipitation System

Reduction /Oxidation

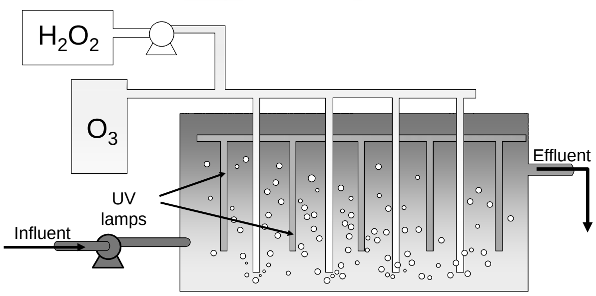
- Chemical reactions
- Advantages
  - Reduces solubility of heavy metals
  - Oxidizes and destroys organics
- Disadvantages
  - Unintended reactions

Cr (VI) Reduction System



ULTRAVIOLET OXIDATION SYSTEM

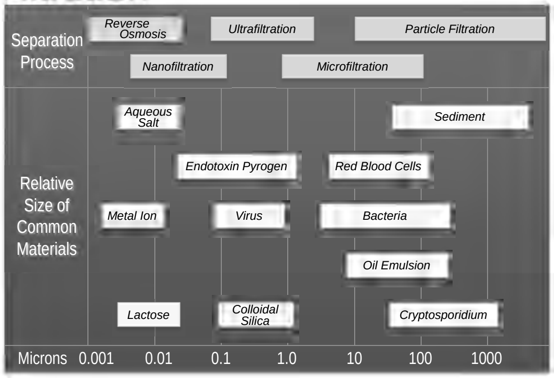
UV Oxidation System



Separation

- Microfiltration
- Reverse osmosis
- Ion exchange

Filtration



Particle Filtration

Dredge, Fox River, WI

Filter Press, Fox River, WI

Microfiltration

Microfiltration is a process which removes contaminants from a fluid by passing though a microporous membrane.

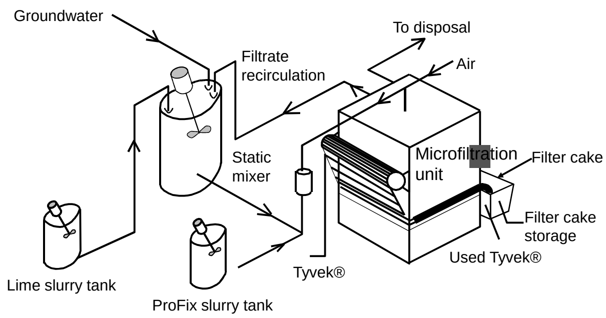
Typical microfiltrations membrane pore size range is 1 to 10 micrometers.

Microfiltration

- Advantage
  - Removes very small particles
- Disadvantages
  - Does not remove dissolved contaminants

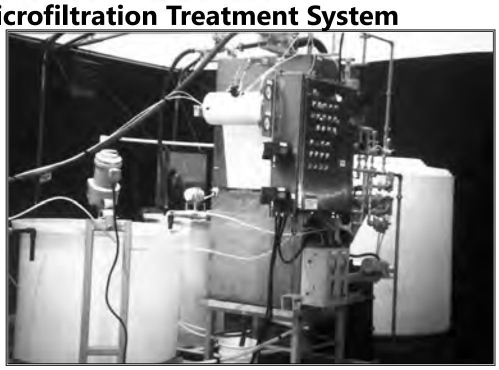
Superfund Site, Palmerton, PA

Du Pont / Oberlin
Microfiltration Treatment System



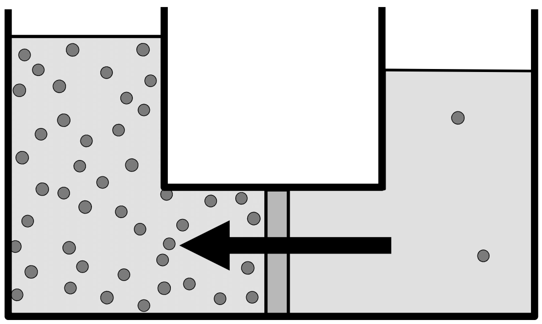
Source: U.S. EPA 1991

Du Pont / Oberlin
Microfiltration Treatment System

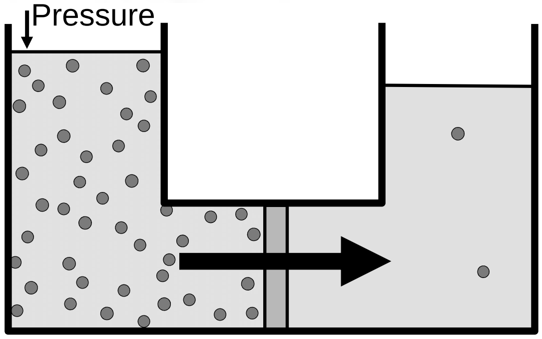


Du Pont / Oberlin
Microfiltration Treatment System

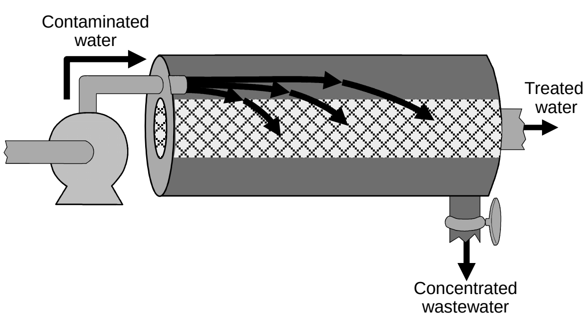
Osmosis



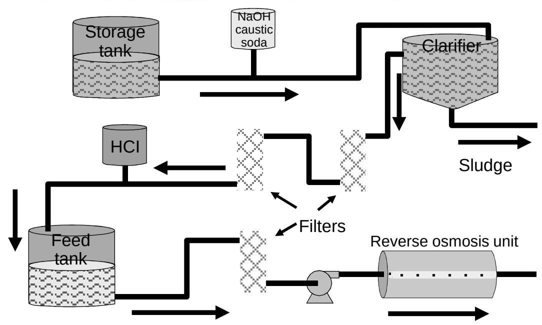
Reverse Osmosis



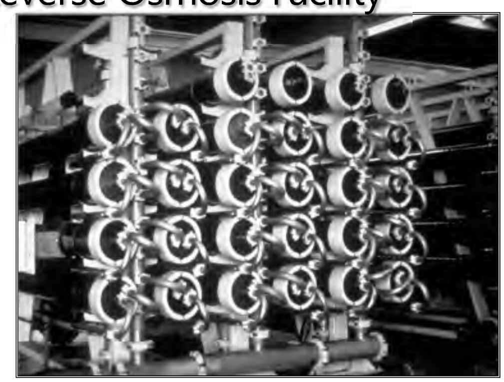
Reverse Osmosis Unit



Reverse Osmosis System



Reverse Osmosis Facility



Cut away of reverse osmosis unit

Ion Exchange

- Removes dissolved metals via transfer of ions
- Uses resin beads

Ion Exchange

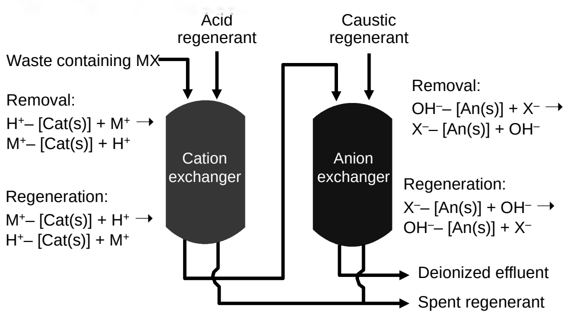
Ion Exchange Advantages

- Removes low concentrations of soluble metal
- Recovers concentrated metal streams for recycling

Ion Exchange Disadvantages

- Suspended solids and organics
- Regeneration chemicals are hazardous

Ion Exchanger



SEDIMENT REMEDIATION

Student Performance Objectives

1. Define Sediments
2. List common sediment remedy options
3. List the advantages and disadvantages for the three common sediment remedy options

Sediment Remediation

EPA

Tetra Tech

Objectives

- Define Sediments
- List common sediment remedy options
- List the advantages and disadvantages for the three common sediment remedy options

Source: USEPA 1999

Sediments

- Sediments - The organic and inorganic materials found at the bottom of a water body. Clay, silt, sand, gravel, decaying organic matter, shells & debris.
- The most common sediment contaminants:
  - Pesticides
  - PCBs
  - PAHs
  - Dissolved phase chlorinated hydrocarbons (to a lesser extent)

Source: USEPA 1999

Sediment Contamination Sources

- Pipeline or outfall discharges
- Chemical spills
- Surface runoff: waste dumps, chemical storage, mines, agricultural or urban areas
- Air emissions: Power plants, incinerators, pesticide applications
- Upwelling of contaminated ground water
- Ships, ship maintenance & in-water structures

Source: USEPA 1999

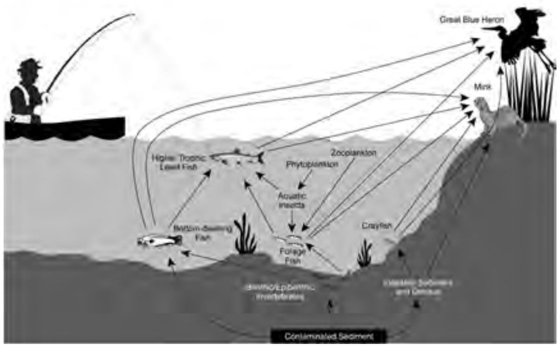
Common Community Concerns

- Health impacts from eating fish/shellfish and recreation
- Ecological impacts on wildlife and aquatic species
- Loss of recreational & subsistence fishing
- Loss of recreational swimming and boating
- Loss of traditional cultural practices by Indian tribes, etc.

Community Economic Concerns

- Economic effects of loss of fisheries
- Economic effects on development and property values
- Economic effects on tourism
- Increased costs of drinking water treatment
- Loss or increased cost of commercial navigation

Human and Ecological Threats



Source: Adapted from EPA Region 5, Sheboygan Harbor and River Site

Sediment Sampling: Chemical

- Sediment grab samplers: Surface sediment chemistry
- Coring devices
- Water column probes: pH and DO
- Surface water samplers: Dissolved and particulate chemical concentrations
- Semi-permeable membrane devices: Dissolved contaminants at the sediment-water interface

Sediment Sampling: Biological

- Benthic analysis: Population and diversity
- Toxicity testing: Acute and long-term lethal effects on organisms
- Tissue sampling: Bioaccumulation, modeling trophic transfer potential, and estimating food web effects
- Caged fish/invertebrate studies: Change in uptake of contaminants by biota

Most Common Sediment Treatment Technologies

- Monitored natural recovery
- In situ capping
- Dredging & Excavation (most common)

Monitored Natural Recovery
Natural Recovery Processes

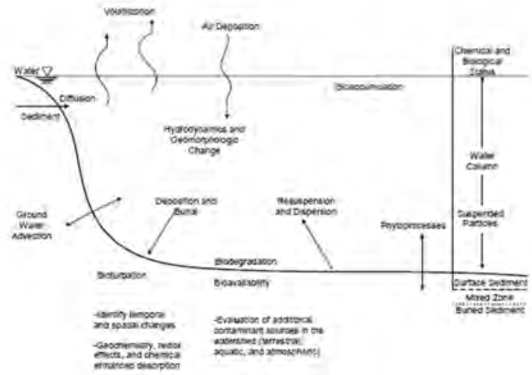
Allows natural processes to contain, destroy, or otherwise reduce the bioavailability or toxicity of the contaminant in the sediment.

This remedy should include site specific cleanup levels, remedial action objectives, and monitoring to assess whether risk is being reduced as planned.

Monitored Natural Recovery
Natural Recovery Processes

- Physical processes
  - Sedimentation, advection, diffusion, dilution, dispersion, bioturbation, volatilization
- Biological processes
  - Biodegradation, biotransformation, phytoremediation, biological stabilization
- Chemical processes
  - Oxidation/reduction, sorption, or other processes resulting in stabilization or reduced bioavailability

Natural Processes



Conditions Conducive to MNR

- Human exposure is low (most important)
- Sediment bed is stable, cohesive, well-armored
- Contaminant concentrations decreasing on their own
- Contaminants are readily biodegradable or transform to lower toxicity forms
- Concentrations are low and cover diffuse area
- Contaminants have low ability to bioaccumulate

Evidence of MNR

- Long-term decreasing trend of contaminant concentrations in:
  - Higher trophic level biota (piscivorous fish)
  - Water column (during low flow)
  - Sediment core contaminant levels
  - Surface sediment

MNR Advantages/Limitations

- Advantages
  - Relatively low implementation costs
  - Non-invasive
- Limitations
  - Leaves contaminants in place
  - Slower to reduce risks than active technologies
  - Often relies on institutional controls such as fish consumption advisories

Most Common Sediment Treatment Technologies

- Monitored natural recovery
- In situ capping
- Dredging & Excavation

In-Situ Cap

In-situ capping is the placement of a subaqueous covering or cap of clean material over contaminated sediment.

In-situ capping is the placement of a subaqueous covering or cap of clean material over contaminated sediment.

In-Situ Cap Primary Functions

Caps reduce risks by:

- Physical isolation:
  - Reduce exposure & bioturbation
- Stabilization:
  - Contaminant & erosion protection to reduce re-suspension
- Chemical isolation:
  - Prevent dissolved and bound contaminants from transporting into water column

Consideration for Selecting Cap Thickness

- Physical:
  - Population density of organisms
  - Sand cap consolidation through compression
- Stabilization:
  - Potential erosion from bed shear stresses due to river, tidal, and wave-induced currents, turbulence generated by ships/vessels, etc.

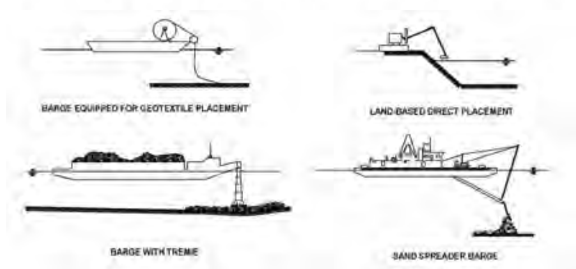
Consideration for Selecting Cap Thickness

- Chemical
  - Gas generation due to anaerobic degradation from organic content, can generate uplift forces on the cap (especially w/ less permeable cap material)

Capping Materials

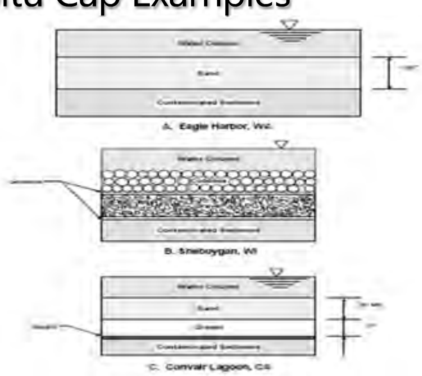
- Upland sand-rich soils (preferred)
- Engineered clay
- Reactive/adsorptive materials: activated carbon, apatite, coke, organoclay, zero-valent iron and zeolite
- Geotextiles: reduce mixing and displacement of cap material
- Impervious materials: geomembranes, clay, concrete, steel, or plastic

In-Situ Capping & Placement Techniques



Source: USEPA 1998d

In-Situ Cap Examples



Source: Modified from U.S. EPA 1998d

In-Situ Capping Advantages/Limitations

- Advantages
  - Quickly reduce exposure
  - Less infrastructure for material handling, dewatering, treatment & disposal
  - Less expensive than dredging or excavation
  - Quick to implement
- Limitations
  - Risk of re-exposure if cap is disturbed
  - Cap materials may not promote native habitat

Most Common Sediment Treatment Technologies

- Monitored natural recovery
- In situ capping
- Dredging & Excavation

Dredging and Excavation

- Dredging: Removal of contaminated sediment while it is submerged
- Excavation: Removal of contaminated sediment after dewatering
- Most often used treatment method at Superfund sites
- Both include transport, treatment and disposal of impacted sediment and water

Site Conditions Conducive to Dredging/Ex

- Suitable disposal site is nearby
- Suitable area for staging and handling
- Navigational dredging is planned
- Water depth is adequate
- Risk reduction outweighs disturbance
- Contaminated sediment overlies clean sediment
- Contaminants cover discrete areas

Dredging Technologies

- Mechanical Dredging
  - Clamshell: Wire supported
  - Enclosed bucket: Wire supported, watertight
  - Articulated mechanical: Backhoe designs
- Hydraulic Dredging
  - Cutterhead: pipeline dredge w/ cutterhead
  - Horizontal auger: pipeline dredge with auger
  - Plain suction: pipeline dredge w/ suction
  - Pneumatic: Air operated submersible pump

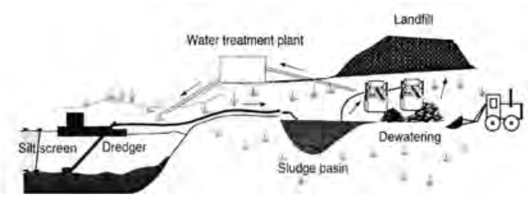
Mechanical Dredge Examples

Source: A = Cable Arm, Corp. B = Barbara Bergen, USEPA)

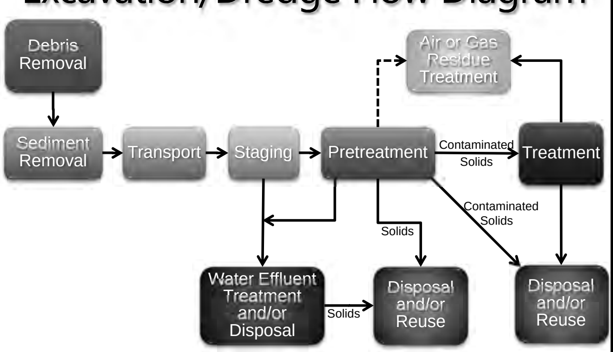
Hydraulic Dredge Examples

Source: A = Jim Hahnenberg USEPA: B = Ernie Watkins USEPA: C = Ellicott Corporation

Dredge Dewatering Example



Excavation/Dredge Flow Diagram



Excavation Dewatering Technologies

- Sheet piling & Cofferdams
- Earthen dams
- Geotubes, inflatable dams
- Rerouting the water body using temporary dams or pipes
- Permanent relocation of the water body

Excavation

Example of excavation following isolation using sheet piling

Source: Pine River/Velsicol, EPA Region 5

Advantages/Limitations of Dredging/Excavation

- Advantages
  - Contaminant removal poses less risk uncertainty
  - Less limitation for water body uses
- Limitations
  - Complex and costly
  - Uncertainty of residual contamination
  - Contaminant losses through re-suspension and volatilization
  - Temporary destruction of aquatic community

Fox River Superfund Site, Case Study

Fox River, WI

Fox River Superfund Site

5 Operable Units (OU) due to large area of PCB contamination

Fox River Superfund Site

- PCB in Sediment includes 39 miles of river and 2700 square miles of Green Bay
- PCBs from a large number of papermills along the river producing and recycling carbonless copy paper (9 PRPs)
- PCBs released directly into the river or after municipal treatment plant
- Fish consumption advisories have been in effect since 1976

Fox River Selected Remedies

- Dredging and off-site disposal
- 7-inch thick engineered cap of sand and armor stone
- 3 to 6-inch sand cover where PCBs <2 ppm
- Long term monitoring for cap integrity and natural attenuation

Fox River Superfund Site

Future Remedies by Year

Year	Dredging		Capping		Sand Covering*	
	Volume (cubic yards)	Operable Units	Acres	Operable Units	Acres	Operable Units
2009	460,000	2, 3, and 4	0	—	0	—
2010	660,000	3 and 4	37	2 and 3	84	2, 3 and 4
2011	510,000	4	32	2 and 3	98	2, 3 and 4
2012	650,000	4	43	2, 3 and 4	67	4
2013	660,000	4	52	4	74	4
2014	610,000	4	66	4	47	4
2015	440,000	4 and 5	63	4	31	4
2016	0	—	28	4	3	4
2017	0	—	94	4 and 5	55	4 and 5
Total	4,000,000	2, 3, 4, and 5	415	2, 3, 4 and 5	459	2, 3, 4 and 5

Fox River Superfund Site

Fox River Map
Pink = Dredging Areas

Dredged approximately 4 million cubic yards of sediment.

Fox River Superfund Site

Fox River Map
Blue = Capping Areas

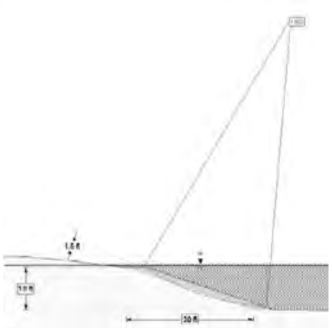
Capped 415 acres

Fox River Superfund Site

Fox River Map
Yellow/Brown = Sand Cover Areas

Approximately 495 acres sand capped

Fox River Capping



Capping Slope Diagram

- 7-inch thick sand and armor stone
- 3-6 inch sand cover where PCBs < 2 ppm

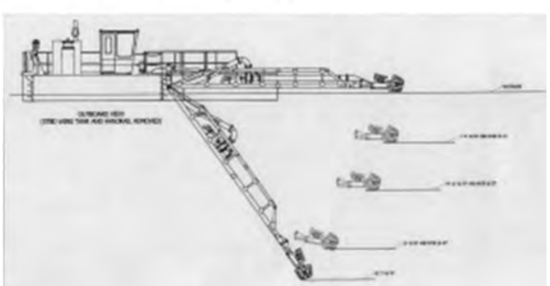
Fox River Dredging

Cutterhead Dredge
& Piping

Piping Suction Pump
& Diesel Engine

Fox River Dredge

Fox River Dredging



Extended Ladder Cutterhead Dredge & Barge

Fox River Dewatering

- Pipe flow to vibrating Screen of gravel and debris > 1/8 inch
- Further hydrocyclone for fine grain sand removal
- Thickening tanks using polymer addition for uniform flow & weir for water removal
- Membrane sediment cake press
- Conveyor to Transport off-site

Fox River Dewatering

Treated Sediment is Transported to landfill or TSCA landfill

Geotube Dewatering

Fox River Effluent Water Treatment

- Sand Filtration: fine vs. course sand
- Bag Filtration
- GAC Filtration
- Diffuser to discharge treated water back to Fox River at ambient flow conditions to avoid disruption

BIOREMEDIATION

Student Performance Objectives

Upon completion of this module you will be able to:

1. Discuss site considerations needed for the use of bioremediation methods.
2. Discuss intrinsic and engineered bioremediation treatment methods
3. Discuss in-situ and ex-situ bioremediation treatment systems.

PRINCIPLES OF BIOREMEDIATION

EPA

TETRA TECH

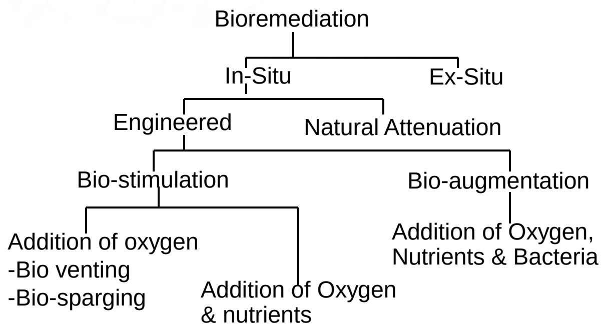
Student Objectives

- Define bioremediation
- Describe a basic oxidation-reduction reaction
- List the different microbial metabolic processes
- List the basic ways that microbes demobilize contaminants
- List three indicators of microbial activity
- List factors that may complicate bioremediation

Bioremediation

The treatment or remediation of contaminated soils, sediments, and groundwater through microbial metabolism.

Bioremediation



Microbial Metabolism

- Microbial metabolism is the basis of bioremediation
- It is the transformation of organic and inorganic compounds by microscopic organisms

Metabolism

- The biochemical transformation that occur in living organisms
- How cells derive energy and basic elements for reproduction
- Energy and essential elements are derived through oxidation-reduction processes

Oxidation-Reduction

The breaking of chemical bonds and transferring electrons from electron donors to electron acceptors.

Microbial Oxidation-Reduction

The organic contaminant often serves as the electron donor, yielding electrons (being oxidized) to microbial compounds (being reduced) to stimulate cell growth and reproduction.

Modes of Metabolism

The three modes of metabolism are:

- Respiration
- Fermentation
- Photosynthesis

Respiration

- Respiration process is either aerobic or anaerobic
- Aerobic respiration uses oxygen as an electron acceptor
- Anaerobic respiration uses a chemical other than oxygen as an electron acceptor such as nitrate, iron, sulfate, and carbon dioxide

Fermentation

An organic compound is used as both electron donor and electron acceptor, converting the compound to fermentation products such as alcohols, organic acids, hydrogen, and carbon dioxide.

Photosynthesis

The metabolic process where plants convert radiant energy into chemical energy, most often stored initially in glucose.

BIOREMEDIATION

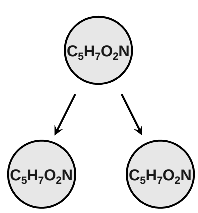
Bioremediation

- The key microorganism involved in bioremediation of organic and inorganic compounds is bacteria.
- Other microorganisms that may be involved in bioremediation are protozoans, fungi, and algae.

Bacterial Life

Bacteria

- Single-celled organisms
- Metabolize soluble food
- Reproduce by binary fission
- Cellular composition:
  - 70 – 90% water
  - 10 – 30% dry mass
    - 92% of dry mass composed of carbon, oxygen, nitrogen, and hydrogen



Bacteria Requirements

Favorable physical and chemical conditions are necessary for optimum bacteria metabolism.

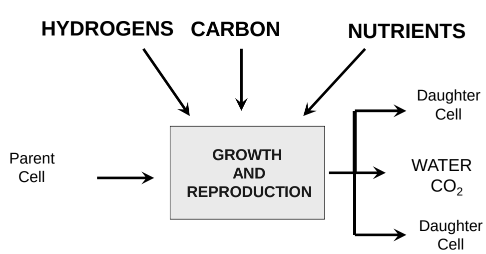
Bacteria Physical Requirements

Physical conditions include:

- pH
- Temperature
- Physical structure for support

Bacteria Chemical Requirements

Chemical requirements include:



Bacteria Chemical Requirements

- Energy Source
  - Chemical compounds (organic or inorganic)
  - Sunlight and Substrates
- Carbon Source
  - Organic Compounds
  - CO2
- Nutrients
  - Nitrogen
  - Phosphorus
  - Trace Nutrients (sulfur, potassium, and iron)

Nutritional Requirements

- Organic and inorganic carbon
  - Organic compounds and CO_2
- Ammonia (NH_3), nitrate (NO_3^-), or nitrogen gas (N_2)
- Various sources of phosphates (PO_4^{3-})
- Trace nutrients
  - Amino acids, sulfate, potassium, magnesium, and iron

Bioremedial Processes

- Aerobic respiration
- Anaerobic respiration
- Fermentation
- Secondary utilization and co-metabolism
- Reductive dehalogenation
- Inorganic compounds as electron donors

Aerobic Microbial Metabolism

$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

Donor Acceptor

Aerobic Microbial Metabolism

ENZYME

$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

Enzymes

- Biological catalysts
- Are not altered by the reaction
- Reaction specific

Bioremedial Processes

Anaerobic Respiration

- Inorganic chemicals are used as electron acceptors
  - Nitrate (NO3-), sulfate (SO42-)
  - Metals (Fe3+, Mn4+)
  - C02

Byproducts = nitrogen gas, hydrogen sulfide, reduced forms of metals, and methane

Anaerobic Microbial Metabolism

C_7H_8 + Nitrate (NO^{3-}) → CO_2 + N2

⇩

Benzylsuccinic acid

↘

Benzoyl Coenzyme-A

↘

Fermentation

- Can play an important role in an anaerobic environment
- Organic contaminant serves as both electron donor and acceptor
- Byproducts can be biodegraded by other species of microbes

Co-metabolism

- Non-beneficial biotransformation
- The microorganism transforms the contaminant but does not benefit from the reaction

Reductive Dehalogenation

- Replacement of a halogen atom with an hydrogen atom.
- Electron donors include hydrogen and low-molecular weight compounds.

Inorganic Compounds as Electron Donors

- Ammonium (NH4+), nitrite (NO2-), reduced iron (Fe2+), reduced manganese (Mn2+), and H2S
- Oxygen is usually the electron acceptor
- Carbon is most commonly taken from atmospheric CO2 (Carbon Fixation)

Indicators of Microbial Activity

- Water chemistry changes
  - Decrease in parent compound, electron acceptor
  - Increase in byproducts
  - Presence of specific metabolic products

$$C_7H_8 + 9O_2 \longrightarrow 7CO_2 + 4H_2O$$

Indicators of Microbial Activity

- Changes in native microbial communities
- Growth of predators

Complicating Factors of Bioremediation

- Unavailability of the contaminant to the microbes
- Toxicity of contaminant to microbes
- Multiple contaminants and natural organic chemicals

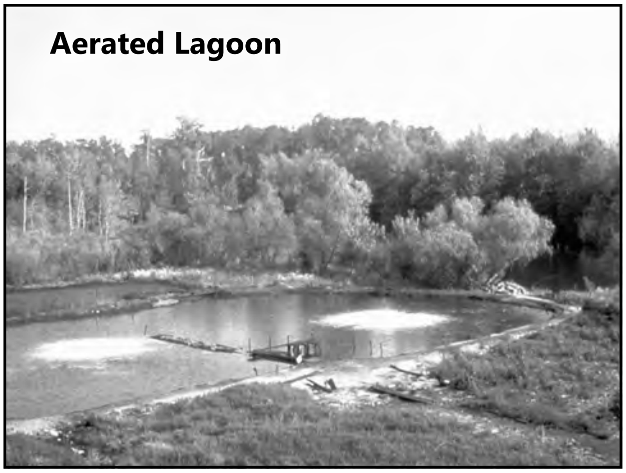
Complicating Factors of Bioremediation

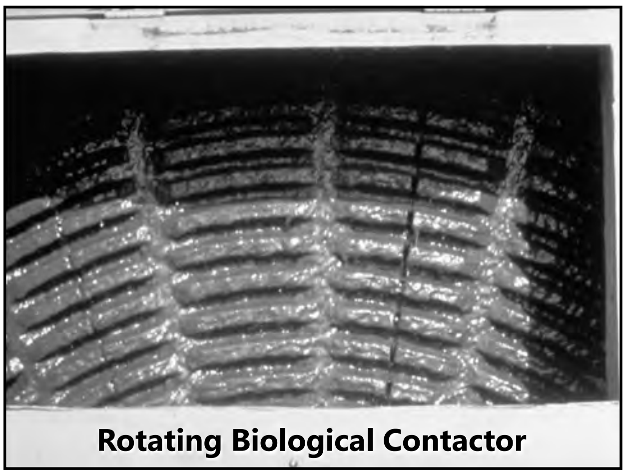
- Incomplete degradation of contaminants
- Inability to remove contaminants to low concentrations
- Aquifer clogging

BIOREMEDIATION SYSTEMS

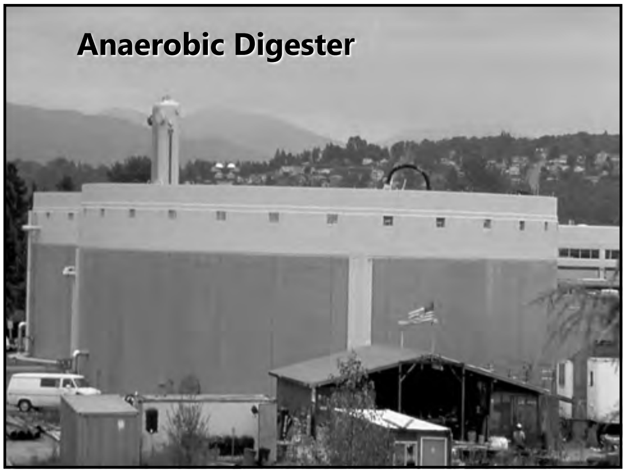
Bioremedation Systems

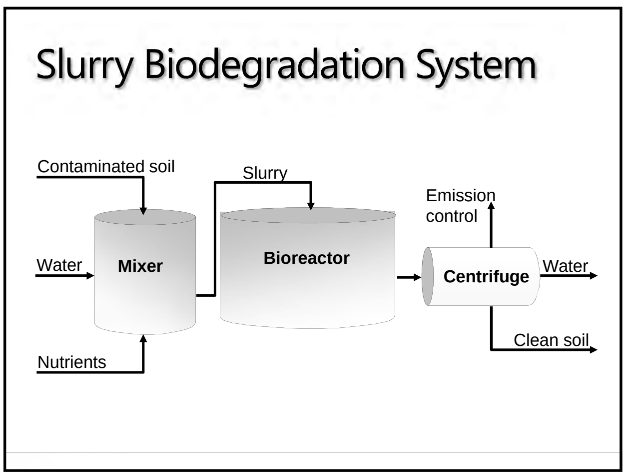
- Aqueous ex-situ treatment systems
  - Trickling filters
  - Aerated lagoon
  - Rotating Biological Contactor
  - Anaerobic digester
- Solid ex-situ treatment system
- In-situ treatment systems

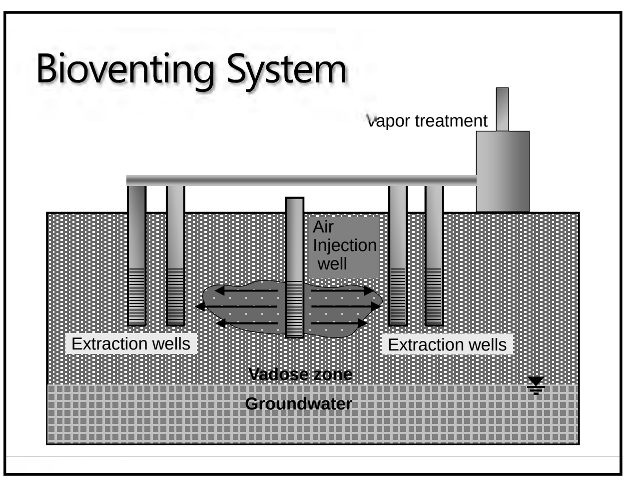

Aerated Lagoon


Rotating Biological Contactor

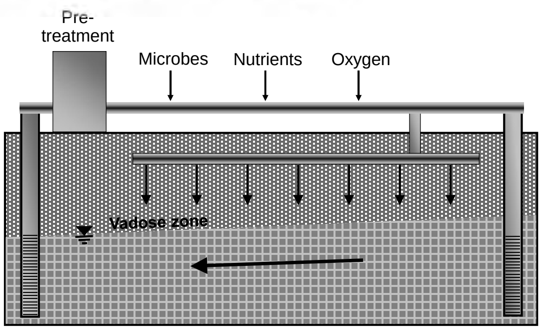

Rotating Biological Contactor


Anaerobic Digester


Slurry Biodegradation System
Contaminated soil
Slurry
Emission control
Water
Mixer
Bioreactor
Centrifuge
Water
Clean soil
Nutrients


Bioventing System
Vapor treatment
Air Injection well
Extraction wells
Extraction wells
Vadose zone
Groundwater

Traditional Insitu System



MONITORED NATURAL ATTENUATION

Student Performance Objectives

Upon completion of this unit, students will be able to:

1. Define monitored natural attenuation
2. Understand monitored natural attenuation processes
3. Review case studies that show monitored natural attenuation processes
4. Understand two screening criteria for monitored natural attenuation applicability

MONITORED NATURAL ATTENUATION

Objectives

- Define monitored natural attenuation
- Understand monitored natural attenuation processes
- Review case studies that show monitored natural attenuation processes
- Understand two screening criteria for monitored natural attenuation applicability

Monitored Natural Attenuation

Monitored natural attenuation (MNA) is the reliance on natural attenuation processes to achieve a site-specific remediation objective within a time frame that is reasonable compared to other more active methods (EPA,1999).

Monitored Natural Attenuation

MNA is often used in conjunction with or as a follow-up process to another active remedial activity.

Monitored Natural Attenuation
Advantages

- An in-situ treatment
- May be a lower cost alternative
- May be effective as a final process to treat residual contaminants

Monitored Natural Attenuation
Disadvantages

- May not be accepted by the regulatory agency or public
- May not treat contaminant within a reasonable time
- May not treat desired contaminants
- Requires detailed site characterization and continued monitoring

Monitored Natural Attenuation

- The MNA natural processes are biological, chemical, and physical reactions.
- Under favorable conditions, these processes either transform contamination to less harmful forms or immobilize contaminants to reduce risks.

Natural Attenuation Processes

Examples of natural processes include:

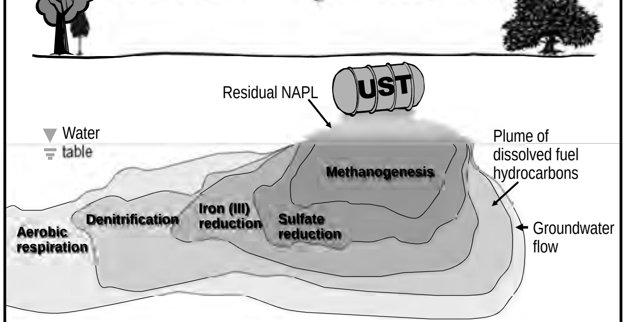
- Biodegradation by subsurface microbes
- Naturally occurring chemical reactions
- Physical sorption to subsurface media
- Natural dilution of contaminants*
- Physical volatilization of contaminants from the subsurface to the atmosphere*

* Not acceptable processes

Monitored Natural Attenuation
Concerns

- MNA is site and contaminant specific.
- The success of MNA depends on many natural environmental conditions which will change as MNA proceeds.

Petroleum Hydrocarbons



For example, biodegradation will continue as long as an adequate supply of electron acceptors is available.

Case Studies

The following case studies show examples of successful and common failures of MNA projects.

Case Studies

South Glen Falls, NY	Natural attenuation of PAHs following source removal
St. Joseph, Michigan	Natural attenuation of a chlorinate solvent
Edwards Air Force Base	No natural attenuation of a chlorinate solvent
Vandenberg Air Force Base	BTEX and MTBE release
Hudson River Sediment	Incomplete natural attenuation of PCBs
Pinal Creek, Arizona	Natural attenuation of inorganic compounds

South Glen Falls, NY

- This case study shows the value of source removal.
- In the 1960s, coal tar generated from an old manufactured gas plant was excavated and reburied in a sand sediment.
- During the 30 years the coal tar was left in place, an 200-foot by 1000-foot contaminated plume developed.

South Glen Falls, NY

- The contaminated plume consisted of PAHs including naphthalene from 0.01 ppm to >2 ppm.
- In 1991, the coal tar-contaminated soil was re-excavated, properly disposed, backfilled with clean native soil.
- Within 4 years of source removal, much of the plume was below detectable levels.

South Glen Falls, NY

Evidence that biodegradation was the primary attenuation process that removed much of the contamination are:

- Depletion of oxygen at the center of the plume where the concentrations were the highest
- Rapid growth of the microbial population that consumed the contamination

South Glen Falls, NY

Additional data that suggests natural biodegradation reduced the contamination once the source was removed:

- Increase of the protozoan population (predator of bacteria) inside the plume
- Detection of a unique transient intermediary metabolite showing biodegradation of the contaminants

St. Joseph, Michigan Superfund Site

- TCE released from a former factory contaminated the groundwater with concentrations as high as 100 ppm.
- A nearby disposal lagoon also leached a large amount of organic matter into the groundwater.

St. Joseph, Michigan Superfund Site

- Microbial activity had completely converted the organic matter into methane, creating a reduced environment that dechlorinated the TCE.
- TCE biodegradation occurred because of the high chemical oxygen demand (COD) placed on the aquifer, as a result of the organic matter that leached from the nearby disposal lagoon.

St. Joseph, Michigan Superfund Site

- Evidence of biotransformation is supported by concentrations of cis-DCE, vinyl chloride, and ethene, daughter products of TCE reductive dechlorination.
- Samples collected near the source show that 8–25% of the TCE had been converted to ethene.

St. Joseph, Michigan Superfund Site

- A site survey shows that the conversion of the TCE to ethene was most complete where methane production and loss of nitrate and sulfate by reduction were the highest.
- Although extensive dechlorination took place, complete breakdown of TCE and its daughter products did not occur.

St. Joseph, Michigan Superfund Site

Indicators of TCE reductive dechlorination are:

- Formation of cis-DCE, VC, and ethene
- Loss of COD in excess of what was needed for dechlorination
- Evidence of anaerobic processes

Edwards Air Force Base, CA

- Between 1958 and 1967, approximately 5,500 gallons of TCE were released creating a large groundwater plume (about 2,800-feet by 2,100 feet).
- Groundwater modeling shows the contaminant had migrated from its source area, however, no degradation of the TCE had occurred.

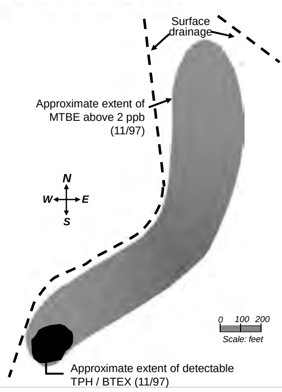
Edwards Air Force Base, CA

- Electron acceptors (nitrate and sulfate) are present in the plume, but there is no dissolved oxygen content or organic material present.
- The probable reason that there is no biotransformation of the TCE is that no primary substrate (organic material) is present to create a reducing condition.

Vandenberg Air Force Base

Vandenberg Air Force Base:

- 572 gallon release of gasoline containing MTBE
- Estimated groundwater velocity is 400 ft/year
- BTEX plume stops within 50–100 feet from source
- MTBE plume is 250 feet wide and extends 1,700 feet from source



Vandenberg Air Force Base

- Natural biodegradation appears to have affected the BTEX, but it had little or no affect on the MTBE.
- In general, simpler and naturally-occurring organic compounds, such as BTEX, are degradable. MTBE is notably resistant to biodegradation because of its stable molecular structure and its reactivity with microbial membranes.

Hudson River Sediment

- A PCB release contaminated a 200 mile stretch of the Hudson River sediment from Hudson Falls to Manhattan. Studies show an incomplete natural attenuation of PCBs in the sediment.
- Studies show aerobic microorganisms present in the sediment. Active aeration pilot studies show co-metabolism created a reduced environment allowing the reductive dechlorination of the PCB.

Hudson River Sediment

- Potential for PCB biodegradation exists in the Hudson River sediment, two requirements must be fulfilled for natural attenuation:
  - A mixing of deep and shallow sediments must occur to link aerobic and anaerobic process. This can occur naturally, but there is no guarantee it will occur often enough to achieve biodegradation.
  - Biodegradation must occur before the PCBs enter the food chain, e.g., the bioaccumulation of PCB in fish tissue.

Hudson River Sediment

- A 1997 study showed significant dechlorination of PCBs, but, even after decades, complete dechlorination has not occurred.
- The rate of dechlorination is insufficient to ensure that monitored natural attenuation will meet regulatory standards.

Pinal Creek, AZ

- Acid drainage from copper mining in Pinal Creek, Arizona area caused a 25-km plume of metal contamination from several unlined mine tailings ponds. It is suspected the pH of the ponds were 2 to 3.
- The acid part of the plume extended 12 km with several metals having concentrations above MCLs.
- Many physical, chemical, and biological processes have affected the metal contaminants.

Pinal Creek, AZ

- Physical dilution likely accounted for a 60% contaminant concentration decrease for the first 2 km of the plume.
- Chemical reaction of the acid plume with natural carbonate material raised the pH to 5-6. This pH raise caused precipitation or sorption of the iron, copper, zinc, and other metals.
- The neutralization reactions depleted the carbonate allowing some metals to continue to migrate to a discharge point in Pinal Creek. The increase in pH and oxygen caused manganese oxides to precipitate.

Pinal Creek, AZ

- The precipitation of the manganese oxides were enhanced by manganese-oxidizing bacteria which resulted in about 20% decrease of the dissolved manganese.
- Concentrations of other dissolved metals decrease because of sorption onto the manganese oxides.
- The natural process reduced the dissolved metals in groundwater. But as the carbonate material become depleted, the source may overwhelm the natural attenuation capacity of the aquifer.

MNA Applicability

MNA Applicability

The success of a project is based on:

- The level of understanding of the dominant attenuation processes
- The probability that site-specific conditions will result in an effective natural attenuation

MNA Applicability

A number of factors must be considered to determine if MNA will be effective:

- Initial Screening of MNA Applicability
- Detailed Evaluation of MNA Effectiveness

Initial Screening of MNA Applicability

Initial Screening of MNA Applicability

- Do regulations allow MNA as a remedial method?
- Has the source been removed to the maximum extent practical?
- Is the plume shrinking such that remediation will be achieved within a reasonable time?
- Are there any receptors that could be affected within a 2-year period?

Initial Screening of MNA Applicability

If the answer is "no" to any of the first three questions or "yes" to the fourth question:

- MNA is not a remedial option at the site

If the answer is "yes" to the first 3 questions and "no" to the fourth question:

- MNA has the potential to be effective at the site, but a detailed evaluation should be conducted

Detailed Evaluation of MNA Effectiveness

Detailed Evaluation of MNA Effectiveness

- Has the site been fully characterized in three dimensions?
- If groundwater is the issue, has the hydraulic conductivity of the most permeable transport zone been measured?
- If groundwater is the issue, has the retarded contaminant transport velocity been estimated?
- Have the geochemical parameters been measured for all monitoring points?

Detailed Evaluation of MNA Effectiveness

- Have rate constants or degradation rates been calculated?
- Is the estimated time to achieve remediation objective reasonable?
- Is there no current or future threat to potential receptors?
  - If yes to all above, then MNA may be effective

MNA Summary

Key components of a MNA corrective action plan include:

- Documentation of adequate source control
- Comprehensive site characterization
- Evaluation of time frame for meeting remediation objectives
- Long-term performance monitoring
- A contingency plan

IN SITU TREATMENTS, PART ONE

Student Performance Objectives

Upon completion of this module you will be able to:

1. Recognize the advantages and disadvantages of in-situ treatment.
2. Identify the different in-situ treatment methods for saturated and unsaturated zones.
3. Describe the principles of natural attenuation, soil vapor extraction, enhanced soil vapor extraction, and air sparging treatment methods.
4. Understand the factors of a successful natural attenuation, soil vapor extraction, enhanced soil vapor extraction, and air sparging treatment system.

IN SITU TREATMENTS

Part One

In situ Treatment

In place treatment of contaminants in soil, sediment, or groundwater using physical, chemical, or biological mechanisms.

Advantages

- Eliminates mass removal process
- Reduces potential exposure
- Reduces surface destruction
- May reduce cost

Disadvantages

- Increases treatment time
- May be difficult to monitor results
- May not treat all contamination
- May cause contaminant to spread

In situ Treatment Methods

	Unsaturated				Saturated		
	Physical	Chemical	Biological		Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓		✓	✓	✓
Soil Vapor Extraction (SVE)	✓						
SVE – Enhancements	✓		✓				✓
Air Sparging					✓		✓
Permeable Reactive Barriers					✓	✓	✓
Chemical Oxidation		✓				✓	
Soil Flushing *	✓	✓			✓	✓	
Bioremediation *			✓				✓
Phytoremediation *			✓				✓
Immobilization *	✓	✓	✓		✓	✓	✓

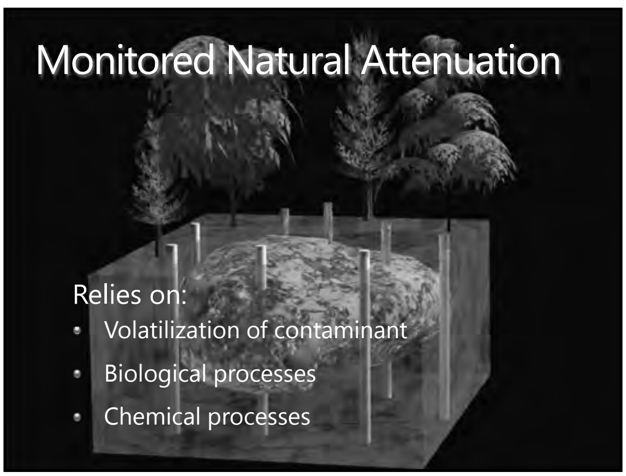
*Covered in other lectures

In situ Treatment Methods

	Unsaturated				Saturated		
	Physical	Chemical	Biological		Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓		✓	✓	✓
Soil Vapor Extraction (SVE)	✓						
SVE – Enhancements	✓		✓				✓
Air Sparging					✓		✓
Permeable Reactive Barriers					✓	✓	✓
Chemical Oxidation		✓				✓	
Soil Flushing *	✓	✓			✓	✓	
Bioremediation *			✓				✓
Phytoremediation *			✓				✓
Immobilization *	✓	✓	✓		✓	✓	✓

*Covered in other lectures


Monitored Natural Attenuation
An *in situ* method that relies on natural processes to remediate contamination.

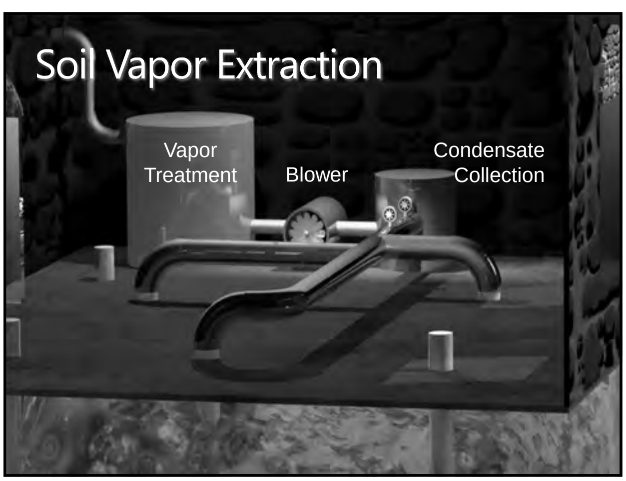

Monitored Natural Attenuation
Relies on:
• Volatilization of contaminant
• Biological processes
• Chemical processes


Monitored Natural Attenuation
Success depends on:
• Type and amount of contaminant
• Size and depth of contaminated area
• Favorable soil and groundwater conditions
• Sufficient time

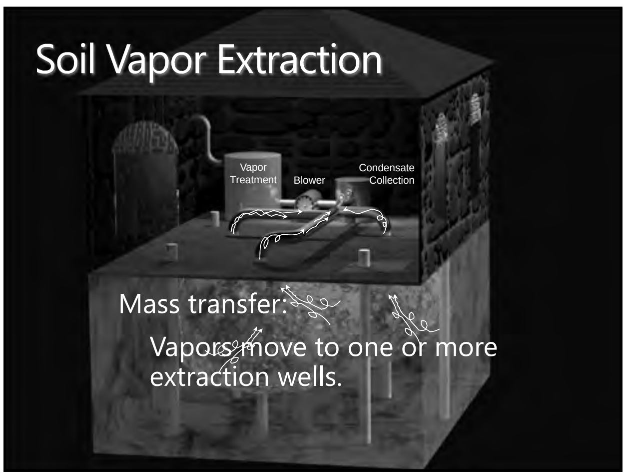
In situ Treatment Methods

	Unsaturated Physical	Unsaturated Chemical	Unsaturated Biological	Saturated Physical	Saturated Chemical	Saturated Biological
Monitored Natural Attenuation	✓	✓	✓	✓	✓	✓
Soil Vapor Extraction (SVE)	✓					
SVE – Enhancements	✓		✓			✓
Air Sparging				✓		✓
Permeable Reactive Barriers				✓	✓	✓
Chemical Oxidation		✓			✓	
Soil Flushing *	✓	✓		✓	✓	
Bioremediation *			✓			✓
Phytoremediation *			✓			✓
Immobilization *	✓	✓	✓	✓	✓	✓

*Covered in other lectures




Soil Vapor Extraction
Vapor Treatment
Blower
Condensate Collection
Flux:
Contaminant vaporizes into the introduced fresh air.


Soil Vapor Extraction
Vapor Treatment
Blower
Condensate Collection
Mass transfer:
Vapors move to one or more extraction wells.


Soil Vapor Extraction
Vapor Treatment
Blower
Condensate Collection
Treatment:
Single- or multi-step process extracts and treats vapors.

Soil Vapor Extraction

Success depends on:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

Soil Vapor Extraction

Remediation manager can only control:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

Soil Vapor Extraction

Remediation manager can only control:

- Contaminant characteristics
- Soil properties
- Site conditions (limited control)
- System design

Soil Vapor Extraction

Success depends on:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

Contaminant Characteristics

The single most important criterion for a successful soil-vapor extraction (SVE) system is the volatility of the contaminant.

Contaminant Characteristics

Volatility of contaminant influenced by :

- Primary factor
  - Henry's Law Constant
- Secondary factors
  - Affinity to medium
  - Contaminant composition

Contaminant Characteristics

Henry's Law Constant (K_H)

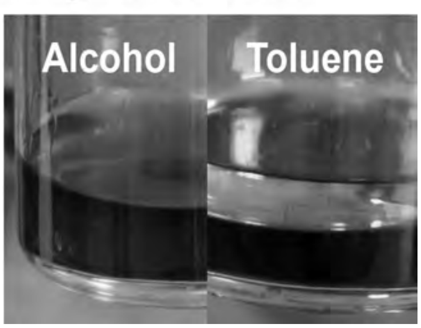
- Relationship between the contaminant's concentration in air and water
- Function of vapor pressure (P_v) and its solubility (C) in water

$$K_H = \frac{P_v}{C}$$

Contaminant Characteristics
Significance of Henry's Law Constant

- Expresses the ability of a contaminant to volatilize from a dissolved phase into a vapor.
  - Approximately ≥ 10^{-3} atm m^3/mole

Solubility Demo Video



Contaminant Characteristics
Organic Carbon Partition Coefficient

Expresses the affinity of a soil to a chemical compound.

K_{OC}

Contaminant Characteristics
Chemical Composition

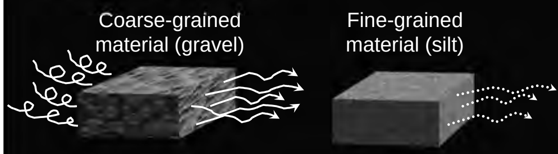
A complex mix of contaminants may impede the effectiveness of an SVE system.

Soil Vapor Extraction

Success depends on:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

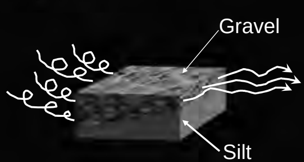
Soil Properties



Soil permeability

- Second only to Henry's Law Constant for success of an SVE system

Soil Properties



Soil permeability is affected by:

- Soil type and heterogeneity

Soil Properties

Soil permeability is affected by:

- Soil type and heterogeneity
- Soil moisture content
  - High soil moisture content will limit vapor advection pathways
  - Optimum soil moisture is less than 10% by weight

Soil Vapor Extraction

Success depends on:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

Site Conditions

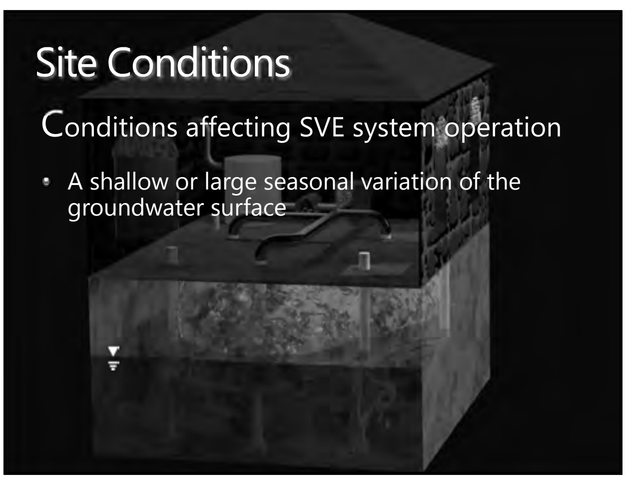
Site conditions refer to above-ground and below-ground conditions, and include:

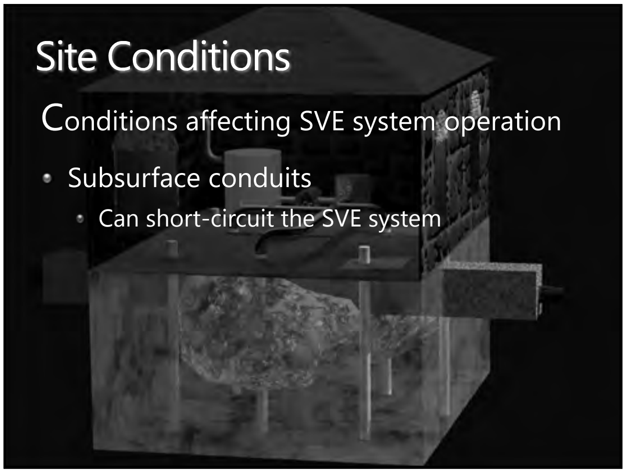
- Depth to groundwater surface
- Subsurface conduits
- Surface caps

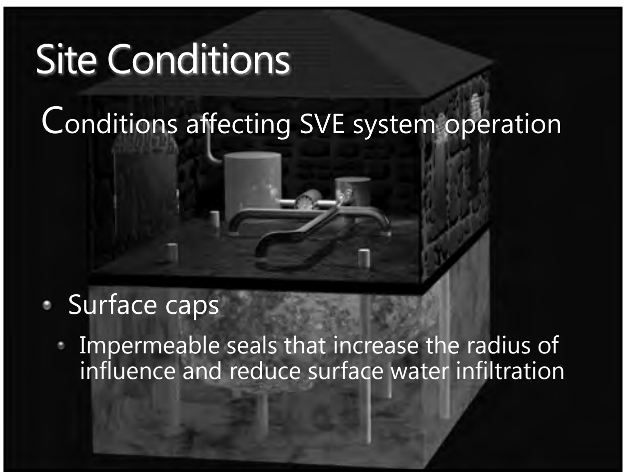
Site Conditions

Conditions affecting SVE system operation

- A shallow or large seasonal variation of the groundwater surface







Soil Vapor Extraction

Success depends on:

- Contaminant characteristics
- Soil properties
- Site conditions
- System design

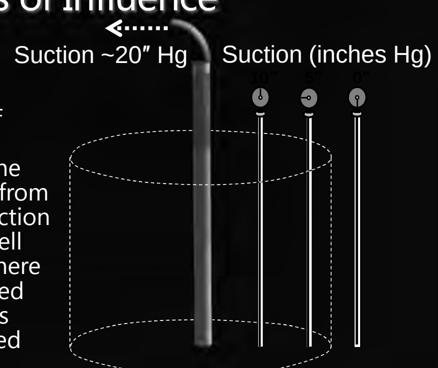
System Design

System design considerations should include:

- Radius of influence (ROI)
- Blower size
- Extraction well design and spacing
- System enhancements

Radius of Influence

Radius of Influence



Radius of influence (ROI) is the distance from the extraction well to well points where the applied vacuum is recognized

Typical SVE Radius of Influence

Homogeneous Soil Type	ROI (in feet)
Coarse sand	>100
Fine sand	60–100
Silt	20–40
Clay	<20

Blower Size

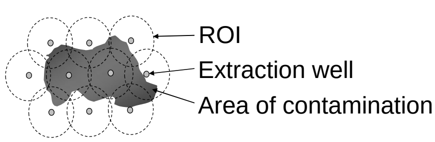
Blowers induce subsurface air flow (vacuum)

Design considerations include:

- Air-flow capacity
- Amount of vacuum produced
- Maintenance costs

Extraction Wells

- Extraction wells are typically 2 in. to 4 in. in diameter, with a screen length of 10–15 ft
- Extraction wells are ideally spaced to achieve an overlapping of the ROI



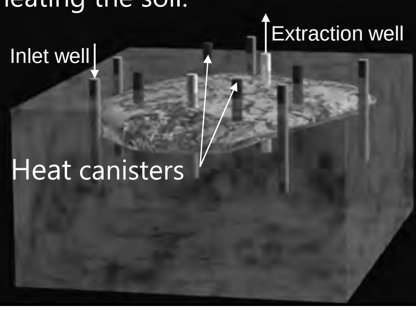
In situ Treatment Methods

	Unsaturated			Saturated		
	Physical	Chemical	Biological	Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓	✓	✓	✓
Soil Vapor Extraction (SVE)	✓					
SVE – Enhancements	✓		✓			✓
Air Sparging				✓		✓
Permeable Reactive Barriers				✓	✓	✓
Chemical Oxidation		✓			✓	
Soil Flushing *	✓	✓		✓	✓	
Bioremediation *			✓			✓
Phytoremediation *			✓			✓
Immobilization *	✓	✓	✓	✓	✓	✓

*Covered in other lectures

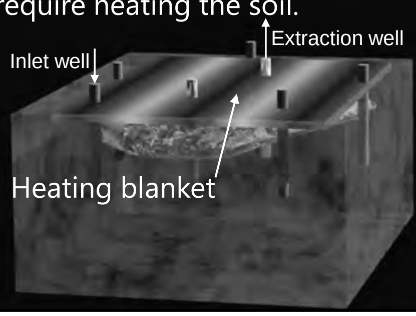
SVE System Enhancements

SVE enhancements generally require heating the soil.



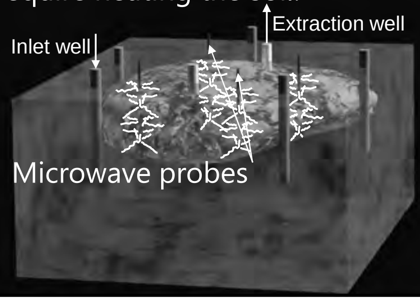
SVE System Enhancements

SVE enhancements generally require heating the soil.



SVE System Enhancements

SVE enhancements generally require heating the soil.



SVE System Enhancements

Heating the soil increases the volatility of the contaminant:

	Temperature		
	10°C	20°C	40°C
Compound	Henry's Law Constant		
TCE	328*	544	1370
Benzene	133	230	619
1,2-Dichloroethane	30	51	134
Methylene chloride	53	89	226

* atm m^3/mole
Source: "*In situ* Treatment Technology" – E. Nyer

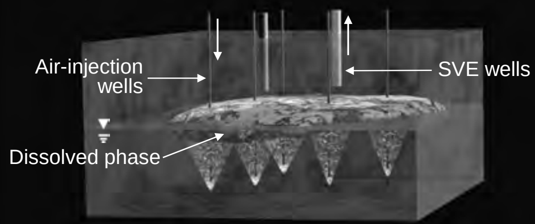
In situ Treatment Methods

	Unsaturated			Saturated		
	Physical	Chemical	Biological	Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓	✓	✓	✓
Soil Vapor Extraction (SVE)	✓					
SVE – Enhancements	✓		✓			✓
Air Sparging				✓		✓
Permeable Reactive Barriers				✓	✓	✓
Chemical Oxidation		✓			✓	
Soil Flushing *	✓	✓		✓	✓	
Bioremediation *			✓			✓
Phytoremediation *			✓			✓
Immobilization *	✓	✓	✓	✓	✓	✓

*Covered in other lectures

Air Sparging

Direct injection of air below the water table



Must be operated in conjunction with a soil-vapor extraction system

Air Sparging

Process can:

- Strip volatile organic compounds (VOCs) from dissolved phase
- Volatilize trapped or sorbed phase contaminants
- Enhance aerobic biodegradation by direct injection of O2

Air Sparging

Success depends on:

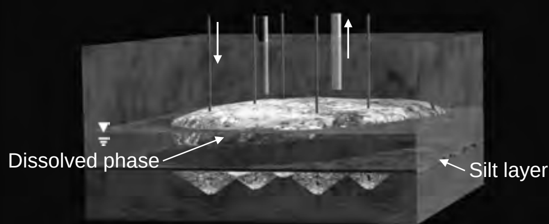
- Contaminant characteristics
- Soil properties
- System design, including:
  - Air distribution (zone of influence)
  - Air injection pressure and flow rates

Air Sparging

In general, the radius of influence for air-sparging wells is between 5 feet and 10 feet.

Air Sparging

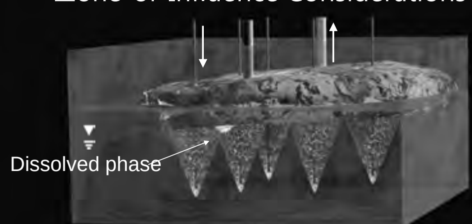
Zone-of-Influence Considerations



- Subtle geologic changes can greatly affect zone of influence

Air Sparging

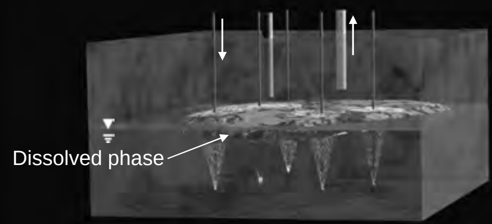
Zone-of-Influence Considerations



- Potential mounding and spreading of contamination

Air Sparging

Zone-of-Influence Considerations



- Airflow paths may develop, creating air channels

Air Sparging

Air injection pressure and flow rates are geology-dependent.

Air pressure for:

- Fine sediment = 12 to 120 in. H_2O (0.4 to 4 psi)
- Coarse sediment = 1 to 10 in. H_2O (0.04 to 0.4 psi)

Air Sparging

Air Injection Considerations

- Higher injection pressures and flow rates do not correspond to better air sparging performance
- Injection rates should be balanced with the SVE system's air withdrawal capacity

Air Sparging
Vapor Treatment

Treatment of extracted vapors from SVE and air sparging systems can include:

- Carbon adsorption
- Thermal oxidation
- Catalytic oxidation
- No treatment

IN SITU TREATMENTS, PART TWO

Student Performance Objectives

Upon completion of this module you will be able to:

1. Describe the advantages, disadvantages, and basic principle of permeable reactive barriers as an in-situ treatment method.
2. Describe the advantages, disadvantages, and basic principle of chemical oxidation as an in-situ treatment method.

IN-SITU TREATMENTS

Part Two

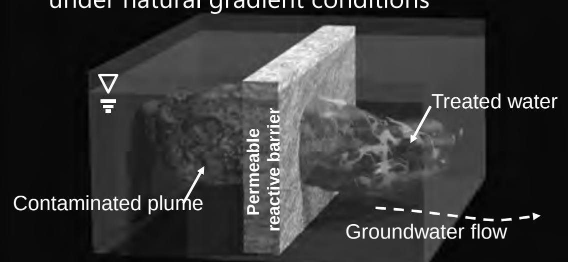
In-situ Treatment Methods

	Unsaturated				Saturated		
	Physical	Chemical	Biological		Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓		✓	✓	✓
Soil Vapor Extraction (SVE)	✓						
SVE – Enhancements	✓		✓				✓
Air Sparging					✓		✓
Permeable Reactive Barriers					✓	✓	✓
Chemical Oxidation		✓				✓	
Soil Flushing *	✓	✓			✓	✓	
Bioremediation *			✓				✓
Phytoremediation *			✓				✓
Immobilization *	✓	✓	✓		✓	✓	✓

*Covered in other lectures

Permeable Reactive Barrier (PRB)

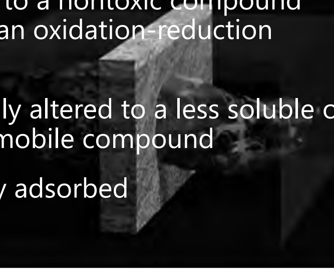
A permeable zone containing reactive material that will intercept and treat contaminated groundwater as it flows under natural gradient conditions



PRB Process

Depending on the contaminant and the PRB material, the contaminant may be:

- Reduced to a nontoxic compound through an oxidation-reduction reaction
- Chemically altered to a less soluble or to an immobile compound
- Physically adsorbed



PRB Advantages

- Proven treatment for organic and inorganic compounds
- Passive system costs less
- Does not disturb surface development
- Generates little waste

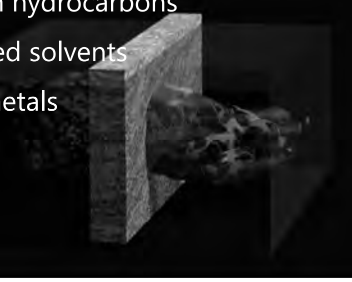
PRB Disadvantages

- Does not treat all compounds
- Must have predictable hydrogeologic flow path
- Difficult to construct > 50 ft. below surface
- Requires time

Effectiveness

PRBs are effective in treating groundwater contaminated with:

- Petroleum hydrocarbons
- Chlorinated solvents
- Soluble metals



Treatable Organic Compounds	Treatable Inorganic Compounds
1,1,1-trichloroethane	chromium
tetrachloroethene	lead
trichloroethene	uranium
cis-1,2-dichloroethene	selenium
trans-1,2-dichloroethene	cadmium
vinyl chloride	sulphate
benzene	nitrate
freon 113	arsenic

PRB System Success

Depends on:

- Contaminant characteristics
- Site characterization
- System design

Contaminant Characteristics

The capabilities of the reactive material ***must match*** the characteristics of the contaminant.

Common PRB Reactive Materials

- Zero-valent Iron (Fe0)
- Biomass
- Oxygen-releasing compounds
- Air sparging curtain
- pH modifiers
- Granular activated carbon

Zero-Valent Iron Reactions

The corrosion of the zero-valent iron (Fe^0) provides the source of electrons that reduce compounds.

Zero-Valent Iron Reactions

Reaction of Fe^0 in saturated state:

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

$2\,H_2O \leftrightarrow 2H^+ + 2OH^-$

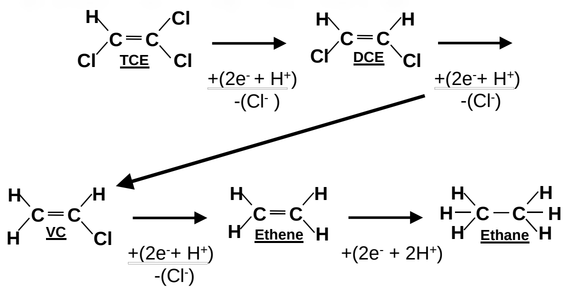
Zero-Valent Iron Reactions
Examples

- Reductive dechlorination
- Chromium (Cr+6) reduction

Reductive Dechlorination

The free electrons ($2e^-$) from the corrosion of Fe^0, plus the $2H^+$ from the water, have the ability to reduce (dechlorinate) chlorinated volatile compounds.

Reductive Dechlorination



Chromium (Cr+6) Reduction

Cr^{+6} under typical aquifer conditions is CrO_4^{2-}

CrO_4^{2-} combined with the free electrons and hydrogen atoms reduces Cr^{+6} to a more stable Cr^{+3}

Site Characterization

Should include an understanding of:

- Hydrogeology
- Contaminant concentration
- Geochemistry and microbiology

Hydrogeology

- Flow path and contaminant distribution
- Aquifer characterization, i.e., permeability, gradient, porosity
- Seasonal or other fluctuations
- Stratigraphy and lithology

Contaminant Concentration

Concentration fluctuations must be considered throughout the life of the system.

Aquifer Geochemistry & Microbiology

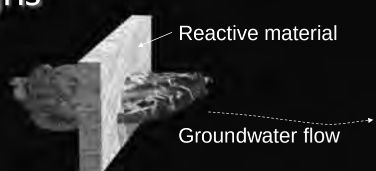
Natural aquifer geochemical and microbial conditions can affect the system design and useful life of the PRB.

Aquifer Geochemistry & Microbiology

- Naturally-dissolved calcium or iron may precipitate and foul the PRB
- Reducing environment may produce:
  - Iron-fouling bacteria (slime)
  - Sulfate-reducing bacteria which could enhance bioremediation

PRB Designs

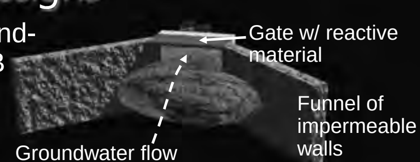
Continuous PRB



- Continuous PRBs are large areas of reactive material designed to assure no bypass of contaminant
- Often constructed by backfilling a trench with reactive material or by injecting a slurry of reactive material

PRB Designs

Funnel-and-gate PRB



- Funnel-and-gate PRBs direct the groundwater to a reactive zone using impermeable walls
- Effective in "low" hydraulic-conductivity aquifers
- Easier to replace or replenish reactive material

Common PRB Design Features

- The PRB design selection is determined by the groundwater velocity and the required residence time in the treatment zone

Groundwater Velocity

- The groundwater velocity through the PRB should be similar to the aquifer groundwater velocity
- Seasonal groundwater fluctuations must be considered in design

Residence Time

- PRB residence time depends on:
  - Contaminant type
  - Contaminant concentration
- Required residence time is based on:
  - Laboratory test
  - Small field test

In-situ Treatment Methods

	Unsaturated				Saturated		
	Physical	Chemical	Biological		Physical	Chemical	Biological
Monitored Natural Attenuation	✓	✓	✓		✓	✓	✓
Soil Vapor Extraction (SVE)	✓						
SVE – Enhancements	✓		✓				✓
Air Sparging					✓		✓
Permeable Reactive Barriers					✓	✓	✓
Chemical Oxidation		✓				✓	
Soil Flushing *	✓	✓			✓	✓	
Bioremediation *			✓				✓
Phytoremediation *			✓				✓
Immobilization *	✓	✓	✓		✓	✓	✓

*Covered in other lectures

In-situ Chemical Oxidation (ISCO)

A treatment process where oxidizing chemicals are placed in direct contact with the contaminant, destroying or immobilizing the contaminant.

An excellent method for source destruction of fuel, solvents, and pesticides in either the saturated or unsaturated zone.

Advantages of ISCO

- No waste generation
- May be less expensive than other treatments
- Low operation and maintenance costs
- Can remediate contaminant source at many depths
- Unobtrusive to surface structures

Disadvantages of ISCO

- May not reach migrated contaminants
- Chemical oxidants are hazardous materials
- Off-gassing of VOCs or chemicals can collect onsite or nearby
- Natural organic material (e.g. peat) may short circuit the process
- May resolubilize stable metals

Treatable Compounds Using ISCO

- Perchloroethene, trichloroethene, dichloroethene, vinyl chloride
- MTBE
- Aromatic hydrocarbons

Untreatable Compounds Using ISCO

- Saturated aliphatic hydrocarbons (e.g., octane, hexane)
- Chlorinated alkanes (e.g., chloroform, carbon tetrachloride)

ISCO System Success

Depends on:

- Matching an oxidant to the contaminant
- Achieving adequate contact between oxidant and contaminant
- Assuring that the oxidant is not consumed by other natural material

Commonly Used Oxidants

- Potassium or sodium permanganate
- Hydrogen peroxide
- Ozone

Permanganate Oxidant

- Very effective oxidizing agent for some chlorinated compounds (e.g., PCE, TCE, DCE, and VC)
- Has strong attraction to electrons in the carbon-carbon double bond

Potassium Permanganate Chemical Process

Potassium permanganate	PCE	Water
$4KMnO_4$ +	$3C_2Cl_4$ +	$4H_2O$

$\longrightarrow 6CO_2 + 4MnO_2 + 4K^+ + 12Cl^- + 8H^-$

Permanganate Property

Dense aqueous solution capable of following the flow paths of DNAPLs

Hydrogen Peroxide Chemical Process

- Oxidant formed by mixing hydrogen peroxide with iron (a metal catalyst), commonly called "Fenton's Reagent"

$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH$

- The hydroxyl radicals (OH) are effective oxidizing agents and are a particularly good treatment for petroleum products

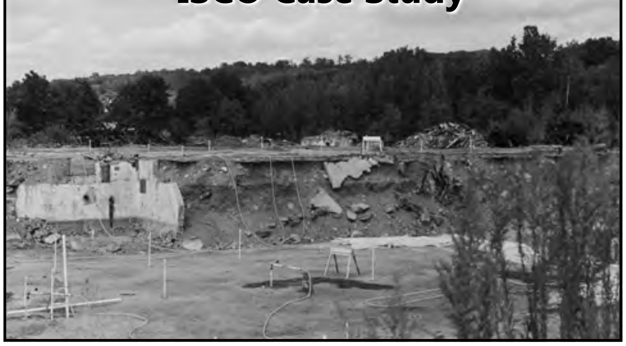
Hydrogen Peroxide Limitations

- Soils with high alkalinity (free carbonate ions) react with Fenton's Reagent
- Low soil permeability

Ozone as Oxidant

- Strongest oxidant
- Effective in treating chlorinated VOCs, PAHs, and BTEX compounds

Fisherville Site Grafton, Massachusetts ISCO Case Study



Permanganate Selection

- Permanganate was selected because it is more stable than peroxide or ozone
  - Less fire/explosion hazard
  - Greater radius of impact through the glacial material at the site
- Permanganate selectively oxidizes carbon double bonds
  - More efficient oxidizer of TCE;
  - More selective oxidizer so less likely it will be consumed by natural organic material (i.e., peat) at the site.
- pH adjustment of aquifer is unnecessary

Time Critical Removal Action

- Treatability Study
- On-Site Injection Testing
- Installation of Temporary Dam in Blackstone Canal
- Full-Scale In Situ Chemical Oxidation (ISCO)

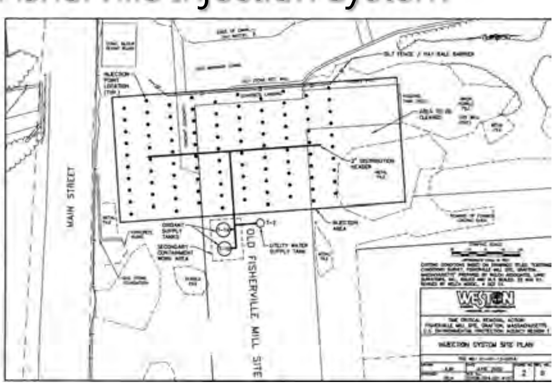
ISCO Treatability Study

On-Site ISCO Injection Testing

In Situ Chemical Oxidation

- Chemical Oxidant is 20% Sodium Permanganate (NaMnO4) Solution
- 100 Injection Wells, 35 to 50 Feet Deep
- 1,244 lbs of (NaMnO4) per Injection Well
- Three Injection Rounds, 50% of Total Injected During First Round, 25% During Subsequent Rounds

Fisherville Injection System

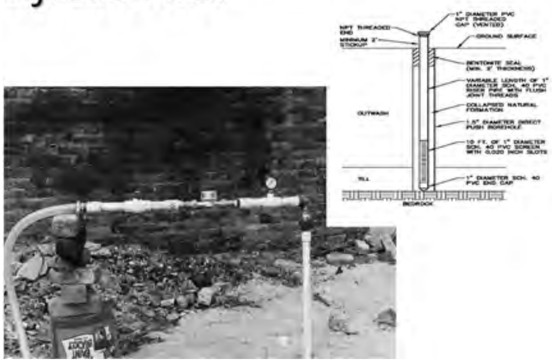


Treatment Area / Injection System

Centrifugal pumps with pressure release valve

Injection Manifold

Injection well



Treatment Chemical Being Pumped

Bailer showing sodium permanganate solution in well immediately offset from injection well

ISCO Conclusions - Success

- The average concentrations in overburden (4 ppm) was reduced to less that 0.1 ppm.
- The cleanup goals were achieved within 16 months for <$2 Million.

SOIL WASHING AND IMMOBILIZATION

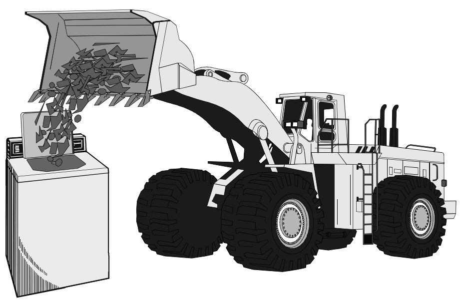
Student Performance Objectives

Upon completion of this module you will be able to:

1. Describe the *in-situ* soil flushing process.
2. Describe the *ex-situ* soil washing process
3. State the application, limitations, advantages, and disadvantages of immobilization technologies.

SOIL WASHING AND IMMOBILIZATION

Soil Washing Treatments

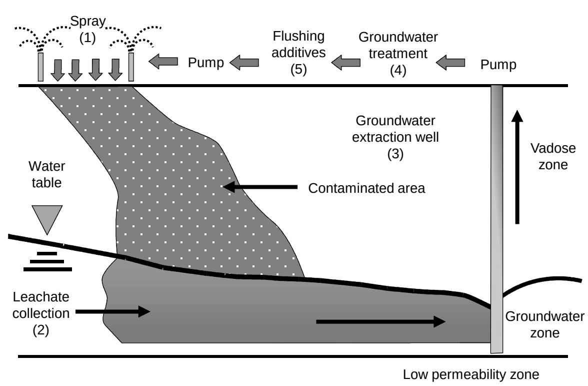


Soil Treatments

- In-situ soil flushing
- Soil washing

In-situ Soil Flushing

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions.



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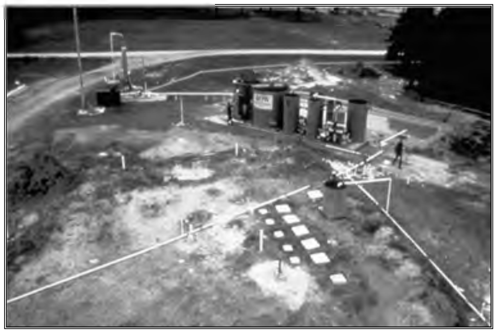
Back Diff Video

Soil Flushing



Soil Flushing

Solvent Selection

- Water
  - Soluble (hydrophilic) organics
  - Octanol/water partition coefficient <10
- Water with surfactant
  - Low solubility (hydrophobic) organics

Solvent Selection

- Acids, chelating agents, or reducing agents
  - Metals
  - Inorganic metal salts

Demonstrated Effectiveness

- Volatile halogenated organics (perchloroethylene, chloromethane)
- Semivolatile nonhalogenated organics (phenols, nitrobenzene)
- Nonvolatile metals (arsenic, lead)

U.S. EPA 1991a

Soil Parameters

- Permeability – affects treatment time and efficiency of contaminant removal
  - ≥1 × 10–3 cm/sec = effective soil flushing
  - <1 × 10–5 cm/sec = limited soil flushing

Soil Parameters

- Moisture content – affects flushing fluid transfer requirements
- Groundwater hydrology – critical in controlling the recovery of injected fluids and contaminants

Process Residuals

- Groundwater treatment
- Flushing additives:
  - Reuse
  - Degradability

Site Requirements

- Underground Injection Control (UIC) permit
- National Pollutant Discharge Elimination System (NPDES)
- Slurry walls or sheet piling for containment
- Berms, dikes, or caps for surface water control

Soil Flushing Limitations

- 1-2 years as concentrations decrease
- Hydraulic control required
- High silt and clay content not applicable
- Surfactants or organic solvents removed
- Bacteria and/or iron fouling
- Additives may interfere with wastewater treatment

Soil Washing

Soil washing is a water-based process for mechanically separating and scrubbing soils ex-situ to remove contaminants.

Soil Washing Treatment

- Onsite, ex-situ, water-based process
- Contamination reduction by particle size separation
- Mechanical washing and separation technique

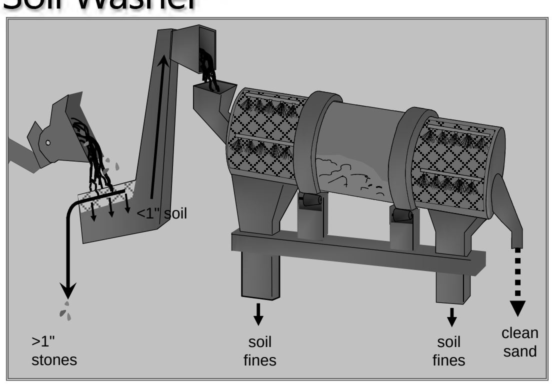
Applicability

- Stand alone or treatment train
- Effective for coarse sand and gravel
- Demonstrated contaminant removal
  - Halogenated volatile organics (perchloroethylene, trichloroethylene)
  - Nonhalogenated volatile organics (phenols, nitrobenzene)
  - Volatile and nonvolatile metals (mercury-volatile, lead-nonvolatile)

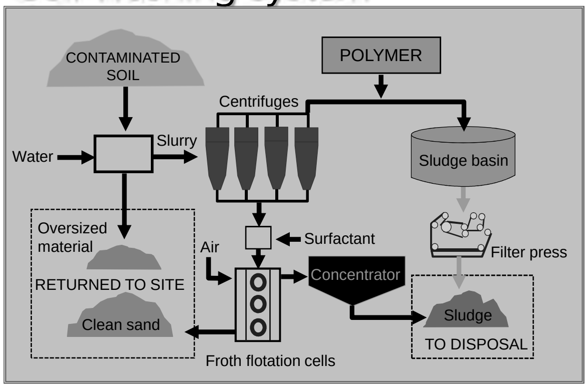
Waste Soil Characterization Parameters

Particle Size Distribution	Comments
>2 mm pretreatment	Oversize requirements
0.25–2 mm	Effective soil washing
0.063–0.25 mm	Limited soil washing
<0.063 mm	Clay and silt fraction, difficult soil washing

Soil Washer



Soil Washing System



Soil Washing

Soil Washing

Soil Washing

Soil Washing

Soil Washing

Soil Washing Residuals

- Wastewater – treatment and recycle
- Vapors – collect and treat
- Oversize soils – return to site
- Fines – further treatment

IMMOBILIZATION

Immobilization General Applications

- Soils, sludges, and sediments
- Lead, cadmium, and similar heavy metals
- Limits mobility (leachability)

Immobilization General Limitations

- Increases waste volume
- Not for organics
- Nondestructive

Predominant Technologies

- Physical
- Chemical
- Thermal
- Biological

Physical Immobilization

- Solidification
- Sludges and sediments
- Clays, vermiculite, and saw dust

Solidification

Chemical Immobilization

- Stabilization
- Cement technologies
- Phosphate technologies
- Matrix formation


New Hampshire Plating Company
Sevenson
Chemical binding of soluble metals to soil


New Hampshire Plating Company
Sevenson
PORTEC
Portec Pugmill


New Hampshire Plating Company
Reagent blending


New Hampshire Plating Company
Loading of treated soil


New Hampshire Plating Company
Sevenson
Blending using a backhoe


Mouat Industries
Columbus, Montana
Chemical reduction of hexavalent chrome (Cr+6)

Mouat Industries
Columbus, Montana

Traub Battery
Sioux Falls, South Dakota

Traub Battery
Sioux Falls, South Dakota

Pug mill used to blend

Thermal Immobilization

- Vitrification
- Primarily radioactive waste
- Electrical resistance or combustion heating

Thermal Immobilization

Thermal Immobilization

Thermal Immobilization

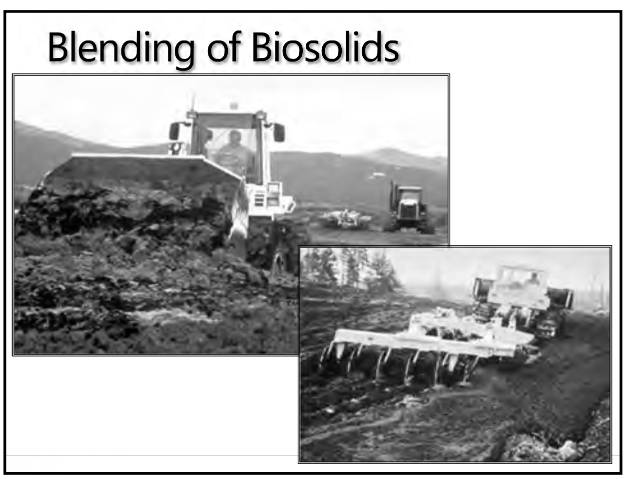
Thermal Immobilization

Biological Immobilization

- Contains as well as immobilizes
- Treats large volume, such as mine tailings


Mine Tailings Leadville, Colorado


Biosolids to be mixed with tailings


Blending of Biosolids

Stabilized Tailings

Immobilization
Advantages

- Treats metals in soils, sludges, and sediments
- Can be used for radioactive and mixed wastes
- Treats large volume mine tailings

Immobilization
Disadvantages

- Increases waste volume
- Not suitable for treating organics
- Requires secondary containment

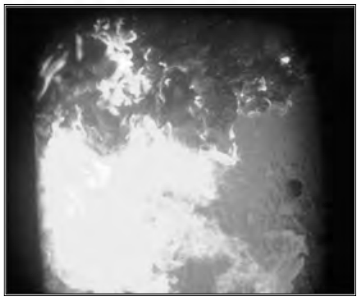
THERMAL TREATMENT

Student Performance Objectives

Upon completion of this module you will be able to:

1. List the applications, limitations, advantages, and disadvantages of thermal treatment.
2. Describe the design and working mechanisms of rotary kiln incinerators.
3. Describe four combustion factors which are needed for an incinerator to properly operate.
4. Describe the design and working mechanisms of thermal desorption systems.
5. Describe the design and working mechanisms of thermal and catalytic oxidizers.

THERMAL TREATMENT



Thermal Treatment Applications

- Treat organic contaminated soils, sediments, and sludges
- Incineration destroys contaminants
- Desorption removes contaminants

Thermal Treatment Limitations

- Does not treat inorganics
- Moisture content
- BTU content

Thermal Treatment Advantages

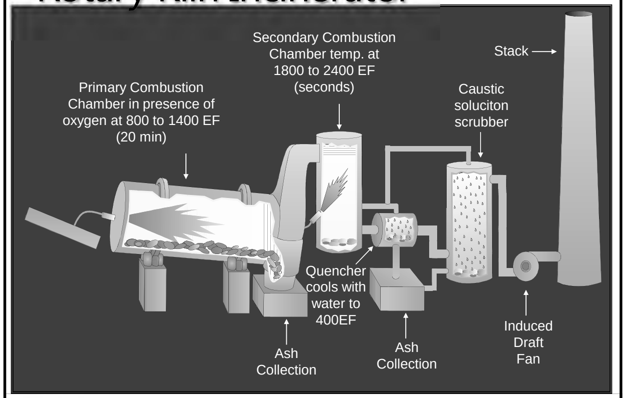
- Contaminant is destroyed
- Established technology
- Volume reduction
- Best demonstrated available technology

Thermal Treatment Disadvantages

- Can be costly
- Possible air pollution problems
- Public disapproval

Rotary Kiln Incinerator

Rotary Kiln Incinerator



Combustion Factors

- Time
- Temperature
- Turbulence
- Oxygen

Waste Characteristics

- Waste with greater than 5,000 Btu/lb
- Moisture or aqueous wastes
- Inorganics that are more than 5% alkali metals
- Halogens
- Volatile met

Portable Rotary Kiln Incinerator

Incinerator Primary Chamber

Incinerator Screw Auger

Incinerator Scrubber with Mixing Tanks

Incinerator Stack

Thermal Desorption

- Volatilizes contaminants
- Condenses and/or treats vapors
- Clean soil returned to the site

Thermal Desorber

Burner Train Within Shroud

Burner Fire Inside Shroud


Discharge


Bag house


Condensers

Thermal Desorption Advantages

- Less expensive than incineration
- Broad application
- Public acceptance
- Recycling potential

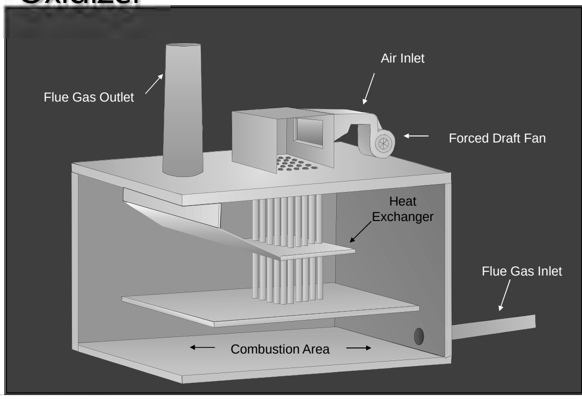
Thermal Desorption Disadvantages

- Further waste treatment may be needed
- Limited soil pH range
- Limited moisture content

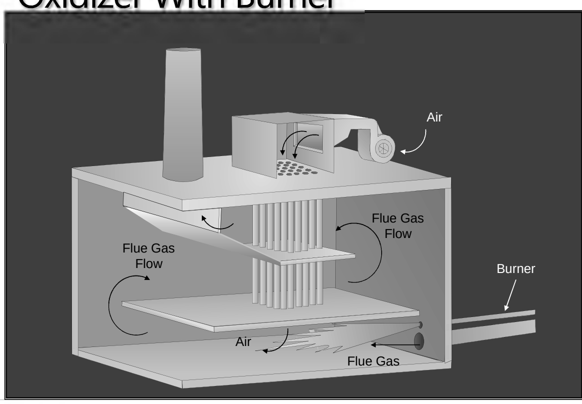
Oxidizers

- Thermal oxidizers
- Catalytic oxidizers

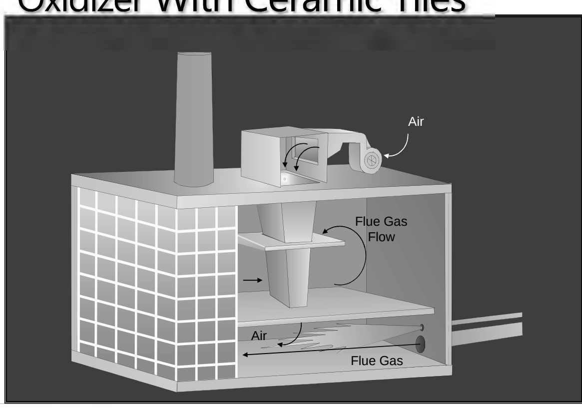
Oxidizer

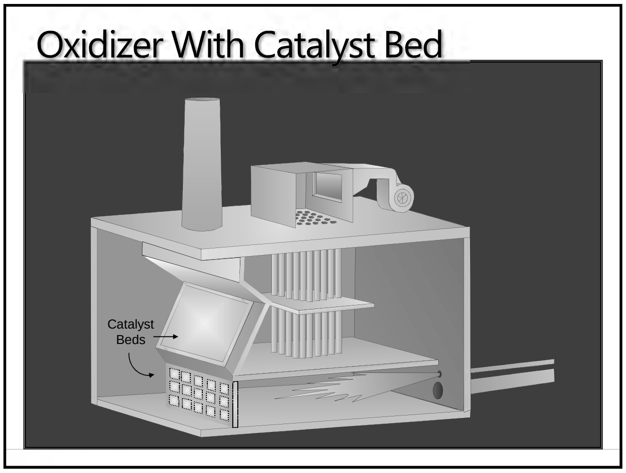


Oxidizer With Burner



Oxidizer With Ceramic Tiles




Oxidizer With Catalyst Bed
Catalyst
Beds

PHYTOREMEDIATION

Student Performance Objectives

Upon completion of this module you will be able to:

1. Define phytoremediation.
2. Describe the working mechanisms of phytoremediation systems.
3. State the advantages and disadvantages of phytoremediation
4. List the conditions under which this technology would be beneficial.

PHYTOREMEDIATION

EPA

Objectives

- Define phytoremediation
- List six phytotechnologies
- List the advantages and disadvantages of phytoremediation technologies
- Review phytoremediation decision trees

Phytoremediation

A set of technologies that use plants for remediating soils, sludges, sediments and water contaminated with organic and inorganic chemicals.

What is Phytoremediation? – United Nations Environment Programme, www.unep.or.jp/ietc/publications/freshwater/fms2/1.asp

Phytotechnology Technical and Regulatory Guidance and Decision Trees. Interstate Technology & Regulatory Council, Feb. 2009, Washington, DC

Phytoremediation

Treatable organic contaminants include:

- petroleum hydrocarbons
- crude oil
- chlorinated compounds
- pesticides
- explosive compounds

Phytoremediation

Treatable inorganic contaminants include:

- salts
- metals
- radioactive materials

Phytoremediation

Phytoremediation can also be defined as the efficient use of plants to remove, detoxify or immobilize environmental contaminants.

Phytoremediation utilizes plants' natural activities and processes, a.k.a. "phyto-technologies" to meet environmental remediation goals.

Phytotechnologies include containment in addition to treatment or removal strategies.

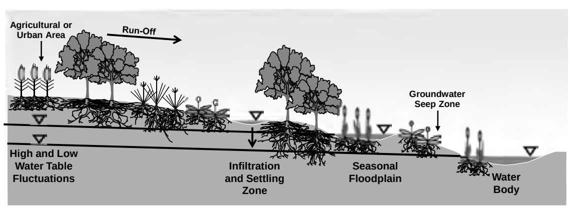
Phytotechnologies

Mechanism	Description	Clean up goals
Phytosequestation	Plant ability to reduce the mobility of a contaminant	Containment (sequesters)
Rhizodegradation	Phytochemicals extruded through roots enhance microbial biodegradation	Remediation by destruction (degrades)
Phytohydraulics	Plant affect on local hydrology	Containment by controlling hydrology (sequesters)
Phytoextraction	Uptake contaminants into the plant	Remediation by removal of plants (extracts)
Phytodegradation	Uptake and break down contaminants within the plant	Remediation by destruction (degrades)
Phytovolatilization	Uptake, translocation, and transpire volatile contaminants.	Remediation by removal through plants (extracts)

Riparian Buffers

Riparian buffers are vegetated areas that protect adjacent water resources from NPS pollution.

These buffers can provide bank stabilization and habitat for aquatic and other wildlife.



Advantages of Phytoremediation

- Considered a green technology and sustainable
- Solar-powered
- Minimal air emissions, water discharge, and secondary waste generation
- Applicable for remote locations

Advantages of Phytoremediation

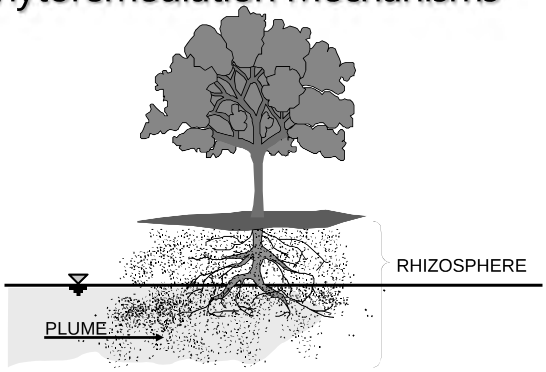
- Favorable public perception
- Improved aesthetics
- Can be used to supplement other remediation approaches or as a polishing step

Disadvantages of Phytoremediation

Major limitations are depth, area, and time

- Depth and area depend on the plant species that is suitable to the site (i.e., root penetration) as well as the site layout and soil characteristics
- Time constraints: phytotechnologies generally take longer than other alternatives and are susceptible to seasonal and daily variations

Phytoremediation Mechanisms



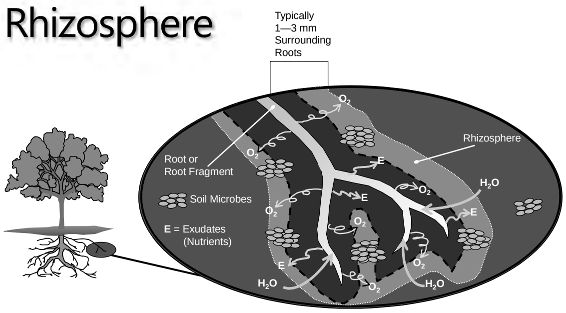
Basic Plant Physiology

Photosynthesis is the process in which plants use carbon dioxide to convert light energy into chemical energy.

Plants:

- uptake water and inorganic dissolved nutrients through the root systems
- exude oxygen into the atmosphere
- exude a source of carbon and oxygen into the soil, greatly enhancing the growth of bacteria and fungi in the immediate vicinity surrounding the roots

Rhizosphere



Photosynthesis

Photosynthesis:

6 CO_2 + 6 H_2O + light energy yields phytochemicals (including carbohydrate) + 6 O_2

Respiration:

Phytochemical (stored chemical energy) + O_2 yields carbohydrates + metabolic energy + CO_2

Growth and metabolism:

Metabolic energy + cell biomass yields biomass production and metabolism

End result: up to 20% of carbon produced by plant goes into rhizosphere

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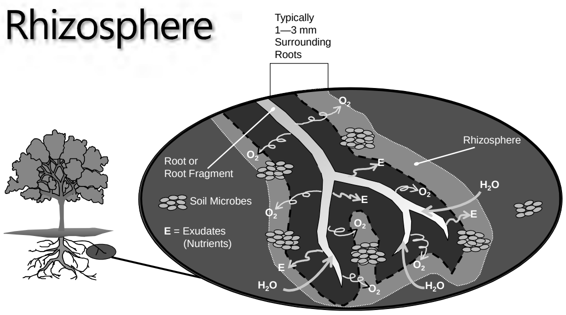
Rhizosphere



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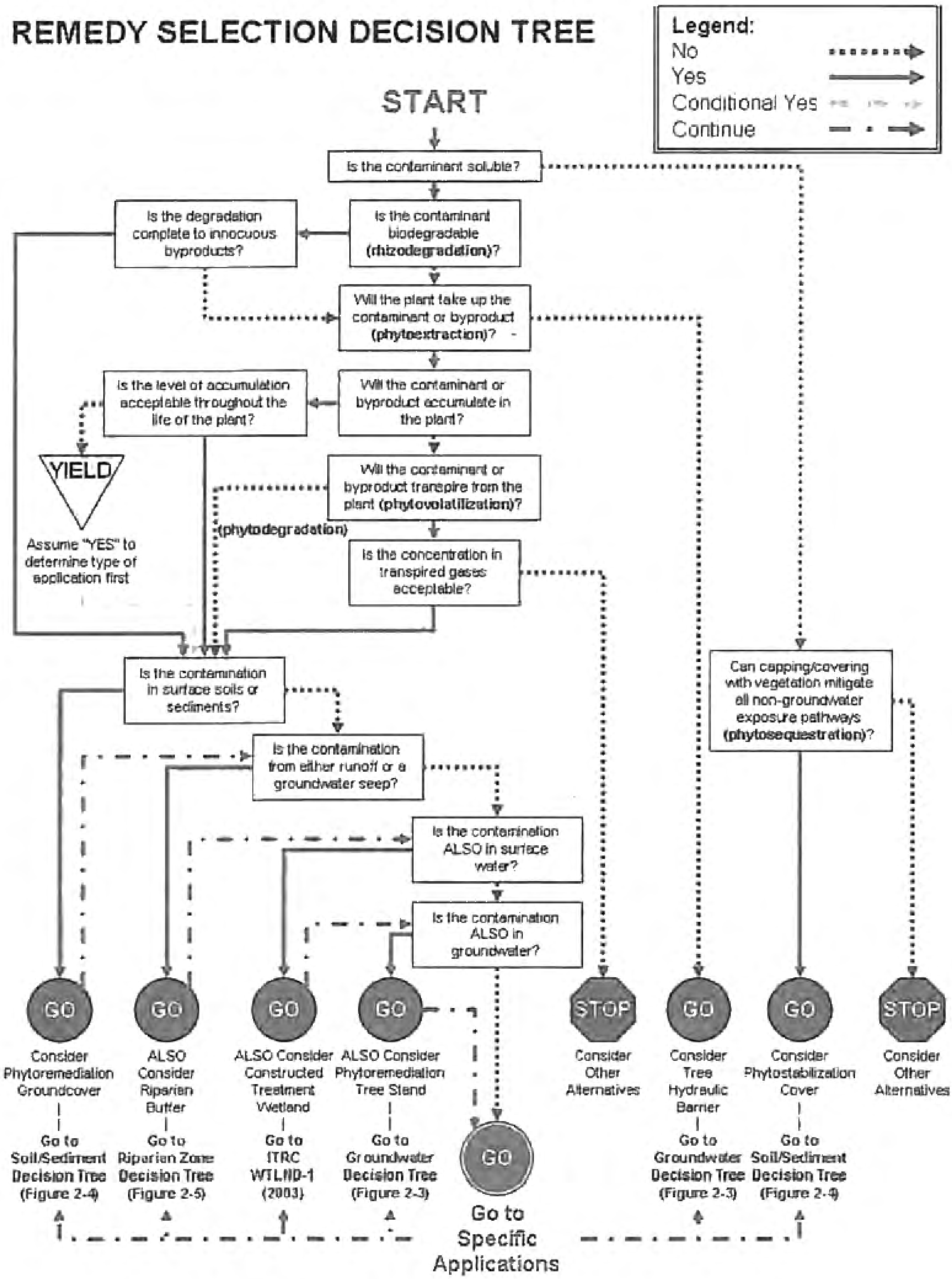
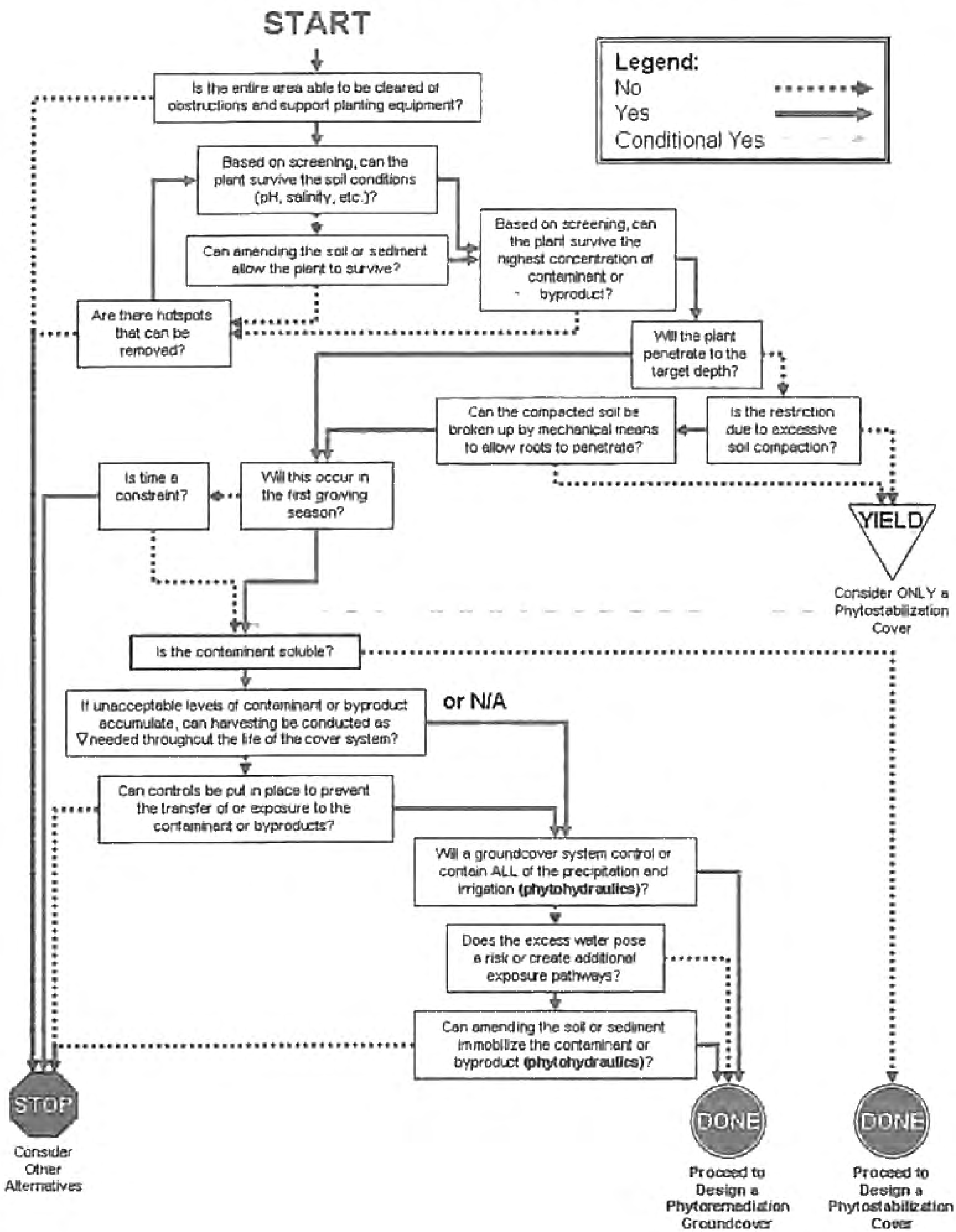
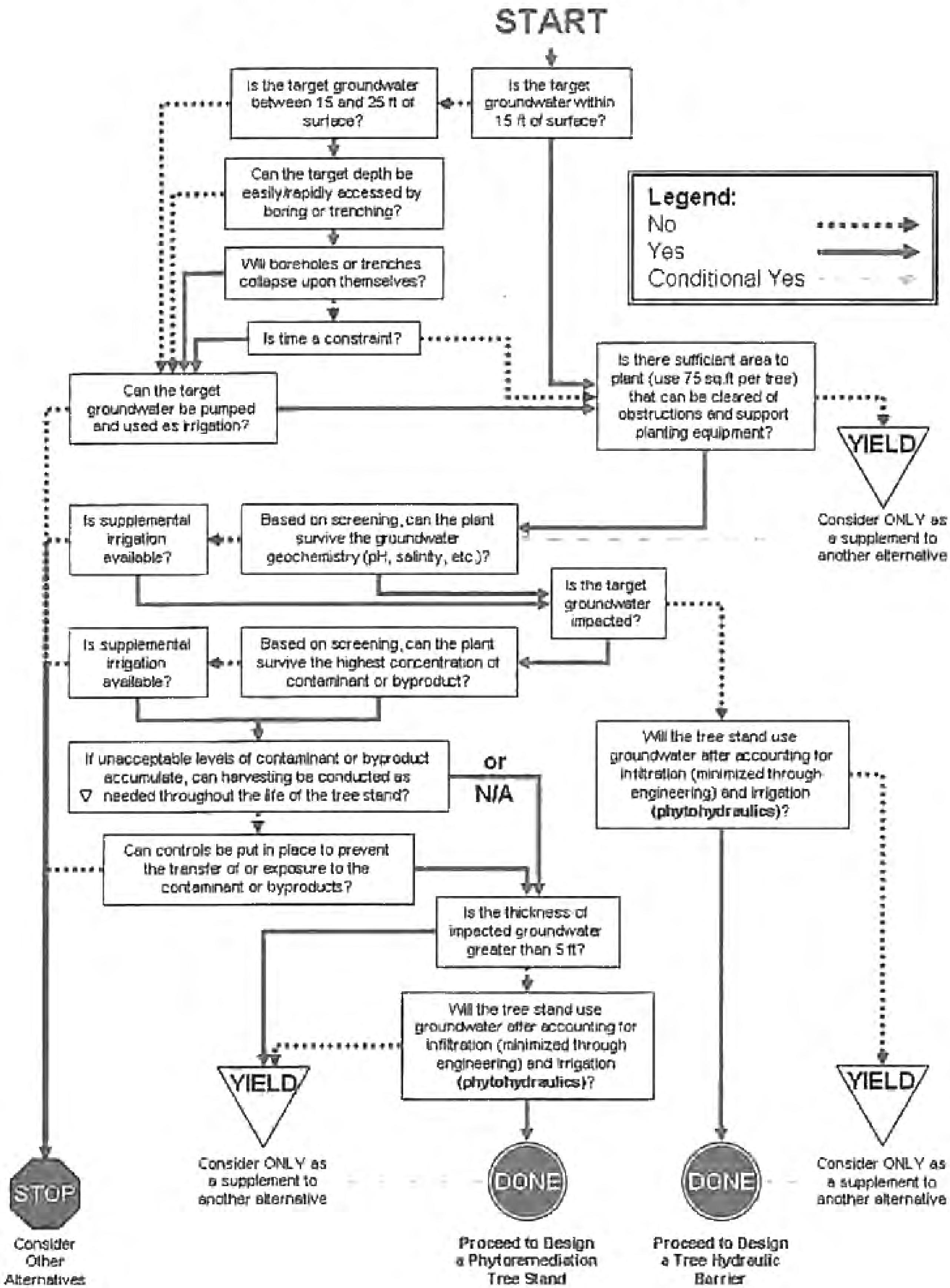

REMEDY SELECTION DECISION TREE
Legend:
No
Yes
Conditional Yes
Continue
START
Is the contaminant soluble?
Is the contaminant biodegradable (rhizodegradation)?
Is the degradation complete to innocuous byproducts?
Will the plant take up the contaminant or byproduct (phytoextraction)?
Will the contaminant or byproduct accumulate in the plant?
Is the level of accumulation acceptable throughout the life of the plant?
YIELD
Assume "YES" to determine type of application first
Will the contaminant or byproduct transpire from the plant (phytovolatilization)?
(phytodegradation)
Is the concentration in transpired gases acceptable?
Is the contamination in surface soils or sediments?
Is the contamination from either runoff or a groundwater seep?
Is the contamination ALSO in surface water?
Is the contamination ALSO in groundwater?
Can capping/covering with vegetation mitigate all non-groundwater exposure pathways (phytosequestration)?
GO
Consider Phytoremediation Groundcover
Go to Soil/Sediment Decision Tree (Figure 2-4)
GO
ALSO Consider Riparian Buffer
Go to Riparian Zone Decision Tree (Figure 2-5)
GO
ALSO Consider Constructed Treatment Wetland
Go to ITRC WTLND-1 (2003)
GO
ALSO Consider Phytoremediation Tree Stand
Go to Groundwater Decision Tree (Figure 2-3)
STOP
Consider Other Alternatives
GO
Consider Tree Hydraulic Barrier
Go to Groundwater Decision Tree (Figure 2-3)
GO
Consider Phytostabilization Cover
Go to Soil/Sediment Decision Tree (Figure 2-4)
STOP
Consider Other Alternatives
GO
Go to Specific Applications

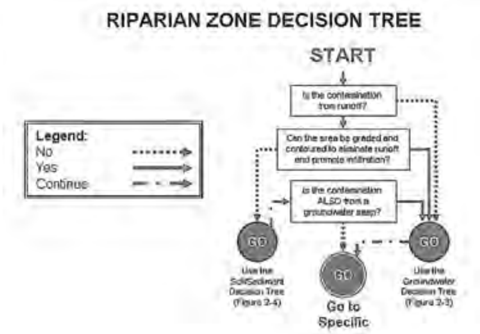
SOIL / SEDIMENT DECISION TREE



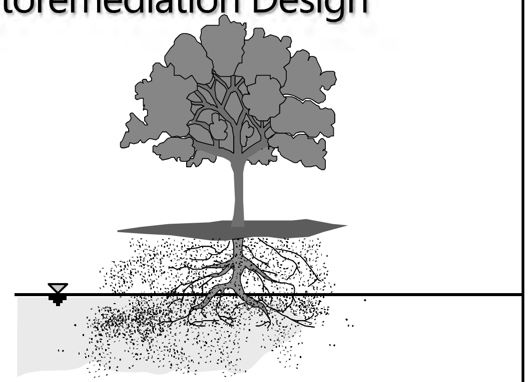
GROUNDWATER DECISION TREE



Riparian Decision Tree



Phytoremediation Design



Design and Implementation

Design depends on site specific conditions such as:

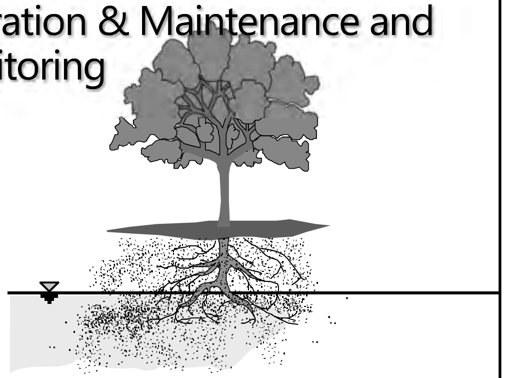
- Climate
- Depth and concentration of the contaminant
- Commercial availability of plants
- Soil conditions (nutrient content salinity)
- Site end use

Design and Implementation

Design cost depends on site specific issues such as:

- Earthwork and labor
- Plant and planting costs
- Soil amendments
- Permits
- Site control (fencing or security)

Phytoremediation Operation & Maintenance and Monitoring



O&M and Monitoring

O&M and Monitoring can last many years

O&M issues may include:

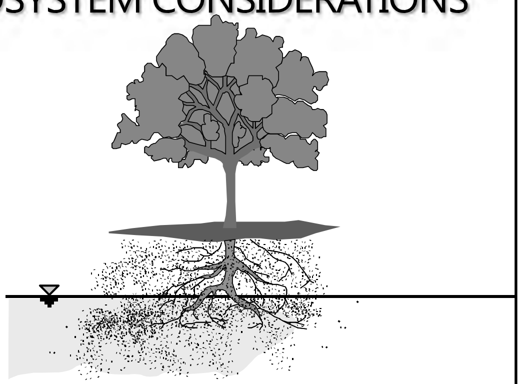
- Irrigation
- Fertilization
- Weed control
- Pest control
- Replanting

O&M and Monitoring

Monitoring includes sampling plant material, and using a conventional remediation monitoring approach such as soil- or groundwater-sample collection and analysis.

Sampling is also conducted to determine if the plant or fruit is safe for consumption.

ECOSYSTEM CONSIDERATIONS



Considerations

- Introduction of non-native plants
- Integration into long-term landscaping use and aesthetic landscaping
- Native plants or plants grown from seed

PROCESS TESTING

Student Performance Objectives

Upon completion of this module you will be able to:

1. List and describe four reasons for performing process testing.
2. List and describe four phases of process testing.
3. Define grab and composite sampling as it applies to process testing.

PROCESS TESTING

Reasons To Perform Process Testing

- Verify clean-up goals
- Ensure proper operation of unit
- Ensure ARARs are being met
- Ensure that public and environment are not being adversely impacted

Process Testing Consists of Four Phases

- Startup
- Shakedown
- Performance Testing
- Production Testing

Startup

- Initial operation on clean material
- Prevent uncontrolled release
- Evaluate mechanical system
- Evaluate controls/alarm system

Startup - Testing

- Unit run at expected operating conditions
- Test computer logic, alarms, monitoring equipment and auto shutoffs
- Calibrate sensors and monitors
- Run unit for 23 of 24 hours to test mechanical soundness

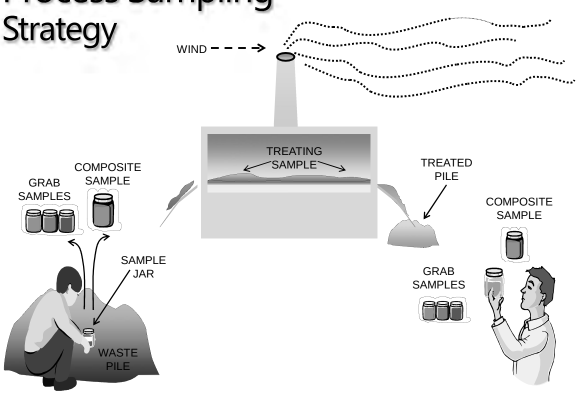
Shakedown

- Similar to startup, but using contaminated material
- System optimization
- Operating parameters checked against remediation results
- Identify matrix specific problems

Performance Testing

- Intensive testing and sampling program
- Meet cleanup goals
- Compliance with ARARs
- Protecting public health
- Establish operating parameters
- Proof of performance (trial burn)

Process Sampling
Strategy



Process Sampling
Media

- Feed streams
- Reagent streams
- Treated materials
- Waste streams

Process Sampling: Air

- Emissions
  - Stack
  - Fugitive
- Strategy
  - Grab
  - Continuous

Process Sampling
Ambient Air

- Workzone
- Fenceline

Production Testing

- Performed on regular basis throughout production
- Ensures that treated material meets clean-up goals
- Usually done as a composite on a per volume basis (i.e. a composite sample each 500 cubic yard pile)

Case Study – FCX Engineering

- Performance test – Low-temperature Thermal Desorber
- Agricultural supply and distribution center
- Disposed of 5,000-10,000 pounds of DDT, DDE and chlordane in trenches

Case Study – FCX Engineering

- Performance test – Low-temperature Thermal Desorber
- Agricultural supply and distribution center
- Disposed of 5,000-10,000 pounds of DDT, DDE and chlordane in trenches

Scope of Work

- Conduct preliminary test
- Perform ambient air sampling
- Conduct meteorological monitoring
- Provide continuous emission monitoring
- Collect stack gas emission samples for particulate, HCl, Cl, VOCs, SVOCs, PCDD/PCDF analyses
- Collect pre- and post-treatment soil samples for analysis

Pre-treatment Soils

- Excavated from beneath concrete slabs and screened to remove debris
- Staged in warehouse

Soil excavated from below warehouse floor

Treatment System

- Six Matrix Constituent Separators (MCS)
- Three condensers
- Three carbon adsorption units
- Three monitoring sheds
- An emission stack

Matrix Constituent Separators

MCS Unit
Closed

MCS Unit
Open

Vapor Condenser

Activated Carbon Units to Remove Contaminant in the Vapor

Monitoring Shed

Emission Stack

Sampling Stations

- Scaffold by the emission stack inside exclusion zone
- Trailers for continuous emissions monitoring (CEM) and sample recovery outside of exclusion zone
- Ambient air sampling stations
- Meteorological sampling station

Ambient Air and Meteorological Sampling Stations

Pre-treatment Soil Sampling

One sample collected from each of 12 trays and composited into one sample for analysis

Emission Sampling

Stack emission test

Emission Sampling

Stack emission test

Emission Sampling

Stack emission test

Emission Sampling

Impingers

Sample recovery from media

Results

- Failed CO due to continued high emissions
- Two options offered

Option 1

- Single stack test without considering CO
- If result passes standard, full scale test performed later after installation of oxidizer or other equivalent system

Option 2

- Full scale stack emission test can be performed without considering CO
- If result passes standard, a CO treatment unit and a CO monitor to ensure the emission of CO is below the emission limit established in the work plan would be installed
- U.S. EPA would then return, testing only for CO

Results

- Option 2 was chosen

TECHNOLOGY SELECTION

Student Performance Objectives

Upon completion of this module you will be able to:

1. State the application, limitations, working mechanisms, advantages and disadvantages of selecting presumptive remedies.
2. State the application, limitations, working mechanisms, advantages and disadvantages of selecting potential remedies.
3. State the application, limitations, working mechanisms, advantages and disadvantages of treatability studies.
4. State the application, limitations, working mechanisms, advantages and disadvantages of technology searches.

TECHNOLOGY SELECTION

Technology Selection

- Presumptive remedies
- Potential remedies
- Treatability studies
- Technology searches

Presumptive Remedies

- Wood treatment sites
- Municipal landfills
- Ex-situ groundwater treatment
- Volatile organic compounds in soil

Wood Treater Sites

- Pentachlorophenol, creosote, and/or chromated copper arsenate
- Biological treatment, incineration, and/or immobilization

Municipal Landfills

- Containment
  - Landfill
  - Groundwater control
  - Leachate collection and treatment
  - Gas collection and treatment

Ex-Situ Groundwater Treatment

- LNAPL recovery
- Air stripping, carbon adsorption, chemical precipitation, ion exchange

Volatile Organic Compounds in Soils

- Soil vapor extraction
- Low temperature desorption
- Incineration

Potential Remedies

- For organics and inorganics
- For water and soil/sludges

Organic Contaminants

- Volatile organics
- Semivolatile to non-volatile organics
- Pesticides

Volatile Organics

- Aqueous
  - Air stripping, air sparging, bioslurping, or in situ biological treatment
- Soils and sludges
  - Soils vapor extraction, soils heating, or bioventing
  - Thermal treatment or in situ biological treatment

Semi-Volatile to Non-Volatile Organics

- Aqueous
  - Carbon adsorption, UV oxidation, chemical or electron beam destruction, and in situ biological treatment
- Soils and sludges
  - Soils flushing, soil washing, chemical extraction
  - Thermal treatment, ex-situ biological treatment

Pesticides

- Aqueous
  - UV oxidation, thermal, carbon adsorption, or biological treatment
  - Dehalogenation
- Soils and sludges
  - Thermal treatment, biological treatment, or dehalogenation
  - Chemical extraction

Inorganics

- Aqueous
  - Chemical treatment, ion exchange, or membrane separation
- Soils and sludges
  - Immobilization, soil washing, chemical or biological extraction
  - Dewatering

Treatability Studies

- Screening and remedy selection studies
- Pilot and full scale studies

Screening and Remedy Selection Studies

- Used when several remedies may work
- Help identify which remedies, if any, meet site clean-up goals
- Help identify the need for the use of multiple remedies

Pilot and Full-Scale Studies

- Used to verify that selected remedies will actually meet clean-up goals
- Help determine design specifications and operating parameters

Technology Searches

- Literature searches
- Internet searches

Literature Searches

- Presumptive remedies for CERCLA sites
- Engineering bulletins for potential remedies
- Treatability studies under CERCLA

Internet Searches

- www.clu-in.org
- www.epareachit.org
- www.frtr.gov
- www.gwrtac.org

FRTR
Remediation Technologies Screening Matrix and Reference Guide, Version 4.0

Home Page

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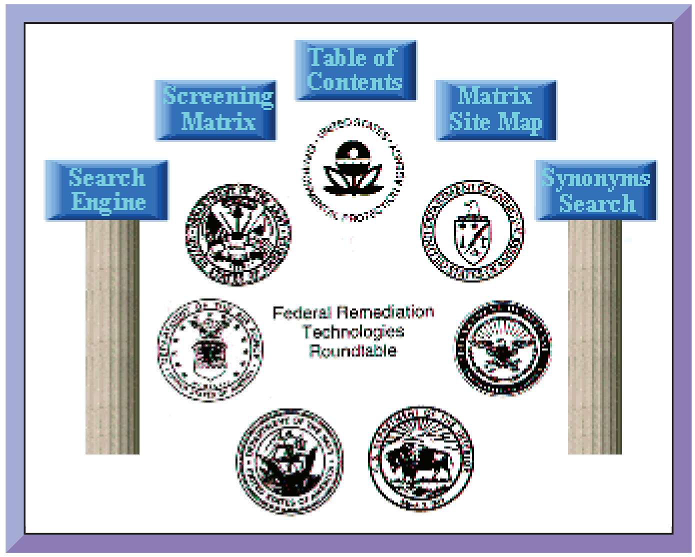
You may access the information in this document in **one of five ways:**



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