Recent Developments in Innovative Treatment Technologies

This document is part of the training materials for the RCRA Corrective Action Workshop on Results-Based Project Management. It contains summaries of EPA statutory authorities, regulations, and guidance materials. In addition, this document is not an EPA regulation and therefore cannot impose legally binding requirements on EPA, States, or the regulated community. EPA may change this document in the future, as appropriate.

Module Objectives

Participants will:

- Be provided an overview of several Innovative Treatment Technologies

- Be provided an overview of EPA policies associated with natural attenuation

Examples of ITT

1. Monitored Natural Attenuation (MNA)
2. NAPL Recovery
   - Dynamic Underground Stripping
   - Six-Phase Heating
   - Bioslurping
   - Gravity
   - Surfactant and Cosolvent Flushing
3. Passive Treatment Walls

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Notes:

Additional Innovative Treatment Technologies addressed in the course sponsored by TIO include:

Thermal, Physical, and Chemical Technologies

- Thermal desorption

- Soil flushing and surfactant enhancements

- Soil washing and Solvent extraction

- Electrokinetic remediation

- Chemical oxidation

Bioremediation Technologies

- Solid-phase bioremediation

- Bioslurping

- Enhanced in situ groundwater remediation

Examples of ITT (Cont'd)…

4. Soil Vapor Extraction (SVE) with enhancements
5. Bioventing
6. Phytoremediation
7. Soil Washing
8. Solvent Extraction
9. In-Situ Oxidation
10. Enhanced In-Situ Bioremediation of Groundwater

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Notes:

A course on Innovative Technologies is sponsored by the Technology Innovation Office (TIO) in the Office of Solid Waste and Emergency Response (OSWER), U.S. Environmental Protection Agency (EPA), and by EPA's Office of Research and Development (ORD). Its purpose is to enhance the ability of participants to consider innovative treatment technologies as cost-effective alternatives to conventional technologies.

For additional information, please reference the following URL:

http://www.epa.gov/swertio1/index.htm

Monitored Natural Attenuation

Is defined as a:

Variety of in situ processes that act without human intervention to reduce the:

- -mass;
- -toxicity;
- -mobility;
- -volume; and
- -concentration

of contaminants in soil or groundwater

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Notes:

The term "monitored natural attenuation" refers to the reliance on natural attenuation processes, within the context of a carefully monitored site cleanup program, to achieve site-specific remedial objectives within a timeframe that is reasonable when compared with other more active methods.

In situ natural attenuation processes include:

-biodegradation

-sorption

-dispersion

-volatilization

-dilution

-chemical transformation

Reference: Monitored Natural Attenuation Final Policy OSWER Directive 9200.4-17P, dated April 21, 1999, EPA document number EPA-540-R-99-009. Hardcopy available in Workshop Toolbook. The document also can be downloaded from the EPA web site at: www.epa.gov/swerust1/directive/d9200417.html

Notes:

Unless #1 is of sufficient quality and duration, #2 and possibly #3 will be required.

Historical data may include soil, groundwater, air, and NAPL phases, and three-dimensional profiles of contaminant concentration changes with time. Once it is known what chemicals and phases were used at the site, the Conceptual Site Model approach may be useful to evaluate chemical distribution among physical phases at the site as part of a monitoring program. Fugacity is one tool for evaluating the distribution of chemicals among physical phases at the site.

Geochemical data includes changes in concentrations of oxygen, iron, nitrate, sulfate, manganese, and methane (terminal electron acceptors).

Field or microcosm studies involve demonstration of biodegradation using site samples with naturally occurring microbial populations. Mineralization studies may be conducted to show biodegradation to CO_2, transformation intermediates may be characterized, and toxicity tests may be used to demonstrate decrease in toxicity. Poisoned control microcosms are used to separate abiotic chemical transformation from biological transformation.

Field-Scale Evaluation of MNA

1. Determine if natural attenuation is occurring using geochemical data

2. Determine groundwater flow and solute transport

3. Locate sources, releases, and receptors

4. Estimate the rate of natural attenuation

5. Compare the rate of transport to the rate of attenuation

6. Compare conditions at point of discharge to acceptable criteria

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Notes:

1. Geochemcial data refers to use of oxygen, iron, nitrate, manganese, sulfate, and carbon dioxide by microorganisms to degrade organic contaminants. Decreases in concentration may indicate use by microorganisms, and therefore add evidence for biodegradation.

2. Groundwater flow and solute transport data are used to determine the rate of transport of the target contaminants taking into account the influence of dilution, sorption, dispersion, and volatilization.

3. Sources, releases, and receptors are identified as part of the Conceptual Site Model and Environmental Indicators evaluation. The absence of contamination in a downgradient well means nothing until it is demonstrated that the downgraident well is in a flow path from the source of contamination. The absence of evidence is not the evidence of absence.

4. Rate of natural attenuation using first order rate kinetic approach is used in the model Bioscreen to evaluate natural attenuation, and has been found appropriate for a variety of sites.

5. Compare rate of transport of target chemicals (plume) to rate of attenuation to determine if plume is expanding or contracting. Can use this information in the evaluation of Environmental Indicators.

6. Are conditions at the point of discharge protective of public health and the environment? Does discharge meet regulatory criteria?

Use of Monitoring Wells in Determination of Natural Attenuation

The absence of evidence
is <u>NOT</u>
evidence of absence

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Notes:

The absence of contamination in a downgradient monitoring wells means nothing until it is demonstrated that the downgradient well is in a flow path from the source of contamination.

Final EPA Directive 9200.4-17P

- Title: "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites"

- Signed on April 21, 1999

- Available at: www.epa.gov/swerust1/directiv/d9200417.htm

- Hard copy also available in Workshop CD

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Notes:

Directive signed by Acting Assistant Administrator, and Directive cover memo signed by EPA Directors from the Office of Solid Waste (RCRA Corrective Action), Office of Emergency and Remedial Response (Superfund), Office of Underground Storage Tanks, Federal Facilities Restoration and Reuse Office, and Technology Innovation Office. Sign-off by these Directors reflects the cross-program coordinated effort that went into the development of the Directive.

Cover memo also includes names and phone numbers of EPA Headquarters, Regional and Office of Research and Development (ORD) contacts representing Superfund, RCRA, and UST programs.

What is the Purpose of Directive?

- Clarifies EPA's policies regarding use of MNA for soils and groundwater

- Appropriate to use as guidance for developing, evaluating, and approving MNA remedies

- Not intended to be detailed technical guidance

- Does not scale back EPA goals for remediation of soils or groundwater

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Notes:

While the directive does not focus in detail on technical aspects of MNA remedies, it does provide an extensive list of references for users to pursue technical guidance.

"EPA remains fully committed to its goals of protecting human health and the environment by remediating contaminated soils, restoring contaminated groundwaters to their beneficial uses, preventing migration of contaminant plumes, and protecting groundwaters and other environmental resources," - EPA Directive 7200.4-17P, page 1.

Definition of MNA in Directive

"The term 'monitored natural attenuation' refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) **to achieve site-specific remediation objectives** within a time frame that is reasonable compared to that offered by other more active methods."

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Notes:

The Directive continues with the following statement regarding natural attenuation processes:

"The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biologic processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include: biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants."

Provides Useful Background Information Dealing With...

- Contaminants of concern, including transformation products

- Specific characteristics associated with MNA for petroleum-related contaminants, chlorinated solvents, and inorganics

- Cross-media transfer of contaminants

- Advantages and disadvantages of MNA

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Notes:

The Directive cautions those considering MNA to recognize that while some (perhaps the more obvious) contaminants may be attenuating, other (perhaps less obvious) contaminants may be resistant to attenuation processes.   For example, those considering MNA for gasoline often focus on the benzene, toluene, ethylbenzene, and xylene (BTEX) component, which has been found in a significant number of settings to attenuate sufficiently to afford adequate protection. However, a common additive to gasoline, methyl tertiary-butyl ether (MTBE), has been found to migrate significant distances and threaten down-gradient water supplies in the same settings where the BTEX component of the plume has stabilized or diminished due to MNA.

MNA remedies, involving cross-media transfer of contamination, should include a site-specific evaluation of the potential risks posed by the contaminant(s) once transferred to a particular medium. The Directive states EPA's preference for MNA remedies that rely more on those processes that destroy or degrade contaminants rather than just transfer them from one medium to another.

Guidance Deals With Topics Including...

- Role of MNA in EPA cleanup programs

- Demonstrating the efficacy of MNA

- Sites where MNA may be appropriate

- Reasonable timeframe

- Remediation of sources

- Performance monitoring

- Contingency remedies

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Some Major Messages

- MNA is appropriate at many, **but NOT all, sites**

- MNA is not a **walk-away, no-action, or presumptive** remedy

- MNA needs to be **technically** justified by the proponent

- MNA needs to address all contaminants of concern, **not just most obvious**

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Some Major Messages (Cont'd)...

- MNA used typically with other **"active"** measures, especially those focused on **sources**

- MNA is __most__ appropriate for groundwater where plume is **already stable or shrinking** (i.e., where plume is not migrating)

- MNA should be able to **achieve objectives in a reasonable timeframe**

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Notes:

Determining what is a reasonable timeframe should be a site-specific decision; however, the Directive recommends that the following factors be considered when evaluating the "reasonableness" of a proposed timeframe associated with an MNA remedy:

- Current as well as future use of the affected resource;
- Relative timeframe in which the aquifer may be needed;
- Subsurface conditions and plume stability, which can change over an extended timeframe;
- Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;
- Uncertainties regarding the mass of contamination in the subsurface and predictive analyses;
- Reliability of monitoring and institutional controls over long periods;
- Public acceptance of the timeframe likely needed to reach objectives; and
- Availability of adequate funding of monitoring over the expected timeframe.

Some Major Messages (Cont'd)...

- Progress should be **carefully monitored**

- **Contingency measures** should be included when MNA is selected based mostly on predictive analysis

- A cleanup is **<u>not</u>** completed until **cleanup objectives** set by implementing Agency **have been achieved**

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NAPL Recovery

- Bioslurping

  - Enhanced recovery using applied vacuum

  - Compare with conventional gravity removal technique

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Bioslurping

- Product and water are withdrawn as a liquid column, slugs, droplets, or vapor

- Smearing of LNAPL product minimized

  - Water table not depressed

  - Horizontal permeability > vertical permeability

- Applied to LNAPLs including petroleum hydrocarbons, gasoline, jet fuels, diesel, and heating oils

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Notes:

Product and water are drawn up the slurp tube as a liquid column, slugs, droplets, or vapor. Product and water can be drawn up as a column provided liquid flows into the well fast enough and depth below the ground surface does not exceed roughly 25 feet; otherwise, product is "slurped" up through the entrainment.

Because the water table is not depressed, vertical "smearing" of light nonaqueous phase liquids (LNAPLs) is minimized. In almost all natural settings, horizontal permeability is greater than vertical permeability.

The liquid stream extracted from the bioslurper well flows through a vapor-liquid separator to the vacuum pump and to an oil-water separator.

Bioventing of soils in the vadose zone is achieved by withdrawing soil vapor from the recovery well.

Bioslurper System
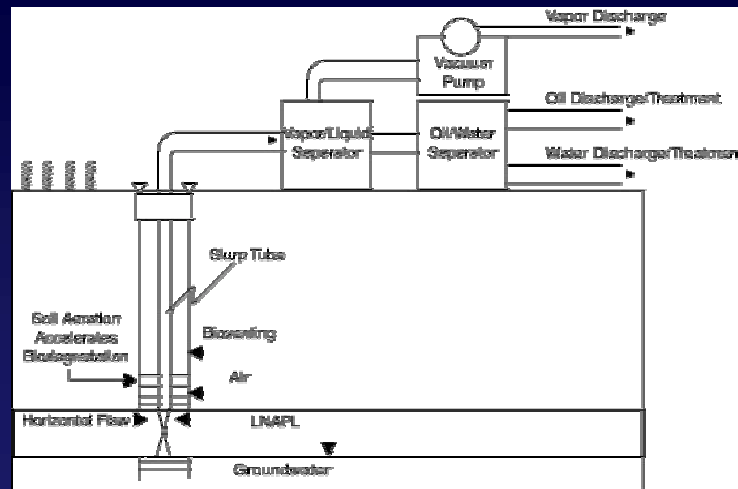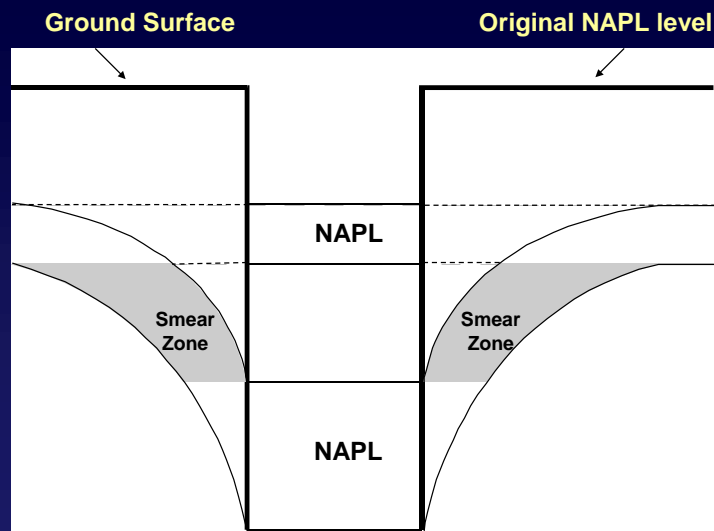
Notes:

Components of the bioslurping system include:

- •Slurp tube extending to LNAPL
- •Vacuum extraction pump
- •Vapor-liquid separator
- •Oil-water separator

A bioslurper system consists of a "slurp" tube that extends into the LNAPL free product layer in the well.

Product is drawn up by the vacuum extraction pump. The system pulls a vacuum of as much as 500 millimeters of mercury (mm Hg) on the recovery well to create a pressure gradient to draw LNAPL into the well. The bioslurper is operated to cause little drawdown in the aquifer, minimizing the quantity of extracted groundwater requiring treatment.

Recovered fluids and vapors are separated so free product can be recovered and recycled. Ground water and soil vapors may be treated (when required) and discharged.

Notes:

Gravity LNAPL recovery is conventional, not innovative, and is shown for comparison with Bioslurping. Water tables depression pump lowers water level and causes of "cone of depression" for LNAPL to enter the recovery well. Change in hydraulic gradient provided by lowering the level of water and LNAPL provides to driving force for LNAPL movement into the recovery well.

Drop in LNAPL level causes "smearing" of NAPL across aquifer due to capillary forces in aquifer material, creating residual saturation of NAPL in pores of aquifer. Residual saturation is more difficult to remove than free product.

The trapped residual in the aquifer material constitutes a continuous source of contamination to groundwater that will persist after product removal from the water table is completed.

Advantages of Bioslurping

- Enhanced recovery due to vacuum driving force
- Non-smearing of aquifer since LNAPL flows horizontally
- Minimal ground water extracted
- Promotes biodegradation
- System can be reconfigured for bioventing

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Notes:

Recovery of product is enhanced over conventional methods because, as opposed to gravity alone (groundwater cone of depression), the vacuum provides a driving force.

Containment flow proceeds along a horizontal flow path that reduces entrapment of product or the "smearing" that is typical of dual pump systems.

Minimal ground water is extracted. Extraction of ground water usually increases costs significantly because of the need for aboveground treatment and potential additional permitting requirements.

As vapor is extracted from the subsurface, oxygen in air drawn from the surface promotes aerobic biodegradation (bioventing) throughout the vadose zone and capillary fringe.

After product recovery is completed, bioslurper system can be reconfigured into a full-time bioventing system to remediate the contamination in the vadose zone.

Limitations of Bioslurping

- Works only with LNAPLs

- Not effective at depths of greater than 25 feet below ground surface

- Requires close monitoring and frequent maintenance

Notes:

Bioslurping works only with LNAPLs.

Contaminants cannot be drawn (pumped) as a column if the free-phase layer is at a depth of greater than 25 feet below ground surface (bgs)

Bioslurping requires close monitoring and frequent maintenance to keep the system operational, because three media (product, vapors, water) must be treated or disposed of simultaneously.

Surfactant and Cosolvent Flushing: Status

- Over 30 field/pilot scale completed or in progress
- About 10 full scale/commercial completed or in progress
- Majority of projects target DNAPLs (TCE)
- Few cosolvent-only projects
- Major Issues
  - Recovery and re-injection (recycling)
  - How surfactants affect bioremediation
  - How flushing can be coupled with other technologies

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Definitely need more cost data. One report on costs from a demonstration site indicated that it was quite expensive, but this was at a demo which is typically an expensive undertaking to demonstrate the efficacy of a technology, not the costs.

Also need to develop uniform ways of determining costs. This is an ongoing battle with many technologies - do you report in $/gall treated or $/soil treated or $/cont. removed or others? Many of the projects report costs in different ways. (RTDF is working on this)

It is also hard to determine how effective the technology was - if you don't know how much dnapl was there to begin with, how do you know the removal efficiency.(RTDF is working on this)

There is a question as to when do you cease application of the s/c. How clean is clean and what are the better technologies to use a polishing steps after bulk napl is removed? (RTDF)

Each state has different reg. On re-injecting treated gw. It is difficult (and expensive) to design systems if in some states you can re-inject h20 that still has cont. in it but in others you can virtually only inject clean h20. (TIO working on this)

Surfactant and Cosolvent Flushing

Description
- Added through trenches or injection wells to mobilize or solubilize NAPLs
- Surfactants enhance mobility of hydrophobic organic compounds by lowering interfacial tension between water and NAPL
- Cosolvents increase solubility
- Recent applications use surfactant/cosolvent mixtures
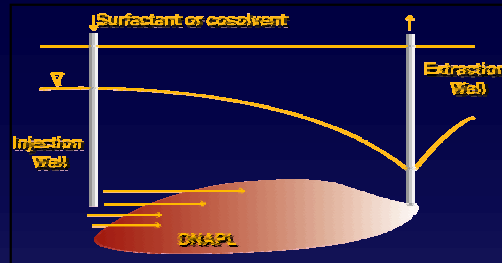
Contaminants Treated
- VOCs, SVOCs
- Petroleum hydrocarbons
- PCBs
- Pesticides

First field tests performed 7 years ago. Most projects are for DNAPLs, but some for LNAPLs.

This is a bulk or residual NAPL removal process more than a polishing step.

Technology under development by various industries and academic institutions. Funding has come from EPA, DOE, DOD. Several consulting firms now do this commercially (INTERA,RADIAN).

Developed mainly because p&t have failed

Many field tests conducted solely for the purpose of feasibility and research and demonstration of the technology. Now the field tests are focused on actually cleaning up sites - one being used at a dry cleaners site in FL.

Surfactants: DOWFAX 8390, Sulfosuccinate, OT/Tween, Triton-x-100

Cosolvents: Alcohol, ethanol, n-pentanol

Often a mixture of surfactants/cosolvents is used

Surfactant and Cosolvent Flushing

Pros

- Treats wide range of contaminants
- Removes NAPLs
- Enhances existing pump and treat systems with little modification

Cons

- Can increase plume size and concentrations
- Difficult to recover surfactants; recovery increases costs
- Difficult to remove contaminants from extracted groundwater with surfactants
- Can cause well fouling
- Some regulatory hurdles for reinjecting treated groundwater

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The hardest part is to identify the DNAPL and quantify how much is there. Several tests have been developed to help with this process.

Difficult to use in heterogeneous low permeability soils.

Lab studies need to be performed to determine the correct surfactant/cosolvent for the project. Each project may require different s/c mixtures due to nature of cont. and site geochemistry.

Large volumes of water, contaminants, and s/c are generated that must be separated and treated at the surface (this is a very costly step).

Some investigators are looking into ultrafiltration, solvent extraction, air stripping, vacuum steam stripping, photochemical treatment to separate h20/cont./s/c.

Because many flushing projects are targeted at DNAPLs there is a concern about mobilizing the dnapl to a clean part of an aquifer or into a new aquifer. This is a significant concern. You need to get hydraulic control to make sure that you are not going to lose any DNAPL.

Passive Treatment Walls
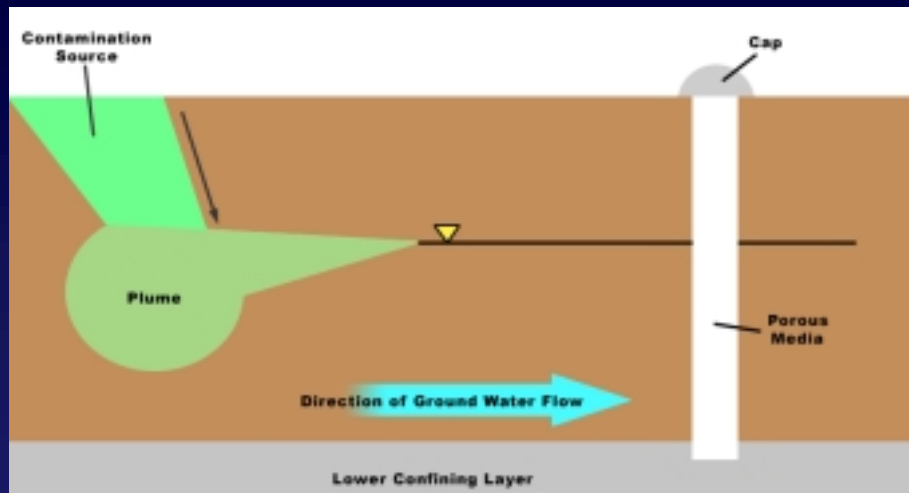
Notes:

An in situ permeable reactive wall is installed downgradient of a groundwater containment plume. The wall will intercept and react with contaminated groundwater. The process represents a low-cost, low-maintenance, remedial alternative for groundwater treatment.

The barrier material consists of a reactive medium that will degrade or retain the containment plume. Construction specifications for the barrier are based on the retention time required for specific contaminants.

Some reactive walls containing zero valent iron have been used to dechlorinate solvents dissolved in groundwater such as trichloroethylene and dichloroethylene.

Passive Wall Process Components

- **Reactive media**
  - zero valent metals (for example, iron filings)
  - chelators
  - sorbent materials (for example, activated carbon)
  - oxygen releasing compounds (ORC)

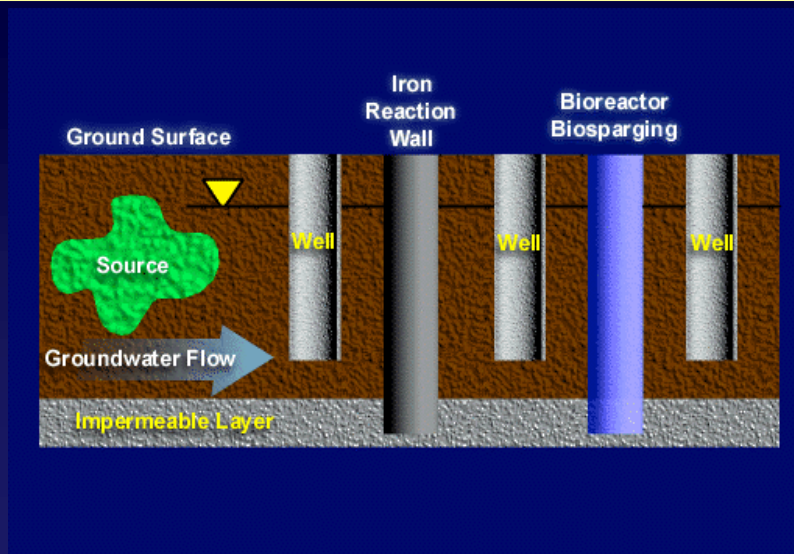- **Vertical barrier and "funnel and gate" components**

Notes:

Passive walls use reactive media to treat contaminant plumes. Such media have included:

-zero valent metals to treat halogenated compounds

-chelators to treat metals

-sorbent materials

-gravel or other porous media through which air is sparged

Design and construction techniques for vertical barrier walls are used to "key" the treatment wall into the aquitard or lower confining layer.

Engineered fill materials commonly are used to construct "funnel and gate" systems to direct groundwater through a relatively impermeable funnel to the permeable and reactive wall (gate), reducing the amount of reactive media needed. The low-permeability funnel is typically constructed of sheet piling or soil-bentonite. Low-permeability capping material, such as concrete or bentonite, is recommended to cover and protect the wall and limit surface infiltration.

Example Process of Using Passive Treatment Walls

Iron Reaction Wall

Bioreactor Biosparging

Ground Surface

Source

Well

Well

Well

Groundwater Flow

Impermeable Layer

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Notes:

Reactive walls may be staged in series to remediate different types of contaminants consecutively or to provide secondary or further treatment. For example, in the illustration above an iron reactive wall could dechlorinate chlorinated hydrocarbons. The resulting hydrocarbon plume could be bioremediated by introducing oxygen. The oxygen could be introduced, for example, through using oxygen-releasing compounds or by sparging with air. The extent and rate of treatment would be monitored through a series of groundwater monitoring wells.

Applications of Passive Treatment Walls

- Contaminated groundwater in shallow contained aquifers

- Organic and inorganic substances

- High concentrations of contaminants

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Notes:

To ensure capture of the contaminant plume, the contaminated water-bearing zone should be isotropic and have a laterally contiguous confining unit. It is important to have site characterization data on groundwater flow rate and direction, hydraulic conductivity, and integrity of the confining layer.

Volatile chlorinated hydrocarbons are easily degraded using iron filings. Sorptive media, such as granular activated carbon (GAC), can treat petroleum hydrocarbons, chlorinated hydrocarbons, and SVOCs. Oxygen-releasing compounds can effectively promote the bioremediation of petroleum hydrocarbons. Research also has been done to demonstrate aerobic co-metabolism of chlorinated solvents. Selected metals such as chromium have been treated in the dissolved phase and converted to less toxic and less mobile valence states.

Concentrations of contaminants generally are not a limiting factor. The size of the contaminant plume and retention time required within the reactive medium dictate the thickness of the wall. Dense nonaqueous phase liquids (DNAPLs), if present, could exhaust or migrate through the permeable treatment media.

Advantages of Passive Treatment Walls

- Effective in meeting contaminant reduction goals

- Minimal Operation and Maintenance (O&M) requirements

- Effective in both high- and low-permeability soils

Notes:

Passive treatment walls are an in situ technology that leaves little or no treatment residuals. Pilot and full-scale projects have shown excellent results in the treatment of volatile organic compounds (VOCs), including perchloroethylene (PCE), trichloroethylene (TCE), and vinyl chloride (VC).

Operation and Maintenance (O&M) requirements for the wall itself are minimal. Monitoring requirements vary according to the specifications of the regulatory authority.

Unlike pump-and-treat systems, SVE, or air sparging, which work best in   high permeability soils, passive treatment walls can work well in low- permeability soils as well.

Limitations of Passive Treatment Walls

- Need contiguous confining layer
- Reactive media may lose reactive capacity in time
- Sorptive media must be replaced periodically
- Biofouling may occur
- Chemical precipitation of dissolved solids may occur
- May not be cost-effective for deep confining layers
- Thorough groundwater modeling is essential

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Notes:

Subsurface characteristics can be limiting. The medium must have a contiguous confining layer into which the wall can be keyed.

Reactive media may lose reactive capacity over time. The medium must be replaced periodically as sorptive sites become saturated.

Biofouling of the medium can occur in the presence of naturally occurring microbial activity and limit the chemical reactivity of the medium.

Depth to the confining layer affects cost. Sheet piling can be used to place barriers inexpensively to depth of about 30 feet. A backhoe and slurry can be used to reach depths of about 50 feet, and a clamshell or longstick backhoe can reach a depth of about 80 feet. However, at depths greater than 30 feet, placement costs increase exponentially.

Groundwater modeling is essential to ensure capture of the plume and adequate retention time in the wall. Funnel and gate systems alter groundwater flow patterns.

Soil Vapor Extraction (SVE) with Enhancements

- SVE is a physical separation technique that volatilizes and recovers contaminants from the soil

- SVE processes include:
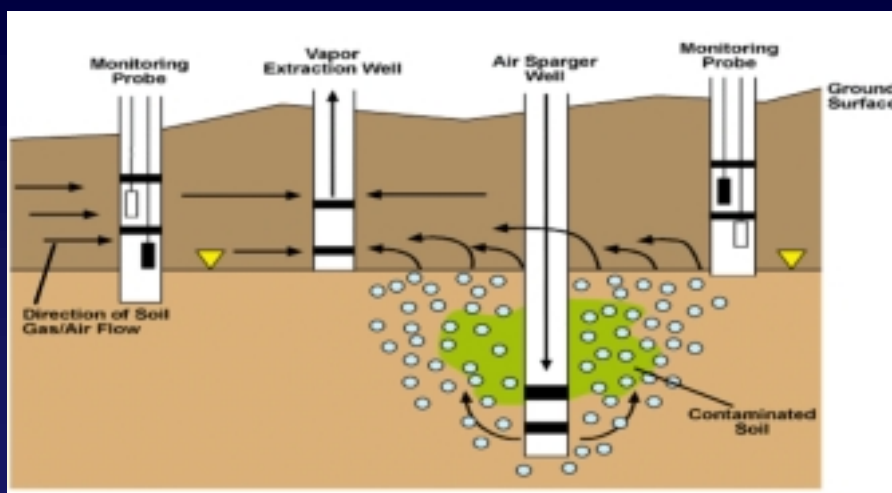 - air sparging
  - directional drilling

Notes:

SVE is an in situ process that removes volatile organic compounds (VOCs) from the vadose zone by application of vacuum through a system of extraction wells placed in the unsaturated zone.

SVE is known by several other names:

-soil venting

-vacuum extraction

-in situ air stripping

-in situ volatilization

-enhanced volatilization

Notes:

Air sparging is a physical separation process that involves injecting air into the saturated zone to volatilize dissolved contaminants. The principle of air sparging is based on the relative tendency of a compound to exist in the vapor phase rather than the dissolved (water) phase. This concept is expressed as Henry's Law.

The technology is particularly applicable for compounds with Henry's Law Constant values greater than 10^{-3} atm-m^3/mole. Refer to TOOLBOOK, tab labeled "Conceptual Site Model (CSM)," and document "SUBSURFACE CONTAMINATION REFERENCE GUIDE," Section 2.2 titled SOIL VACUUM EXTRACTION.

When air sparging is employed, compressed air is forced into the saturated zone through an injection well screened beneath the water table. As air moves through the saturated zone, VOCs present in the water are stripped and travel to the unsaturated zone. The sparged vapors are captured in the unsaturated zone by vapor extraction wells and treated above ground.

Injection wells may be either vertical or horizontal. Refer to the next section on directional drilling.

Air Sparging System
(More Accurate Perception)

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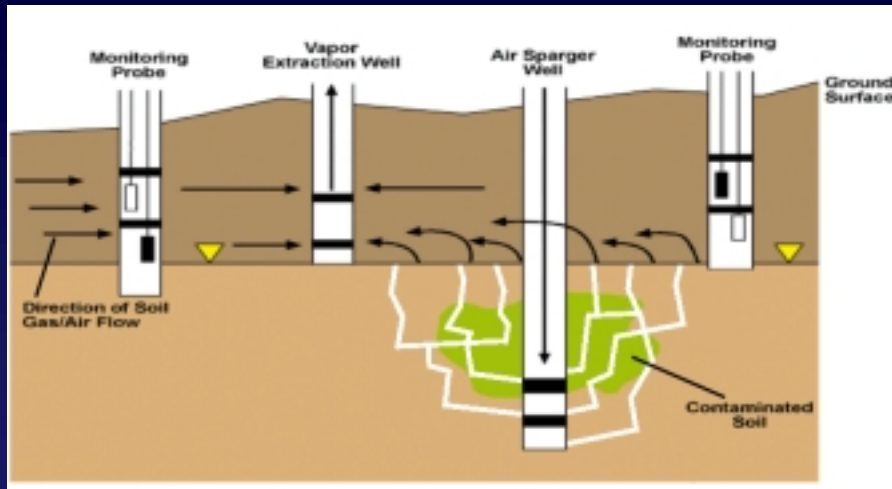
Applications of Air Sparging

- Unconfined aquifer

- Permeable (coarse-grained) soils

- Shallow contaminant plumes

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Notes:

Air sparging is applicable only under unconfined aquifer conditions. Confining layers restrict vertical air flow and prevent the recovery of sparged contaminants.

Air sparging is implemented most easily and effectively in homogenous, coarse-grained (permeable) soils. Coarse soils provide a medium for even distribution of air, allowing for optimum mass transfer efficiencies and more effective removal of VOCs.

Air sparging is employed most commonly for contaminant plumes present at less than 30 feet below the water table. Although air sparging can be implemented at greater depths, the potential for uncontrolled migration of sparge vapors increases with increasing depth because of the potential for channeling along subsurface features. Sufficient vadose zone depth is also required to enable the vapor recovery system to perform adequately.

Applications at field scale has been primarily for BTEX contamination.

Limitations in Air Sparging

- Contaminant mobilization

- Limited effectiveness in heterogeneous soils

- Limited effectiveness in impermeable, fine-grained soils

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Notes:

Sparging may influence the movement of contaminants in an aquifer more than the natural gradient. The lateral migration of air within the saturated zone generally will be accompanied by a lateral spread of the dissolved contaminant plume. Where dense nonacqueous phase liquids (DNAPLs) are present, air sparging activities have been observed to disperse the separate phase, increasing the size and concentration of the VOC plume. The overall design of all remediation systems should incorporate measures to control the potential spread of the contaminants.

The effectiveness of air sparging is limited by the presence of soil heterogeneities, which can channel sparge vapor flow and result in inefficient mass transfer. As a result, the remediation time frame in heterogeneous soil may be dictated by the time required for contaminants to diffuse from zones of lower permeability to those of higher permeability.

Sparging in impermeable, fine-grained soils may result in formation of fractures or development of gas pockets. Injection of high-pressure air into an impermeable soil may cause fracture paths and vapors flow, resulting in poor contact between sparge vapors and contaminated soils. Pockets of gas may decrease soil permeability and impede the effectiveness of an air sparge system. They can also cause lateral displacement of groundwater, which, in the absence of groundwater controls, can result in lateral displacement of contaminants.

DIRECTIONAL DRILLING
Horizontal Drilling Process

Well Screen and Casing

Directional Drilling Unit

Backreaming Tool

Drilling String
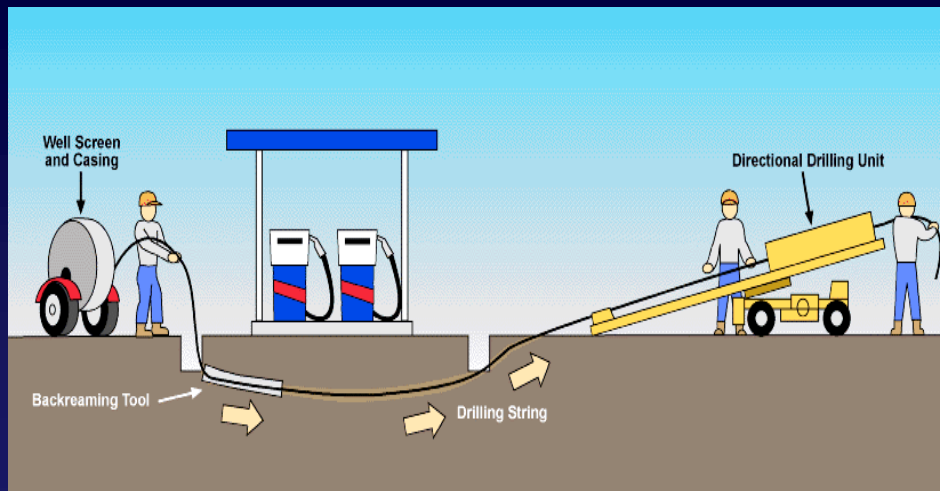
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Notes:

Directional drilling employs specialized drill bits to advance curved boreholes in a controlled arc for installation of horizontal wells or manifolds for SVE and sparging technologies.

The borehole is initiated at a shallow angle, typically 5 to 30 degrees to the ground surface. After the arrival at a target depth, the drilling tool is reoriented to drill a horizontal borehole. Electronic sensors located in the drill tool guidance system provide orientation, location, and depth data to the driller.

Directionally drilled boreholes can be completed blind, terminating in the subsurface, or can be reoriented upward to return to the ground surface.

Advantages of Directional Drilling

- Allows application of SVE in areas not accessible by vertical drilling

- Concentrates remediation along the geometry of the contaminated zone and eliminates need for multiple vertical wells

- Allows placement of well screen immediately above the water table and over an extended area

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Notes:

Directional drilling technologies allow application of SVE in areas not generally accessible by vertical drilling techniques, such as under large aboveground structures.

Directional drilling can also increase the efficiency of SVE by concentrating subsurface remedial activities along the geometry of the contaminated zone and by increasing the zone of influence of a single extraction well. In extensive operations, use of horizontal wells can eliminate the need for numerous vertical wells, eliminating the need for redundant hardware for SVE systems.

Horizontal wells allow the placement of extraction well screens immediately above the water table and over an extended area.

Limitations of Directional Drilling

- Installation difficult for:
  - Low permeability soils
  - Cobbles and coarse gravels

- Costs increase dramatically with depth

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Notes:

Installation of horizontal wells in soils and clays can be difficult because of the reduction of the specific capacity of the well caused by the smearing of silts and clays against the borehole wall. This can result in lower effective permeabilities.

The presence of cobbles and coarse gravels may complicate horizontal drilling and result in increased costs for well installation.

Horizontal wells are most commonly installed to depths of 50 feet to 80 feet, but have been installed to depths of 235 feet. Approach lengths and installation costs increase considerably with well depth.

Bioventing

- Treatment supplies oxygen in the vadose zone

- Oxygen is used by microorganisms in soil to initiate aerobic biochemical conversion and degradation of hydrocarbons

  For benzene, complete biodegradation (biological mineralization) is described as follows:

$$C_6H_6 + 7.5\,O_2 \longrightarrow 6\,CO_2 + 3\,H_2O$$

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Notes:

Bioventing is an in situ technology that supplies oxygen to the subsurface vadose zone to enhance the aerobic microbial biodegradation of contaminants.

Bioventing provides oxygen to unsaturated soils by injection of air or another source of oxygen, such as hydrogen peroxide or oxygen releasing compounds (ORCs). Oxygen also can be introduced by vacuum extraction wells that simply draw air from the surface or from inlet wells. The oxygen is used by indigenous microorganisms.

Bioventing generally is effective for nonchlorinated hydrocarbons, such as petroleum and creosote compounds, and hydrocarbons with low numbers of chlorine atoms, such as vinyl chloride.

Research has shown that oxygen concentrations as low as 2% by volume in soil are sufficient to stimulate aerobic biodegradation.

Schematic of Bioventing

Air Injection   Vacuum

Contaminated Soil   Soil Gas Monitoring

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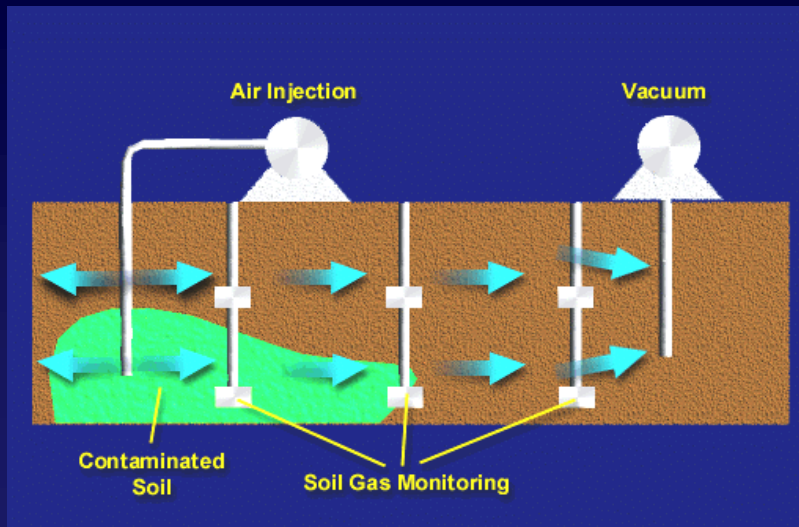
Notes:

Bioventing may incorporate air extraction wells or air injection wells. Air extraction wells draw air from the ground surface through contaminated soils, while air injection wells push air into the subsurface.

If volatile contaminants can be controlled as shown in the diagram above, VOCs can also be treated using bioventing to biodegrade contaminants below ground surface, thus eliminating emissions to the surface and the need for above-ground treatment systems.

Sometimes SVE systems are used in conjunction with bioventing systems. Following removal of volatile contaminants, SVE systems may be converted to bioventing systems by reducing extraction flow rates. Use of an SVE system in a bioventing capacity targets less volatile contaminants, and may reduce operating costs by decreasing vapor treatment requirements or eliminating them altogether.

Application of Bioventing

- Permeable unsaturated soil

- Temperature affects rate of reaction

- Aerobically biodegradable fuel hydrocarbons and some chlorinated VOCs

- Hydrocarbons that cannot be removed by SVE alone

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Notes:

Bioventing is most appropriate for permeable, unsaturated soil where air (as the carrier for oxygen) can be moved through the soil to supply oxygen for biodegradation to the contaminated area.

The temperature of the subsurface generally affects the rate of biodegradation. The higher the temperature, over the range of 5° to 35° centigrade, the faster the rate of treatment. However, where subsurface environments are naturally cold (e.g., Alaska) indigenous microorganisms are acclimated to optimum performance at natural environmental temperatures.

Bioventing is designed primarily to treat aerobically biodegradable and semivolatile fuel hydrocarbon constituents (BTEX). However, some chlorinated volatile organic compounds (e.g., vinyl chloride) are aerobically biodegradable and are appropriate for the application of bioventing. And some chlorinated compounds, such as TCE, can be co-metabolically biodegraded under aerobic conditions when a substrate is provided (methane for TCE).

Bioventing is also applicable to less volatile compounds, for example, higher molecular weight polycyclic aromatic hydrocarbon (PAH) compounds, that do not readily partition to the air phase, but are aerobically biodegradable.

Limitations of Bioventing

- Limited to aerobically biodegradable chemicals

- Limited effectiveness in:
  - Low permeability soils
 - Soil with low moisture content

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Notes:

Chemicals that are not aerobically biodegradable are not amenable to treatment using bioventing (for example, perchloroethylene (PCE) or carbon tetrachloride (CT)).

Low-permeability soils limit the ability to supply oxygen to the contaminated area, thus reducing or eliminating biodegradation.

Low moisture content in soil reduces microrganism activity and results in reduced biodegradation rate and extent, even when oxygen is present through the application of bioventing. Because bioventing tends to dessicate soils, moisture may need to be added to soil through surface irrigation to maintain adequate moisture for microorganisms.
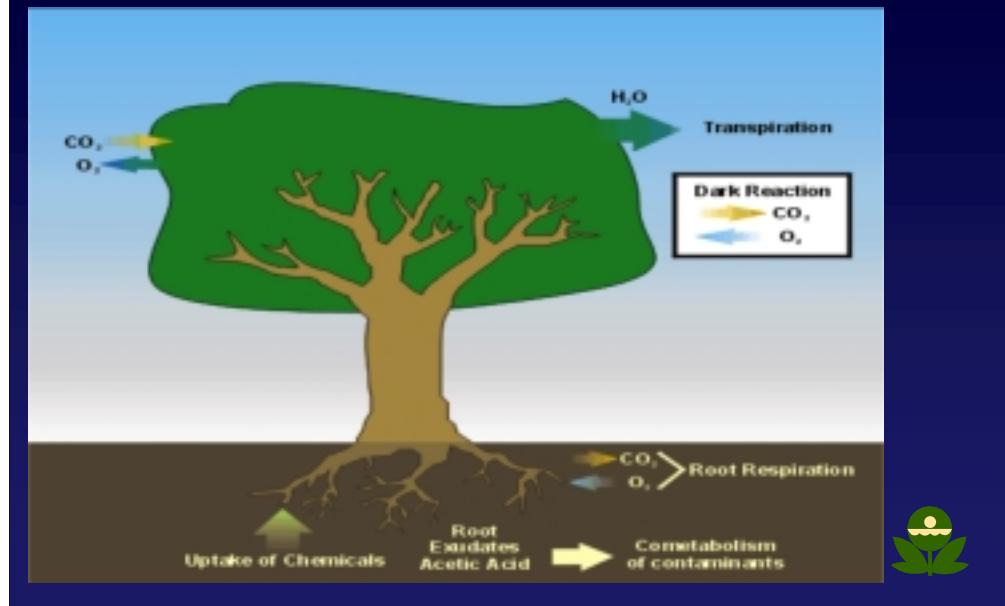
Notes:

Phytoremediation is the use of plants to remove, contain, accumulate, or degrade environmental contaminants in soil, groundwater, surface water, sediment, and air. That definition applies to all biological, chemical, and physical processes that are influenced by plants and that aid in the cleanup of contaminated substances.

Plants can be used in site remediation through degradation and mineralization of organic chemicals and through accumulation and concentration of inorganic chemicals, including heavy metals, from soil into above ground plant tissues.

Phytoremediation is still in the relative early stages of development and is being field-tested at various sites in the United States.

Types of Contaminants and Plants

Contaminants

BTEX

PAH

Chlorinated Solvents

Metals

Nutrients

Pesticides

Explosives

Radionuclides

Plants

Trees (poplar, willow, cottonwood, birch)

Grasses (Bermuda, rye, sorghum, fescue)

Legumes (clover, alfalfa)

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Notes:

Contaminants that are potentially treatable using phytoremediation include nonhalogenated and halogenated organic chemicals, inorganic chemicals (nutrients, metals, and radionuclides), pesticides, and explosives. For chemicals that are hydrophobic (associated with the soil solid phase), plant roots may be used to bring microorganisms in the plant root zone (rhizosphere) into contact with the chemicals.

Plant types that are used depend upon the depth of contamination, ability of plants to grow in a given climate, and site specific situations.

At Aberdeen Proving Grounds, 183 hybrid poplars were planted at a cost of $15,000 over a one-acre site to remediate groundwater contaminated with 170 mg/L 1,1,2,2-tetrachloroethane and 61 mg/L trichloroethyene (TCE). Although groundwater concentrations have not been reported, tree tissue data indicate that evapotranspiration of volatile contaminants occurs.

At the Edward Sears site in New Jersey, 208 hybrid poplars were planted at a cost of $25,000 over a one-half-acre area to remediate groundwater contaminated with PCE and TCE. While TCE was reduced from 28 ug/L to 1 ug/L in 9 months, results thus far cannot be used to differentiate between evapotranspiration or soil volatilization.

Mechanisms of Phytoremediaton

- Extraction of chemicals
- Stabilization of soils
- Degradation of chemicals within the plant or root zone
- Volatilization of chemicals
- Hydraulic control of leachate
- Vegetative caps

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Notes:

Hyperaccumulators are defined as plants that transport metals from the soil and contain more than 0.1 percent, dry-weight basis, of Ni, Co, Cu, Cr, or Pb, or 1.0 percent of Zn or Mn.

Volatilization of chemicals, while less desirable than degradation, may be preferable to the prolonged risk of groundwater contamination.

Hydraulic control (phytohydraulics) uses plants with high transpiration rates to take up large quantities of water and reduce subsurface water content, thereby achieving hydraulic control of the site to prevent further migration of contaminants.

Limitations of Phytoremediation

- Limited to shallow soil, streams, and groundwater
- Longer remediation time
- Toxicity and fate of degradation products is unknown
- Potential for contaminants to enter food chain
- Design must incorporate soil and climate conditions

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Notes:

Phytoremediation is limited to the depth and extent of root zone establishment. For hydraulic control, it is limited to the depth to which it can affect water movement.

Longer remediation times are required due to several factors, including rate of plant establishment, rate of growth of the root zone, and low biological activity (low rate) in colder seasons.

Degradation products may be toxic and more mobile or less amenable to phytoremediation than the parent contaminant. More research is necessary to address this topic.

Contaminants may enter the food chain through uptake into grasses and parts of trees that are subsequently consumed.

In matching a species for a particular containment application at a site, criteria related to site soil and climate must be considered. Locally available indigenous plants are generally best suited for establishment and growth.

Soil Washing

- Soil washing is an aqueous based ex situ technology that uses mechanical processes to separate and wash soil particles

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Notes:

Soil washing removes contaminants in two ways: (1) dissolution or suspension of contaminants in the wash solution, and (2) separates particles by size.

Contaminants associate more with organic carbon, silt, and clay by sorption (fine grained soil mineral fraction)

Contaminants associate less with sand and gravel (coarse grained soil mineral fraction

Aqueous Soil Washing Process
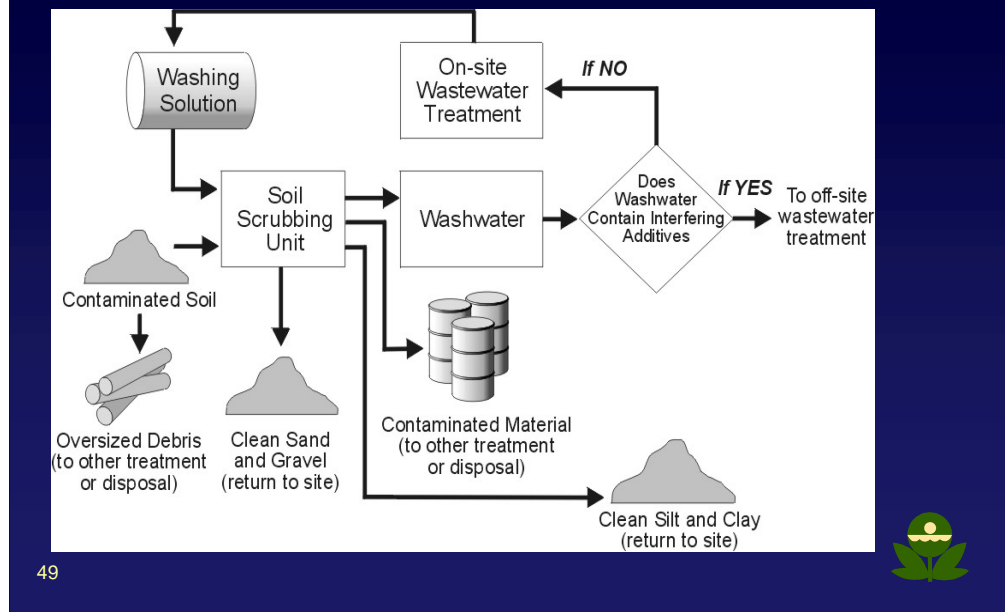
Notes:

Four phases of soil washing:

1. Soil Preparation. Pretreatment of soil to remove oversized material. Creates a more homogeneous feed stream for delivery to the soil washing/scrubbing plant. Common sizes removed are ½ inch and larger. Example, at the Libby Montana, wood preservative site, contaminated soil was deparated into two classes: (1) materials larger than ½ inch diameter, and (2) materials smaller than ½ inch. Example, soil for the Electric Power Research Institute was separated into two fractions: (1) larger than soil particles (2 millimeters in diameter), and (2) soil particles (sand, silt, and clay). Particle classification and separation is a function of the type and requirements of the soil washing unit.

2. Soil Washing. Aqueous washing solution removes pollutants from solids. Washing methods include surface attrition, acid or base amendment for solubilization, mixing with solvents for dissolving contaminants released from solid to the liquid fraction. Solids are separated and sent for further processing.

3. Wastewater Treatment. Wastewater will contain primarily fine-grained solids, dissolved salts, organic humic compounds, free floating hydrocarbons, etc.

4. Management of Residuals. May be disposed in a regulated landfill, or may require further treatment.

Advantages of Soil Washing

- Relatively low-cost alternative for separating wastes

- Closed treatment system that permits control of ambient volatile emissions

- Can reduce the volume of contaminated media and the concentrations of contaminants

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Notes:

Soil washing can be used as a pretreatment step to concentrate contaminants and reduce the volume of wastes that require further treatment, thereby reducing the overall costs of a cleanup project.

Because the technology is primarily a separation and volume reduction process, it frequently is used with other technologies.

Examples: Wood preserving site (Libby, Montana), and EPRI sites with PCP contamination. Separation by material sizes provided a strategy to both reduce the volume of more highly contaminated materials, and concentrate contaminants for treatment in smaller reactors where better process control could be applied.

Limitations of Soil Washing

- Wash-water additives may make it necessary to treat wastewater before discharge.

- Effectiveness very much depends on soil conditions and nature of contaminants.

- Further treatment is usually required.

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Notes:

Introduction of additives such as surfactants, acids, bases, etc., may require treatment of wastewater before discharge.

Most soil washing processes are relatively ineffective on soils with high clay and silt content.

Further treatment on concentrated contaminants, fine-grained soils, and wash-water may be required.

Costs quoted by soil washing vendors included in EPA REACH IT range from $30 to $195 per ton.

Solvent Extraction Process
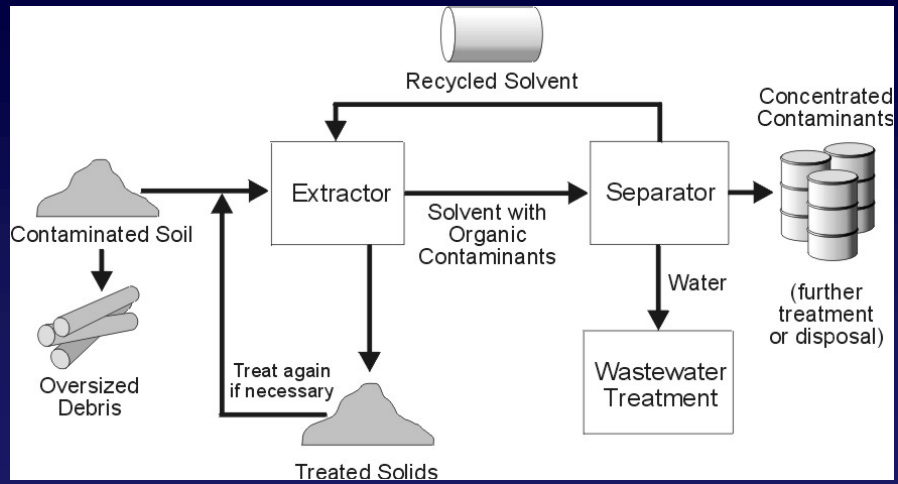
Notes:

Process description:

1. Feed preparation
2. Extraction
3. Recovery of solvents and organic compounds
4. Separation of solids

Methanol has been used at Hill Air Force Base, Utah, for sites contaminated by fire training activities. Methanol partitions the contaminants from the solid soil phase into the solution phase. The solution phase is recovered and reused.

Methanol has been used to treat containerized soil contaminated with PCP and other wood preservative chemicals including PAHs. The solvent extraction process was combined with photodegradation technology to degrade the organic chemicals in the extracted solvent on site within a period of a few hours.

Notes:

Extraction efficiencies of 90 to 98 percent on PCB sediments have been reported.

Vendors costs range from $30 to $800 per ton of contaminated soil.

Example of the application of the solvent ethanol for pentachlorophenol (PCP) removal from contaminated soil. Treatment combination used was solvent extraction, followed by photodegradation of chemicals in the solvent phase.

Limitations of Solvent Extraction

- Traces of solvent may remain in the treated solids

- Least effective on very high molecular weight organics

- Can become expensive if solvent reuse is not possible

- Generally not applicable for inorganic contaminated soil

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Notes:

Traces of organic solvent may remain in the treated soils, therefore, toxicity of the solvent is an important consideration.

Often high ratios of solvent:soil are required for contaminant removal.

Often a combination of solvents are best, rather than one solvent, which can increase costs of treatment.

Treatability studies should be performed to determine effective combinations of solvents, rate of extraction, and solvent reuse aspects.

In Situ Oxidation

Description

- Injection of strong oxidants
  - Fenton's Reagent, hydrogen peroxide, or potassium permanganate
- Oxidation and/or dechlorination process
- Best for compounds with unsaturated carbon-carbon bonds
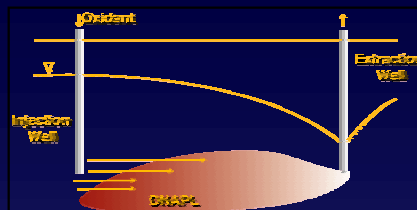
Contaminants Treated
- VOCs
- SVOCs
- Petroleum hydrocarbons

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Fenton's Reagent - reaction between hydrogen peroxide and ferrous iron (II) to generate a hydroxyl radical (this radical is second only to fluorine in oxidation potential)

Complete oxidation of organic compounds yields innocuous by-products commonly founds in nature, primarily carbon dioxide and water

In Situ Oxidation:
Status

- Over 50 full-scale cleanups for BTEX

- 42 field demonstrations on chlorinated solvents

- At least four vendors

- More study needed on long-term effectiveness on chemicals not oxidized initially (rebound)

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Vendors:

In-Situ Oxidative Technologies

- ISOTEC process using Fenton's reagent chemistry (hydrogen peroxide and proprietary iron-based catalysts) - can completely oxidize most petro and aromatic hydrocarbons, chl solvents, pesticides and herbicides

- 3 full scale projects in design, 14 full scale projects constructed (primarily in NJ), 3 full scale cleanups

Geo-Cleanse International, Inc. (GCI)

- Geo-Cleanser Process uses Fenton's reagent chemistry (H_2O_2 and ferrous sulfate)

- injected reagents are not envr hazardous, intermediate products are natural, nonhazardous mono and fatty acids, end products are CO_2 and H_2O, and in the case of chl solvents, chloride ion. Remaining reagents decompose to water and O_2 and provide nutrients for natural remediation processes, or precipitate as nonhazardous metallic salts

- been applied successfully at 40 commercial sites for full scale cleanups

- cost is $2 - $25/lb/contaminant (excludes excavation, permitting, and disposal of residues)

Potential Vendor:

BSI Environmental

- uses Fenton's for soil and sludge contamination (ex situ)

- potential for in situ gw treatment

- 1 full scale

- cost is 100K - 220K/yd^3 (excluding excavation, permitting, and disposal of residues)

In Situ Oxidation

Pros	Cons
• Destroys NAPL • Permanent solution • Low capital • Low energy • Rapid cleanup and closure • Enhances existing pump and treat systems with little modification	• Contaminant volatilization (BTEX) • May require large quantities of oxidizing agent • Possible incomplete oxidation or formation of intermediate contaminants • Other carbon sources compete for oxidant • May require multiple injections

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Pros:

low cost - no permanent structures or monthly maintenance fees

minimal site disruption - ability to remediate under structures and pavement, around utilities, and without interrupting site operation or closing facilities

time - reduces contaminant levels within hours and contaminant reduction is verifiable within days

Cons:

certain organics can not be effectively oxidized by Fenton's reaction including methylene chloride, alcohols, and ketones

Enhanced *In Situ* Bio-Remediation of Groundwater
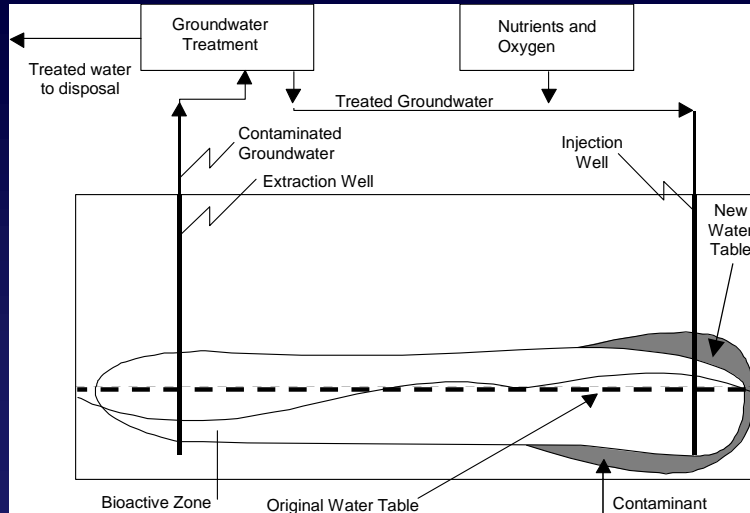
Notes:

Promotes and accelerates the natural biodegradation process in saturated soil.

Generally consists of a water recirculation system, aboveground treatment of ground water, conditioning infiltrating water with nutrients, and an oxygen source.

One design option consists of central withdrawals of ground water and reinfiltration through injection wells, surface ponds, or infiltration galleries at several locations around the outer border of the treated area. Hydrological control or engineered barriers (slurry wall) can be used to isolate the site.

Generally, the groundwater is withdrawn at a higher rate than it is infiltrated. Surplus is discharged off-site after being treated to meet permit requirements.

To support biodegradation in the subsurface, and aboveground treatment system may be used to degrade contaminants in the withdrawn ground water and to condition the water before reinfiltration.

Types of In Situ Bioremediation Processes

- Aerobic processes

- Anaerobic processes

- Cometabolic processes

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Notes:

Aerobic biodegradation involves the use of dimolecular oxygen (O2) by microorganisms and the oxidation of organic contaminants. Highly oxidized compounds such as PCE and TCE are impossible or difficult to biodegrade aerobically because they cannot donate electrons. These oxidized compounds can, however, be reduced under anaerobic conditions.

Anaerobic biodegradation occurs without O2 as the electron acceptor. Inorganic electron acceptors in the subsurface include: nitrate ($NO3-$) ferric iron ($Fe+^3$), sulfate ($SO4-^2$), and manganese ($Mn+4$). Adequately characterizing a plume for electron acceptors is critical to understanding , predicting, and controlling the likely bioremediation processes.

Cometabolism is a process in which organic contaminants are degraded fortuitously (by accident) by the enzymes of microbes metabolizing substrates for food and energy. Therefore, the chemical undergoing cometabolism does not provide energy or food for the microorganism, and actually microbial energy and enzymes in the process of transformation.

Notes:

Infiltration:

Injection wells drilled into the saturized zone are the most direct method for providing electron acceptor and nutrients.

Infiltration galleries or surface applications can reduce installation costs, however, direct contact with ground water is less assured.

Electron acceptor:

Aerobic biodegradation provides the most rapid reactions, and the amount of contaminant biodegraded is proportional to the amount of oxygen added. Oxygen concentrations that can be achieved at 50 F include: for air, 10mg/L; for oxygen saturated water, 40 mg/L, and for hydrogen peroxide at 200 mg/L, 94 mg/L of oxygen.

A method to potentially improve the delivery of oxygen is through the use of oxygen releasing compounds (ORC) that are placed in the bottom of injection wells.

Hydrogen peroxide at less than 100 mg/L can inhibit bacterial activity, and upon reaction to provide O2 may "degas" oxygen out of the saturated zone and into the unsaturated zone. An example of this occurred at the Champion International Site in Libby, Montana, where concentration of O2 in the unsaturated soil above the H2O2 injection well was up to 40% by volume.

The reaction of NO3- (electron acceptor) with toulene, is shown below:
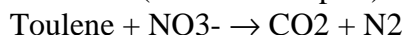
$$Toulene + NO3- \rightarrow CO2 + N2$$
About 4 – 7 ppm NO3- are required to degrade 1ppm of hydrocarbon

The need for addition of nutrients depends upon the amount and bioavailability of nutrients present at the contaminated site. Nitrogen (N) and phosphorus (P) are generally considered to be required to accomplish aerobic biodegradation of carbon and the amount of N and P required is based on the amount of carbon contaminant. The ratio that is generally used is: C:N:P = 100:10:1 (by weight)

Applications of Enhanced In Situ Groundwater Remediation

- Treats two media (soil and water) simultaneously

- Broadly applicable for organic compounds

- Considered a natural process with public acceptance

- Routinely used at UST sites and wood preserving sites

Notes:

Technology is more cost effective at sites where both soil and ground water are treated that, for example, conventional pump and treat technology where the water is first pumped from the subsurface, and then must be treated separately in an above ground reactor.

The process also reduces toxicity upon biodegradation of the parent compounds and intermediates.

Example includes the Champion International Site in Libby, Montana, for treatment of wood preserving wastes including creosote, containing PAHs and pentachlorophenol (PCP). Reference: Champion International Superfund Site, Libby, Montana Field Performance Evaluation. Bioremediation Unit: In Situ Bioremediation of the Upper Aquifer. EPA/600/R-97/044, U.S. EPA Office of Research and Development, Washington, D.C. August, 1997. Another example is traverse city, Michigan, under the direction of the Kerr Environmental Research Laboratory, Ada, Oklahoma (Dr. John Wilson).

Limitations of Enhanced In Situ Groundwater Remediation

- Contaminants must be biodegradable

- Requires extensive site characterization

- Mobility of contaminants may require the use of an aboveground water treatment system

- Depth to groundwater and cleanup levels may limit applicability

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Notes:

Site characterization is required to determine both applicability and performance of the technology.

Addition of water witrh nutrients and oxygen (or other electron acceptor) may increase the level of the water table and cause spreading/mobilization of contaminated water at the site. This would generate the need for contaminant, either hydraulic or structural, or both.

Careful process control is critical to technology performance. For example, addition of too much H2O2 may inhibit biodegradation and addition of any oxygen may oxidize reduced iron that causes precipitation and reduce water flow rates. H2O2 may degas in the subsurface and influence permeability and release oxygen into the vadose zone.