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Compatibility of Alternative Chlorinated Solvent Source Treatment Strategies with Monitored Natural Attenuation

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Introduction

One of the most powerful and promising strategies for optimizing environmental restoration is the use of combinations of technologies rather than a single technology to reach the target cleanup goals. The U. S. Environmental Protection Agency (EPA 1998, 1999) explicitly recognized the value of using a combination of technologies in their guidance on the use of monitored natural attenuation:

> "*EPA, therefore, expects that monitored natural attenuation typically will be used in conjunction with active remediation measures (e.g., source control), or as a follow-up to active remediation measures that have already been implemented.*"

A combined approach benefits from the ability to match the invasiveness and aggressiveness of the remedial action to the amount of contamination and level of risk. This matching process is particularly important for recalcitrant contaminants such as chlorinated solvents. Highly contaminated areas justify more intense remediation action(s) while minimally contaminated areas are suited to natural or even passive methods. A logical extension of this concept is the need to transition technologies through time as sites become cleaner. The extended approach, sometimes described as a "technology train," responds to changing conditions with the goal of optimizing cleanup. Importantly, an efficient technology train comprises actions that are compatible with each other. Each action must condition and/or deliver the target site to the next action in a proper state. For example, if a site is transitioning to an anaerobic-passive technology, then the ideal predecessor technology would minimize residual oxygen and residual electron acceptors left in the site. In this case, a predecessor technology such as in situ chemical oxidation (using Fenton's Reagent, persulfate, or the like) that generates high levels of residual dissolved oxygen and solid peroxides would be less desirable than alternatives than do not generate these conditions.

The U. S. Department of Energy (DOE) is actively working to clean up legacy contamination from its operations. Notably, DOE is responsible for the cleanup of many sites where the contamination includes chlorinated solvents (or chlorinated volatile organic contaminants (CVOCs)). At some sites, groundwater plumes containing CVOCs tend to become relatively large. Estimates for times to remediate sites often ranges up to 100s of years for these large plumes. As a result, the CVOC plumes are a concern to DOE, regulators and stakeholders. In response to this challenge, DOE initiated a project to "provide the technical and policy support to facilitate implementing appropriate passive cleanup… leading to responsible completion of active remediation activities at high risk DOE waste sites." As part of this effort, input from regulators and stakeholders is used to assure that the technical development efforts are properly selected and targeted. Regulator and stakeholder collaboration has included briefings in Tennessee, Washington, south Carolina and Georgia, briefings to the advisory boards at the DOE Hanford, Savannah River, and Oak Ridge reservations, and a joint development effort with the Interstate Technology and Regulatory Council. One of the items highlighted in the meetings, notably by the Savannah River Site (SRS) Citizens Advisory Board (CAB), is the potential compatibility (or incompatibility) between the source treatment techniques and MNA. The SRS CAB requested a specific assessment of this issue by the project team. In the sections below, a general evaluation of the compatibility of various source treatment and plume treatment technologies with monitored natural attenuation and enhanced passive remediation for chlorinated solvents is documented.

The Soil and Groundwater Project Team at SRS prepares the former M Area Settling Basin Area for Steam Treatment to Remove Residual Chlorinated Solvents from the Soil and Groundwater (Photographer Roland Collins)

Summary of Conditions Suited to Monitored Natural Attenuation and Enhanced Passive Remediation

In the 1990s MNA was championed by a small group of EPA and U. S. Department of Defense (DOD) scientists who recognized that enlisting the forces of nature in site remediation (i.e., MNA) could be effective in meeting cleanup goals. These scientists also determined that MNA, when compared to alternative active treatments, generally reduces costs and collateral environmental impacts. Their efforts led to the publication of technical guidance (EPA, 1998; Wiedemeier et al., 1995) and policy directives (EPA, 1999). Figure 1 is a synopsis of the technical protocol and regulatory protocol development timeline for MNA for both petroleum hydrocarbons and chlorinated solvents. It is clear from the timeline that development of MNA for petroleum hydrocarbons, because the underlying processes are inherently more robust and simple, occurred earlier than the development of MNA for CVOCs. Moreover, MNA of petroleum hydrocarbons is now widely accepted and used. MNA processes for CVOCs are more complex and nuanced and the general viability, robustness and utility of the CVOC protocols are still being determined.

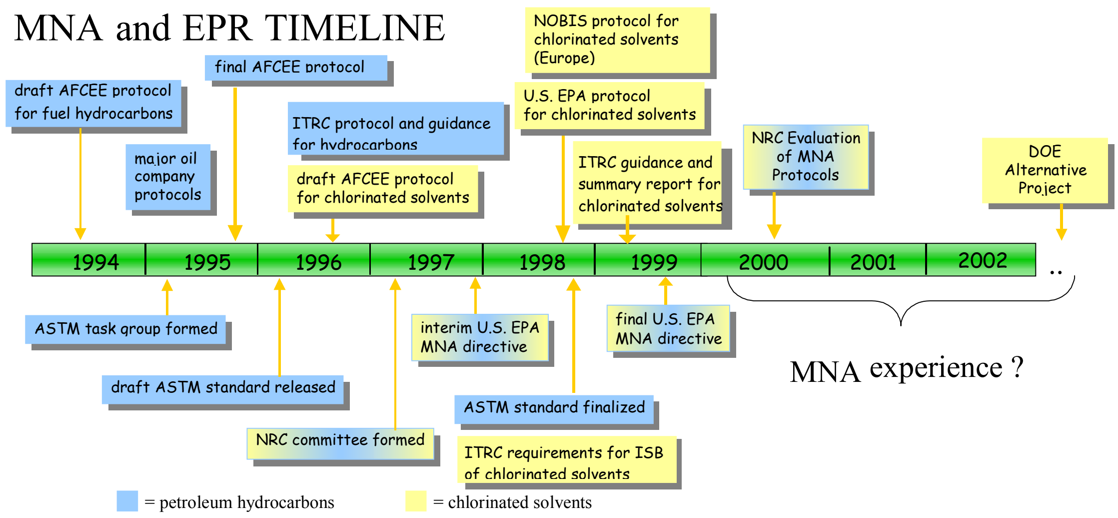


Figure 1. Recent Historical Development of MNA/EPR for Petroleum Hydrocarbons and Chlorinated Solvents (after Wiedemeier and Barden, 2002)

CVOCs are subject to a variety of physical, chemical, or biological processes that lead to their attenuation, including biological degradation, abiotic degradation, sorption, and dispersion. While degradation processes are the most desirable, all of these mechanisms can play a role in MNA and EPR. The DOE Alternative Project is emphasizing a mass balance concept to support MNA and EPR. A strategy of balancing attenuation capacity with potential for contaminant loading from the source leads directly to technically based approaches for encouraging the beneficial use of natural processes and for improving documentation of performance while minimizing costs and mitigating any adverse collateral impacts.

This "attenuation capacity" based paradigm has the potential to build on traditional measures of plume stability and geochemical footprints. The ideas support recommendations from the EPA that stress natural attenuation is most appropriate when used in conjunction with engineered reduction of contaminant sources or as a follow up measure. The precise manner in which active remediation and MNA/EPR are combined depends on the attenuation capacity of the system. If the attenuation capacity is relatively small, then active measures will be needed to remove or immobilize a significant proportion of the contaminant source. If the natural attenuation capacity is relatively large (or if it can be enhanced appropriately), less active source treatment should be performed. In either case, it is necessary to verify and quantify the attenuation capacity to effectively implement this approach. The proposed loading-capacity paradigm integrates well with the DNAPL source mass-flux measurement research. Tools to measure mass flux are being developed and tested and will offer the means for providing the critical input data to the mass balance approach.

Environmental remediation technologies can be viewed on a continuum ranging from source excavation on one end to MNA on the other end (Figure 2). This continuum represents potential technologies and strategies to be used during the period of remediation. Over time these approaches reduce and attenuate risks to meet the remediation goals. This results in a final status where the site requires no further action. As drawn, aggressive technologies such as direct *in situ* chemical destruction and thermal methods fall near the left of the continuum. Baseline pump and treat, active bioremediation and similar methods are near the center of the continuum. Permeable treatment systems fall to the right. Importantly, the area adjacent to MNA on the continuum has been designated EPR.

The simple definition provided above is the key to defining the allowable boundary of EPR. For sites where contaminant delivery from the source is less than the naturally sustainable attenuation capacity, MNA/EPR is viable. For sites where the contaminant delivery is greater than the attenuation capacity, but the attenuation processes or contaminant loading can be sustainably modified to achieve the required balance, then EPR is viable. Conversely, for sites where contaminant delivery from the source is greater than the sustainable attenuation capacity, then active remediation will be necessary. This continuum eliminates the historical dichotomy that has been strictly drawn between active remediation and natural attenuation. When combined with the attenuation capacity paradigm, the continuum provides a quantitative basis for determining when MNA and EPR are useful and appropriate and what activities logically fit into the classifications. Importantly, a majority of contaminated sites will require a sequence of activities for responsible cleanup – often including source removal/destruction combined with treatment of a primary contaminant plume (the soil and groundwater that contain moderate to high concentrations). Virtually all sites will have a monitored natural attenuation component, either in the more dilute portion of the plume or after transitioning from more active treatment actions. The capacity based definitions and continuum will support a technical determination of how and when to transition from active remediation to MNA/EPR.

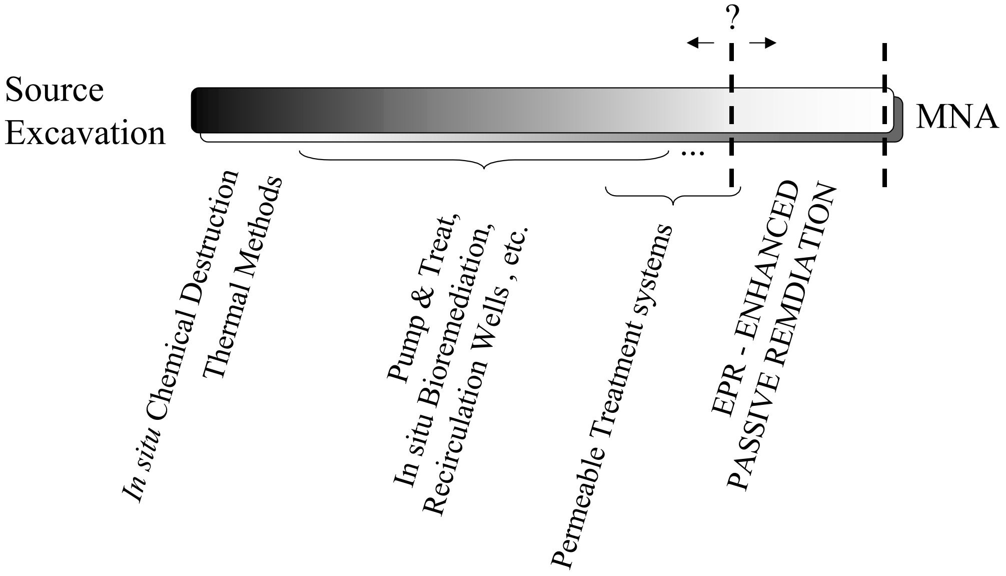
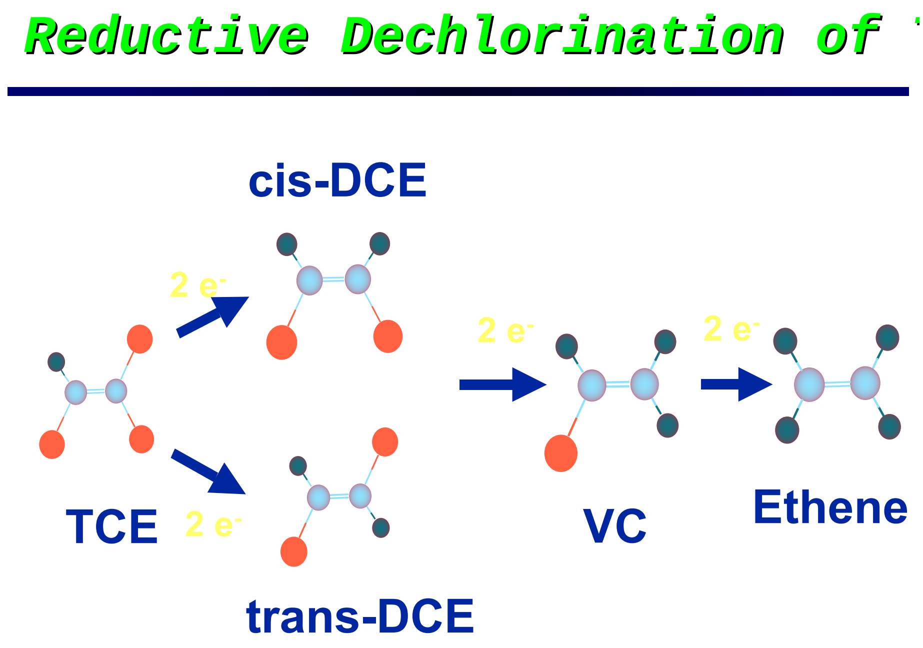


FIGURE 2. Continuum of Individual Remediation Technologies

For CVOCs, anaerobic biological destruction processes (Figure 3) are traditionally considered a primary MNA mechanism (McGuire et al, 2004; Wiedemeier et al., 1999). The pathway for this mechanism includes the degradation intermediates dichloroethene, vinyl chloride and ethene. This microbial activity requires strongly anaerobic conditions and the presence of anaerobic microorganisms possessing reductive dehalogenation capability. In cases where natural conditions do not support active anaerobic reductive dehalogenation, research is underway to determine the efficacy of biostimulation (addition of carbon sources to produce anaerobic conditions) as well as bioaugmentation (addition of anaerobic halorespiring bacteria) to achieve *in situ* anaerobic biodegradation of chlorinated solvents. This research has focused on active bioremediation systems as well as deploying long-lived amendments to generate an enhanced passive remediation condition. Correct conditions and the presence of appropriate microorganisms will commonly result in effective degradation of chlorinated solvents. Recent data suggest that anaerobic abiotic destruction may also play a significant role in cVOC destruction and aerobic biodegradation is active and effective for daughter products such as dichloroethene and vinyl chloride.



Reductive Dechlorination of

Figure 3. Pathway for stepwise reductive dechlorination of Trichloroethylene.

There are a few important geochemical controls on the anaerobic biotic and abiotic cVOC degradation processes. Because the cVOCs are serving as terminal electron acceptors, the environment must first be depleted of all other potential terminal electron acceptors with higher energy levels, e.g. nitrate and sulfate (Figure 4) and be in the region of methanogenesis (methane production). However, some sites are known to go into what is referred to as a ‘stall’ where reductive dechlorination stops at either cis-DCE or vinyl chloride. Usually this stall is caused by lack of the correct microbial community, or by high concentrations of competing terminal electron acceptors. Additionally, the conditions need to be within acceptable ranges for temperature, pH, and moisture. Macronutrients (primarily nitrogen and phosphorous) are also necessary.

For purposes of a summary analysis, MNA and EPR for near-source cVOCs degradation are optimally anaerobic. If daughter products with fewer chlorines predominate (or if they are produced by a source treatment method) then the optimal conditions shift from anaerobic to aerobic. The other MNA and EPR mechanisms (e.g., sorption, dispersion, etc.) may also be influenced by source treatment methods and the manner in which they are altered is summarized in the supplementary material provided in the Appendix.

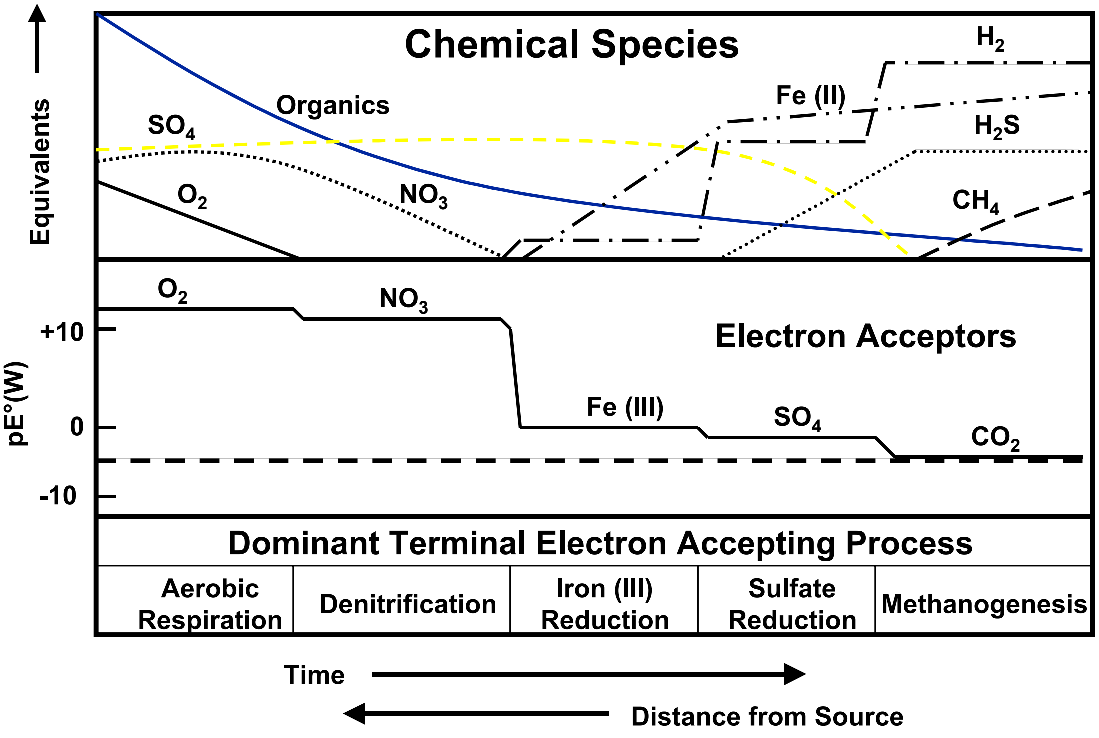


Figure 4. Critical chemical species, electron acceptors, and redox processes in relationship to bounding conditions necessary for reductive dechlorination of TCE (dashed line).

Summary of Source Treatment Methods Evaluated

Technologies have been categorized into: source removal technologies and plume control and elimination technologies. Source control technologies discussed include physical removal (excavation), chemical extraction (e.g., surfactant or cosolvent flushing), physical containment, chemical destruction (e.g., chemical oxidants), and energy based enhancements (e.g., various types of heating, electroosmosis, and sonic). We did not evaluate physical improvements to facilitate mass transfer (e.g., fracturing and soil mixing) and plume control and elimination technologies (pump and treat, chemical reactive barrier, and bioremediation) because they are not explicitly source treatment methods. These related technologies would also influence the status of a contaminated site and its suitability for MNA and EPR. A more detailed description of the technologies is provided in the supplementary material provided in the Appendix.

Summary of Results

An assessment of the various potential technologies is provided in the technology matrix (Figure 5) and in the associated discussion below. In generating the matrix, each technology was placed on a designated row and each of the relevant attenuation mechanisms was placed its designated column. The compatibility of the technology with MNA, vis-à-vis its influence on each attenuation mechanism is designated using a graphical symbol. Monitored Natural Attenuation and its ideal requirements are described above. If a source treatment technology improved a site's compatibility with MNA or results in an enhancement (EPR), then it is assigned a green dot. If a technology is neutral and has no substantive impact (either positive or negative) on an attenuation mechanism, then it is assigned an open dot. If a technology adversely impacts an attenuation process, then it is assigned a black dot.

A few of the designations are noteworthy on this table. One of these is the influence of thermal treatments such as steam or electrical resistance heating on the potential for MNA based biological processes – Does the heat irreparably damage the microbial community and reduce the potential for future biological MNA or EPR? If there is an impact, is it temporary or long-term? These questions, as with many similar issues, are the topic of current research efforts in EPA, DOE and DOD. The graphical designation in the table is based on the early findings. Related to heat treatment, for example, study of an SRS steam heating site (the M Area solvent storage tank dynamic underground stripping project) indicated that a diverse and functional microbial community can be measured even while the site is still cooling after an extended period of thermal treatment (Fliermans, 2003). This type of finding is encouraging as it suggests that, except in the most extreme cases, that the robustness of natural systems may protect the ability to rely on MNA even after aggressive source treatment. Also included on the table is an example of how source treatment actions can be adjusted to maximize future compatibility with MNA and even to enhance future MNA (i.e., the EPR concept). The example is from a recent report (DOE, 2003) in which a scientific team recommended adding a long-lived electron donor to the backfill for a planned excavation. In the referenced report, the backfill was combined with a hydraulic control that passively draws water back toward the excavation (for discharge at the base of a nearby escarpment). The result of these actions would be a long-lived passive treatment that has a potential performance life that is potentially sufficient to meet remediation goals. Creative combinations such as this are possible for many of the listed technologies and should be encouraged.

Attenuation Process → Source Treatment Method ↓	**Reduced loading / flux**	**Biotic degradation**		**Abiotic degradation**		**Sorption**	**Dispersion**
		of parent solvents	of daughter compounds	of parent solvents	of daughter compounds		
Physical Removal							
excavation	🟢 / ○	○	○	○	○	○	○
excavation with electron donor (e.g. peat) added to backfill	🟢	🟢	○	🟢	○	🟢 / ○	○
soil vapor extraction	🟢	○	○	○	○	○	○
Chemical Extraction Methods							
cosolvents	🟢	🟢	○	🟢	○	○	○
surfactants	🟢	○	○	○	○	○	○
Physical Containment							
walls/caps/floors	🟢	🟢	○	○	○	○	🟢
Chemical Oxidation							
peroxide/permanganate/persulfate	🟢	●	🟢	●	○	○	○
Energy Based Treatments							
electrical resistance heating (e.g., six phase)	🟢	?	○	○	○	○	○
steam heating (e.g., DUS)	🟢	○	○	○	○	○	○
hydrous pyrolysis (steam heating with added air/oxygen)	🟢	● / ○	🟢	● / ○	○	○	○
radio frequency heating	🟢	?	○	○	○	○	○
electro-osmosis	🟢	?	○	○	○	○	○
sonic	🟢 / ○	?	○	○	○	○	○

🟢 = technology benefits or enhances the designated natural attenuation process
○ = neutral -- the technology does not substantively impact the designated natural attenuation process
● = negative -- the technology provides adverse conditions for the designated natural attenuation process
note -- short-term impacts (e.g., oxygen introduced by SVE) that dissipate quickly after completion do not influence rating

Figure 5. Summary Technology Matrix showing the compatibility of source treatment methods with natural attenuation for cVOCs.

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Appendix

Supporting Information on Source Treatment Methods

A summary assessment of the various potential technologies is provided in the technology matrix; more detail on the technologies is provided below. Technologies have been categorized into: source removal technologies and plume control and elimination technologies. Source control technologies discussed include physical removal (excavation), chemical extraction (e.g., surfactant or cosolvent flushing), physical containment, chemical destruction (e.g., chemical oxidants), energy based enhancements (e.g., various types of heating, electroosmosis, and sonic), and physical improvements to facilitate mass transfer (e.g., fracturing and soil mixing). Plume control and elimination technologies include pump and treat, chemical reactive barrier, and bioremediation. A synopsis for each technology is provided in turn. Monitored Natural Attenuation and its ideal requirements are described above.

Source Control Technologies

Physical Removal

Excavation

This is a baseline and preferred removal technology for very shallow accessible source zone contaminants. In many cases, physical removal is infeasible because of scale (the migration of CVOCs into a large subsurface volume) the limitations imposed by existing facilities, surface and underground infrastructure, and safety (slope and structural). Physical removal also generates large amounts of secondary waste that requires further handling, transport and disposal. Costs for excavation given these limitations is often excessive and the benefits of excavation may not justify the costs given the associated risks. In the limited number of cases where a substantive portion of the source can be removed, this approach will reduce contaminant release from the source. Excavation is generally neutral in its impacts on the natural attenuation processes tabulated in the technology matrix.

Excavation with Electron Donor Added to the Backfill

On a site-specific basis, the various source technologies described herein can be adjusted to optimize their performance and possibly even provide the necessary attenuation to reach cleanup goals. This section describes such a scenario in which excavation is supplemented by amended backfill and hydraulic modification (DOE 2003) as shown in Figure 6.

Given a source removal action and the proximity of the escarpment, this set of actions represents a low cost and viable strategy. A pipe could be drilled through the bottom of the pit at a downward angle until it exits the escarpment, or a siphon tube could be run from the bottom of the pit over the escarpment and down to an elevation below the intake of the pipe to provide a natural siphon (see Figure 6). Draining the pit would cause groundwater to flow towards the pit and thus capture much of the contaminated water in the area. A strategy involving either MNA, or a combination of bioremediation and stabilization could be used to further control the plume and eventually reach a low risk state. Horizontal wells could be drilled in other directions at the time that the drain is installed to insure that the plume is not escaping the passive collection system. Further, the pit could be filled with permeable material and layered with stabilizers, reactive barriers, and biostimulants, eg. phosphate, iron, and electron donor, to passively remediate and stabilize the remaining contaminant. This strategy leverages with the source removal excavation and requires little new infrastructure or maintenance.

For purposes of the technology matrix, the incorporation of additional concepts into the excavation improves the linkage of the source treatment to the future natural attenuation necessary to complete the remediation at the site.

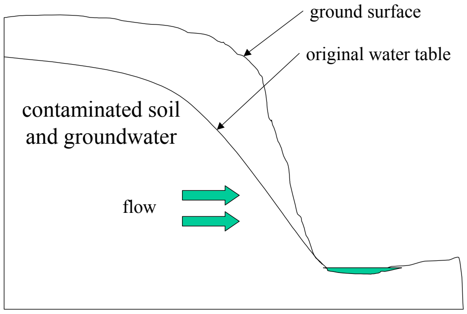
Soil Vapor Extraction (SVE) and Related Technologies Such as "Dual Phase Extraction"

SVE is a baseline method that has been successfully used under a wide range of source zone conditions. The biggest limitation to use of SVE is low permeability in source zone sediments and a high degree of heterogeneity. In these conditions, the more permeable material is remediated quickly (circa years) while the less permeable material is remediated much more slowly (circa decades or centuries). Thus, while SVE is likely to be an important component of the cleanup of residual source solvent at most sites, various enhancements should be considered as appropriate to improve mass transfer and removal rates. Related methods, such as dual media extraction, are being performed by a large number of companies. These related technologies are based on removing as much water as possible by pumping and then cleaning up the sediment using the more efficient SVE approach (i.e., air is a more efficient VOC extraction medium than water). The water removal can be accomplished on a local scale by using a high vacuum suction tube in the SVE well or, on a slightly larger scale, by using intensive pumping of a small number of closely spaced wells. Dual media extraction is promising for small solvent source sites in relatively permeable and homogeneous geological conditions. Specific attributes that make dual media extraction promising include: 1) residual solvent present in the capillary fringe and shallow groundwater, 2) minimal solvent source deep in aquifer zone(s) beneath the water table, and 3) avoiding implementation at sites with either very high or very low permeability.

Soil vapor extraction will reduce contaminant release from a residual source area. The process does introduce air into the treatment zone, but this is an ephemeral impact that dissipates quickly following cessation of SVE. Thus, this process is generally neutral in its impact for future natural attenuation of CVOCs.

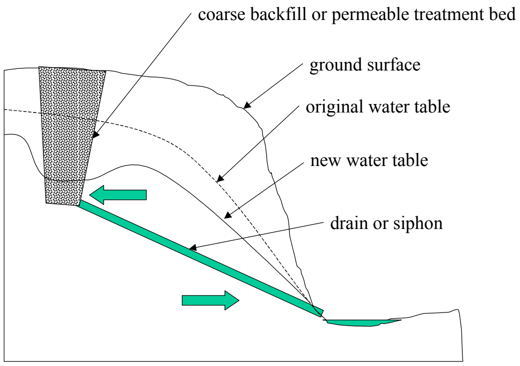
Figure 6. Simplified Diagrams of an Excavation Plus Modified Backfill and Hydrology. (a) baseline conditions, b) cross section of Geodrain, c) site configuration options

a)



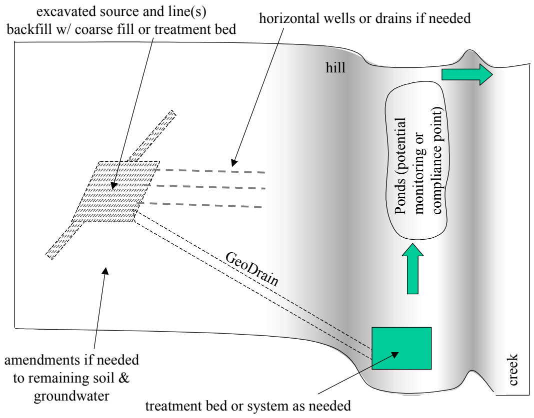
Baseline Conditions

b)



Basic GeoDrain
(see text for description of options)

c)



Chemical Extraction

Surfactant Flushing

This technology uses surfactant solutions to solubilize or mobilize source solvent. Because surfactant flushing requires delivery and capture of reagent and requires intimate contact of the reagent with the source solvents the technology is poorly suited to solvent sources in heterogeneous and/or low permeability sediments.. In the appropriate setting, surfactant amendments allow solvents to be removed in a few pore volumes of flushing rather than the hundreds or thousands of pore volumes required if the solvent is dissolving into water. This technology has been studied for many years by various universities (SUNY Buffalo, University of Texas, University of Oklahoma, University of Florida, University of Waterloo, and others) and by Duke Engineering and Services Company. The process requires rigorous control on the injected and extracted fluids to assure that the source zone is swept by the injected reagent and to assure that the mobilized/solubilized CVOC is effectively captured. A key element to the success is optimizing the use of the relatively expensive surfactants by developing recycle systems, more efficient surfactants, or other strategies. This technology has been applied with limited success at sites with favorable source and geological conditions. Specific attributes that make this technology promising include: 1) relatively small and well defined solvent target in permeable material below the water table, 2) solvent present throughout the formation, and 3) competent confining zones to help control undesirable migration away from the treatment zone. Because it involves injection and extraction of reagent, this class of technology would have limited applicability above the water table and to clean up heterogeneous or fine-grained sediments. Recent research in this field is focused on surfactant recycle and reducing the buoyancy of mobilized CVOC for more effective control and capture.

Surfactant Flushing will reduce contaminant release from a residual source area. Otherwise, this process is generally neutral in its impact for future natural attenuation of CVOCs.

Co-solvent Flushing

This technology is very similar to surfactant flushing in theory and approach, except that co-solvents (e.g., alcohols and other such solvents) are used instead of aqueous surfactants. Because co-solvent flushing requires delivery and capture of reagent and requires intimate contact of the reagent with the source solvents, it would have similar limitation. Co-solvent based remediation has been deployed by universities (e.g., Clemson University) with some success. In addition to research on reducing the buoyancy of the mobilized source solvent, co-solvent researchers are examining increasing the density of the reagent fluid to more effectively target “bottom-dwelling” dense solvent layers.

Cosolvent Flushing will reduce contaminant release from a residual source area. Also, many investigators are documenting that some of the cosolvents (e.g., ethanol) are suitable electron donor and that cosolvent flushing may leave a residual condition where natural attenuation is enhanced.

Physical Containment

Source Zone Isolation Methods

These methods include slurry walls, caps, sheet pile walls, grout injection/mixing, silica gel injection, and related geotechnical techniques. These methods attempt to stabilize and address solvents by removing them from the active transport pathways in the soil and groundwater system. Because of the low concentrations needed to meet regulatory goals (e.g., μg/L or ppb levels), isolation methods are not generally successful in meeting regulatory goals (unless combined with other technologies such as electron donor addition to stimulate biological dgradation).

In a general sense, physical containment methods will reduce the release of CVOC from a source area and potentially improve conditions for natural attenuation of parent compounds by limiting the oxygen in the system.

Chemical Destruction

In Situ Oxidation

This technology uses reagents to destroy DNAPLs in place. Because in situ oxidation requires delivery of reagent and requires intimate contact of the reagent with the source solvents, it is limited in effectiveness in heterogeneous and/or low permeability sediments. Typical reagents include Fenton's reagent (hydrogen peroxide and reduced iron), permanganate solution, or persulfate solution. These reagents are strong oxidizers that "burn" the DNAPL in a saturated or vadose zone setting. As the reagent is added, it reacts vigorously and often induces bubbling and mixing – a process that may enhance contact of the reagent with the target DNAPL under some conditions. Several variants of in situ oxidation methods have been deployed commercially. A key element to the success is performing the work rapidly with a minimal volume of reagent. Sites with highly reduced conditions (conditions that would scavenge reagent away from the desired DNAPL destruction) would be poorly suited to this technology class. Specific attributes that make this technology promising include: 1) relatively small and well-defined DNAPL target in permeable material, 2) DNAPL present throughout the formation, and 3) competent confining zones to help control reagent delivery. Because it involves injection of reagent, this class of technology would have limited applicability to clean up heterogeneous fine-grained layers.

Of the source treatment methods considered herein, in situ oxidation is the least compatible with the anaerobic biodegradation that is typically a central element in CVOC natural attenuation. In situ oxidation leaves a high amount of residual electron acceptor in the form of dissolved oxygen and, more importantly, solid peroxides and other highly oxidized compounds. These buffer the dissolved oxygen to high levels for long periods of time. In a pilot test at SRS, dissolved oxygen levels in monitoring wells at a site treated with Fenton's Reagent remained elevated (at about 30 to 40 mg/L versus 5 to 10 mg/L) for several years following completion of the remediation. A high dissolved oxygen is not harmful and can be often be beneficial. When viewed in terms of the conditions needed for CVOC natural attenuation, the post chemical oxidation conditions are not optimal.

Energy Based Enhancements

Joule Heating

This technology directly "injects" AC power into the subsurface to heat the soil through self-resistive ("Joule") heating. Through resistance to the flow of electricity in the bulk soil/groundwater, heat is generated. Thus, the ground itself acts in a manner analogous to the heating element in a small radiant home or office heater.

This process normally requires some moisture to be maintained in the heated zone. Since the area immediately adjacent to the electrodes heats faster than the overall treatment zone, injection of small amounts of water or electrolyte solution is often required to allow the ground to be heated to temperatures near 100° C. A relatively successful commercial variant is called six-phase heating. Dividing the power into six phases (rather than the traditional three phases of line power) helps avoid problems because the power density near each electrode is reduced and the overall power pattern is more uniform. An advantage of six-phase heating for vadose zone contamination is that power and heat are preferentially directed into fine grained or clayey layers. These layers tend to be moister and they have been shown to be the long-term solvent reservoir in many layered geological systems such as A/M Area at Savannah River. Six-phase heating was developed by the Pacific Northwest National Laboratory and has been licensed for commercial implementation. This process was originally funded and developed by the DOE Office of Technology Development. The first field test of six-phase heating was performed at the Savannah River Site in South Carolina. This test successfully heated a shallow contaminated clay zone underlying the former process sewer line leading to the M Area Settling Basin. Six-phase heating is potentially applicable to similar solvent source targets as steam but with less robustness to heat below the water table and the possible need for closer borehole spacing to install electrodes. Six-phase heating is likely to be more robust than steam for low permeability conditions.

Heating to temperatures near 100° C will impact the microbial population. Recent data for steam based treatment suggests that the subsurface environment may be resilient to this impact and the population will recover rapidly following treatment. Moreover, the cooldown period (which can last for years) is subject to more rapid microbial processes because of the increased temperature. Thus, while this remains an important question that is worthy of research, the matrix identifies microbial impacts as neutral.

Steam Flushing and Steam with Hydrous Pyrolysis Oxidation

This technology uses steam to sweep residual solvent from the subsurface and to deliver heat. Because steam flushing requires delivery of a fluid and general contact of the fluid or its energy with the source solvents, it would have limited applicability to low permeability sediments. Steam flushing is a crossover method originally developed and studied for enhanced oil removal to increase the productivity of oil wells and oil fields. In fact, early development work related to this technology was performed at the

Lawrence Berkeley Nantional Laboratory (LBNL) and the Lawrence Livermore National Laboratory (LLNL). The primary mechanism of oil/solvent removal is concentration of the contaminant phase along the expanding steam front and collection at strategic locations. Typically, steam based remediation systems use a set of wells to deliver steam and move the contaminant phase towards "interior" collection wells to minimize the potential for spreading. In addition to the primary mode of action, steam provides heat energy to increase the mass transfer of contaminants from fine-grained materials and increases contaminant vapor pressure and solubility. A final benefit of steam and other in situ heating methods is that a fraction of the organic phase will break down in the subsurface in the presence of heat and oxygen. Steam is an extremely effective fluid for cleaning soil and groundwater. It delivers its energy efficiently in a minimal condensed volume (much of the energy is released as the steam front condenses). Steam is less dense than water. Thus, it will tend to be most effective and efficient in the vadose zone and in areas below the water table where the entire aquifer is contaminated rather than just a thin layer at the bottom of the treatment zone. Natural layering of sediments and careful design and operation will also limit the tendency of the steam to override the water table.

There are a few commercial variants of steam heating. The most successful and widely used are by licensees of the LLNL steam remediation processes. These particular processes are known as Dynamic Underground Stripping (DUS) and Hydrous Pyrolysis Oxidation (HPO) for the steam sweep and the abiotic oxidation process, respectively. The steam variant of "DUS with HPO" was developed with the support of the DOE Office of Technology Development. In virtually all variants of in situ steam treatment, the steam is injected at high pressures and spreads rapidly through the formation. Heat is transferred to the formation and the steam front expands as the treatment zone reaches target temperatures near the boiling point of water. The rapid expansion of the steam zone reduces the required number of access points compared to many alternative technologies such as six-phase heating or the reagent-based destruction/mobilization/solubilization methods.

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Radio Frequency (RF) Heating and Similar Methods

Heating occurs internally through a dielectric mechanism in which molecular dipoles interact with the electromagnetic wave. The induced molecular distortion and/or motion is translated from mechanical to thermal energy. The effectiveness of the dipole coupling and the power absorbed is a function of the frequency and amplitude of the RF field and the dielectric properties of the sediments. These properties, in turn, are a function of soil composition, moisture content, and temperature. RF heating works initially through interaction with the pore water and water of hydration but is capable of continued heating to temperatures above 100 degrees C by interaction with the minerals. Typical frequencies applicable to soils are in the range of 1 to 100 MHz. The frequency band has been set aside by the Federal Communications Commission for industrial, scientific and medical use with expedited approval in this range and, as a result, the technology has been studied for enhanced oil recovery and successfully deployed for pilot solvent source cleanup at SRS (Jarosch et al., 1994). Different applicator configurations are possible. The two most common are a dipole for application in a borehole, and a "triplate array" for treatment of a fixed volume block. RF heating was developed primarily by researchers from the Illinois Institute of Technology Research Institute (IITRI).

Because of the cost of the RF generator and matching network, and poor efficiency with respect to the original power source (<70%), RF heating has not had as much commercial success as Joule heating. Related technologies such as in situ microwave heating have also been proposed in the past. Unfortunately, as discussed above, microwave frequencies are too high for effective volumetric heating and these systems only heat a thin layer immediately adjacent to the applicator.

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ElectroOsmosis

This technology exploits electrokinetic phenomena in which ions in the diffuse double layer near soil particles move in response to a DC electric field and induced water movement. Electro-osmosis in porous media, such as clays, is possible because of the structured electrical double layer of negative and positive ions formed at typical solid-liquid interfaces. For soil particles, the double layer consists of a fixed layer of negative charges associated with the solid phase and a diffuse aqueous layer of positive ions. Application of an electric potential on the double layer results in a driving force for displacement of the two layers toward the respective electrodes; i.e., the positively charged layer to the cathode and the negatively charged layer to the anode. Since the particles in the soils are immobile, the fixed layer of the negative ions is unable to move. However, the positive ions can move within the diffuse layer and drag water toward the cathode (EPA, 1990). While the basics of this technology are well established from industrial applications in dewatering and clay consolidation, reliable performance for remediation applications has yet to be established. DOE has invested significant resources in the development of this technology with some success documented for organic contaminants (e.g., the Lasagne consortium tests at Paducah and similar pilot studies at LLNL) as well as limited success in direct extraction of metals and radionuclides ("electrokinetics").

In saturated or nearly saturated sediments, the electroosmotic conductivity is directly proportional to the permitivity of the pore water solution, the zeta potential of the soil, and inversely proportional to the viscosity of the fluid. Importantly, electroosmotic conductivity is essentially independent of hydraulic conductivity. For typical fine-grained sediments with a hydraulic conductivity of 10^{-7} to 10^{-12} m/s, electroosmotic conductivities range from 10^{-4} to 10^{-5} cm^2/volt/s. Therefore, reasonable induced voltage gradients on the order of V/cm will increase water flow velocities by several orders of magnitude (assuming typical hydraulic gradients of 0.1 and below). There have been many problems with electroosmosis systems. Water electrolysis at the electrodes can generate large excursions of pH. This, in turn can result in unstable operation and/or metals dissolution and precipitation. Also, for organics, the method is limited to the soluble fraction and will not remove residual nonaqueous phase solvents in the system. The technology is most applicable to saturated or near saturated sediments with low permeability (e.g., $< 10^{-5}$ m/s hydraulic conductivity). Within this bound, the method has low power consumption and will induce a relatively uniform flow that is "independent" of heterogeneity. Because it extracts the dissolved phase only, the method has limited applicability in source zones with solvent trapped in pools or isolated pores (unless combined with another technology).

Electroosmosis will reduce contaminant release from a residual source area. Otherwise, this process is generally neutral in its impact for future natural attenuation of CVOCs.

Sonic Enhancement

This technology uses low frequency sonic energy to improve mass transfer and enhance recovery in pump and treat systems such as soil vapor extraction. As with several of the energy techniques, this method was originally studied to support enhanced oil recovery and has recently been proposed for enhancing environmental cleanup of organic contaminants. Researchers have actively studied this technology in Europe (e.g., University of Delft in the Netherlands) and in the United States (e.g., Weiss and Associates and more recently P. Kearl at the Oak Ridge Grand Junction Office). DOE invested significantly in commercial development. There are several hypothesized mechanisms for the increased mass transfer, including vibration of contaminants in and out of pore throats, vibration of the matrix itself, generation of thermal energy, and others. None of these has been clearly demonstrated or quantitatively confirmed. Further, tests to date show that the effectiveness of the method tapers off rapidly and much of the residual solvent in a system (circa 80%) does not respond to this enhancement. Thus, the technique has shown limited success to date and would likely have limited effectiveness at many sites.

Sonic methods should have minimal impact on MNA potential.

The following technology descriptions are not explicit source treatment technologies and do not appear in the matrix. They are described here for completeness and to emphasize the idea that environmental cleanup requires a combination of technologies.

Physical Improvements to Facilitate Mass Transfer

Fracturing

Fracturing involves using air or water to generate controlled fractures in the subsurface, improve mass transfer and enhance recovery in pump and treat systems. Fracturing technologies are subject to problems in the presence of significant cultural interferences, significant heterogeneity, slope stability concerns, and the need to deliver large amounts of propping solids to keep the fracture open.

Soil Mixing

This is a standard commercial technology used for foundation stabilization when grout is injected during the mixing. The method has also received significant use for environmental cleanup by using chemical reagents (e.g., oxidants), rather than grout to destroy contaminants, or chemical reagents combined with grouts to stabilize contaminants. Such standard implementations might be applicable to niche portions of the CVOC sources.

Plume control and elimination technologies

Pump and Treat

This is a baseline that provides good performance for dissolved contaminants that can be efficiently collected using wells or trenches. Pump and treat is limited by the continued presence of a residual source and the high degree of heterogeneity. Pump and treat is also limited in the dilute portions of plumes where small amounts of contaminant are collected in large amounts of water.

Chemical Reactive Barrier

This technology utilizes a treatment material in a permeable trench or structure. The intercepted water is treated as it flows through the system and “clean” water is discharged. This technology has been the subject of active research throughout the world with investment by universities (Waterloo and others), companies (e.g., Envirometal Technologies, Inc. and others), and all relevant federal agencies. The most common treatment material for VOCs is granular iron (“zero-valent iron”), amended granular iron, sorbents derived from industrial byproducts, or waste organic material for redox control. In the case of iron, the barrier provides an environment that dehalogenates chlorinated VOCs as they pass through because of the high energy of the surface corrosion reaction and the high surface area. The primary problems with this technology relate to the chemistry of the water exiting the barrier, which often has a high pH (>10) and no dissolved oxygen. Other problems include low treatment flow rate, especially in low permeability materials, sometimes expensive installation, and unknown lifetime of the barrier materials.

Bioremediation

Bioremediation is an in situ treatment technology routinely applicable to organic contaminants. Heterogeneous and low permeability subsurface media complicate the delivery of nutrients. In general, bioremediation exhibits low health and safety risks and has high social acceptability. Classical bioremediation schemes and involve the timely addition of electron donors, electron acceptors and nutrients being flushed through the contaminant plume, resulting in toxicant degradation within months to years. Alternative delivery concepts are also possible. If nutrients were delivered in a manner such that time was not of the essence, then less aggressive bioremediation activities could, over time, compliment plume abatement and add value in terms of contaminant reduction per dollar spent.