WSRC-TR-2003-00330
June 18, 2004

POTENTIAL ENHANCEMENTS TO NATURAL ATTTENUATION: LINES OF INQUIRY SUPPORTING ENHANCED PASSIVE REMEDIATION OF CHLORINATED SOLVENTS

June 18, 2004

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Prepared for the United States Department of Energy under Contract No. DE-AC09-96-SR18500

POTENTIAL ENHANCEMENTS TO NATURAL ATTENUATION: LINES OF INQUIRY SUPPORTING ENHANCED PASSIVE REMEDIATION OF CHLORINATED SOLVENTS

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OVERVIEW

The Department of Energy (DOE) is sponsoring an initiative to facilitate efficient, effective and responsible use of Monitored Natural Attenuation (MNA) and Enhanced Passive Remediation (EPR) for chlorinated solvents. This Office of Environmental Management (EM) "Alternative Project," focuses on providing *scientific and policy support for MNA/EPR.* A broadly representative working group of scientists supports the project along with partnerships with regulatory organizations such as the Interstate Technology and Regulatory Council and the U.S. Environmental Protection Agency (EPA). The initial product of the technical working group was a summary report that articulated the conceptual approach and central scientific tenants of the project, and that identified a prioritized listing of technical targets for field research. This report documented the process in which: 1) scientific ground rules were developed, 2) lines of inquiry were identified and then critically evaluated, 3) promising applied research topics were highlighted in the various lines of inquiry, and 4) these were discussed and prioritized. The summary report will serve as a resource to guide management and decision-making throughout the period of the subject MNA/EPR Alternative Project. To support and more fully document the information presented in the summary report, we are publishing a series of supplemental documents that present the full texts from the technical analyses within the various lines of inquiry (see listing). The following report – documenting our evaluation of the state of the science of the characterization and monitoring process and tools-- is one of those supplemental documents.

Summary Report:
Natural and Passive Remediation of Chlorinated Solvents: Critical Evaluation of Science and Technology Targets, WSRC-TR-2003-00328

Supplemental documents:
Baseline Natural Attenuation Processes: Lines of Inquiry Supporting Monitored Natural Attenuation of Chlorinated Solvents, WSRC-TR-2003-00329
Potential Enhancements to Natural Attenuation: Lines of Inquiry Supporting Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00330
Multiple Lines of Evidence Supporting Natural Attenuation: Lines of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00331
Potential Enhancements to the Characterization and Monitoring of Natural Attenuation: Lines of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00332
Historical and Retrospective Survey of Monitored Natural Attenuation: A Line of Inquiry Supporting Monitored Natural Attenuation and Enhanced Passive Remediation of Chlorinated Solvents, WSRC-TR-2003-00333

Historically, the recognition, evaluation and reliance on natural processes for remediation and final polishing of contaminated sites have been problematical. Over the past fifteen years, however, significant progress has been made due to the efforts of regulatory and federal agencies such as the EPA and the U.S. Department of Defense (DoD), and others. This progress has taken the form of regulatory protocols and case studies from attempted implementation. To be successful, the DOE Alternative Project must link to, and build upon, this progress. A key component of responsibly advancing the technical basis for the use of MNA/EPR was documenting the baseline processes and tools that are used to characterize a site to determine if

MNA or EPR is appropriate and then to monitor the attenuating processes if MNA and/or EPR are viable, the state of the science for each process and class of technologies and areas for additional science. This document discusses processes/strategies used for enhancing mechanisms to support MNA and EPR.

Complete Text for Potential Enhancements to Natural Attenuation Writings

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List of Acronyms

ACP	Ashtabula Closure Project
cis-DCE	cis-1,2-dichloroethene
cVOC	Chlorinated volatile organic compound
DCE	Dichloroethene
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
EISB	Enhanced in situ bioremediation
EM	Environmental Management
EPA	United States Environmental Protection Agency
EPR	Enhanced Passive Remediation
ESTCP	Environmental Security Technology Certification Program
KCP	Kansas City Plant
MNA	Monitored Natural Attenuation
NAL	naphthalene
PCB	Polychlorinated biphenyl
PCE	Tetrachlorethene
SERDP	Strategic Environmental Research and Development Program
TCE	Trichloroethene
VC	Vinyl Chloride

Chemical Formulae

C-14	carbon 14 isotope
N	nitrogen

1.0 Introduction

The physical, chemical, and biological components of the natural attenuation capacity will have an impact on the magnitude of the flux of contaminants reaching a receptor. However, these processes may not be sufficiently robust to reduce the flux to within acceptable limits in undisturbed systems. Therefore, this section considers what potential actions might be feasible that will enhance their effectiveness by stimulating a natural process to be more active, work faster (improved kinetics), proceed to a more favorable end-state, or to improve the overall attenuation of contaminants beyond what is occurring naturally. The fundamental question is, "Can we either manipulate the system (e.g. hydrology) and/or the processes to achieve a desired end-state?"

There are several major objectives of any proposed enhancements. Enhancements must (a) increase attenuation of the contaminant (and/or decrease the flux of contaminants from the source that is feeding the plume) and (b) once implemented, be sustainable with little or no further interference. In this line of inquiry we consider a range of enhancements to the following general processes:

- Microbiological degradation
- Abiological processes
- Plant-based processes
- Large-scale hydrologic processes

1.1 Role of the line of inquiry

We know that certain natural biological, chemical, and physical processes take place in the subsurface that either degrade, retard migration, or disperse (i.e. dilute) chlorinated solvents. Each contributes to the overall reduction of contaminant fluxes. We also know, however, that some of these processes do not work efficiently enough for some natural systems to provide sufficient attenuation within a plume to meet regulatory requirements. For example, under certain circumstances native bacteria provide incomplete degradation of the solvents such that toxic intermediate constituents such as dichloroethene (DCE) or vinyl chloride (VC) are formed, but not destroyed at appreciable rates. Are there ways to stimulate the existing consortia (or add new, more favorable bacteria) to more completely degrade contaminants? Will such an enhancement, once implemented, be sustainable with little or no further intervention?

A second example is related to abiological processes such as abiological degradation or sorption. Are there ways to produce sustainable changes in these processes such that the rate of degradation is increased or the rate of desorption relative to that for sorption changes in favor of increased retardation and decreased flux of contaminants?

With respect to plants (herbaceous and woody) there are several dimensions to the possibility of enhancements. For example, can one take steps to improve the ability of the native plants to uptake and transpire or metabolize the contaminant? Can one enhance the biochemical processes naturally taking place in the root zone of native plants to increase the in situ destruction of the contaminants? Alternatively, one can consider introducing a new suite of plants that have been selected to have special properties for removing the contaminant either due to enhanced uptake/metabolism (e.g. hyperaccumulators) or improved/refined root-based reactions. Finally, careful manipulation of the type of trees introduced, their density of growth, and their specific placement relative to the contaminant plume can manipulate the amount of uptake and transpiration of groundwater and thereby modify the groundwater flow system or the amount of infiltration reaching the water table. The purpose of this enhancement is to manipulate the groundwater flow system in desirable ways or reduce the flux of contaminants reaching the aquifer from a contaminated source zone.

Large-scale hydrologic manipulation is designed to either fully or partially isolate the source of the plume or modify the flow system throughout the plume footprint by simple engineered methods in order to reduce the mass flux of contaminants within limits that can be accommodated by other natural attenuation processes. These can include various forms of surface caps and covers as well as subsurface engineered barriers that reduce the flux of contaminants by altering groundwater flow patterns.

In summary, the following sections will develop potential lines of inquiry that may lead to strategies for enhancing the effectiveness of natural attenuation processes. Figure 1 identifies these lines of inquiry at a high level. Detailed discussion of them is contained in sections 2 through 4.

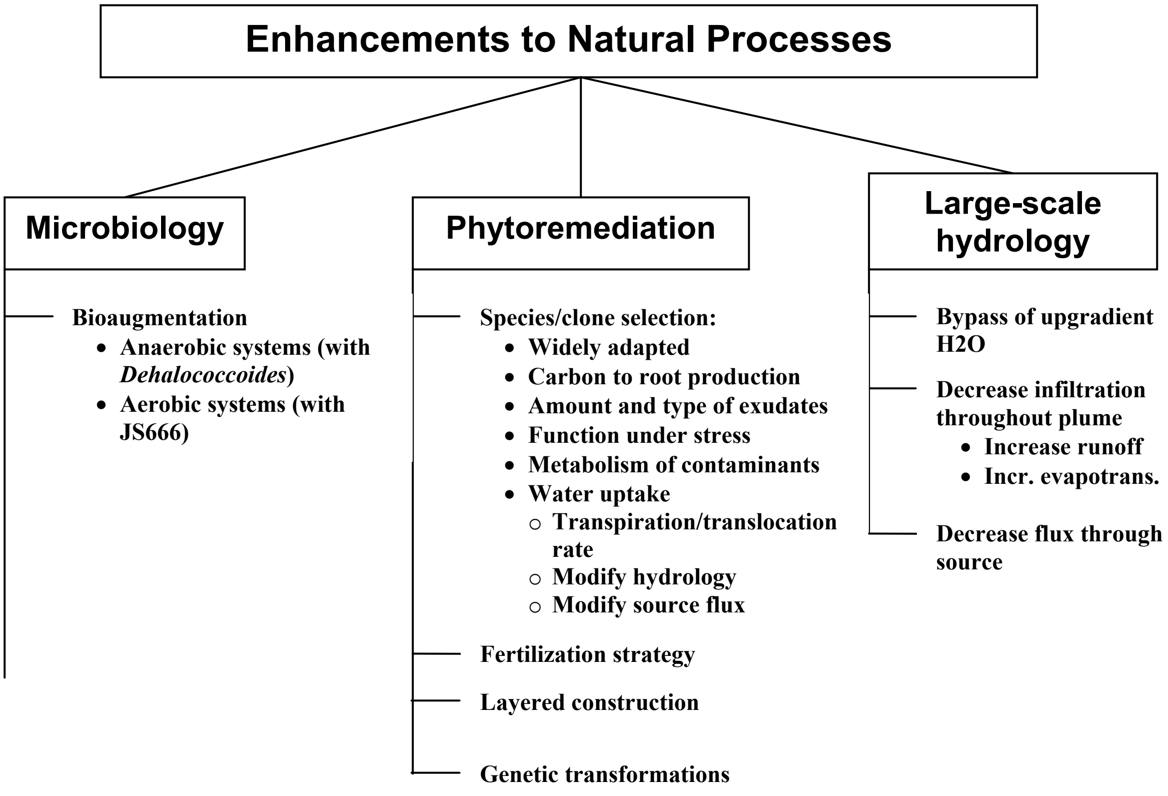


Figure 1. Lines of inquiry for the principle components of natural attenuation where enhancements may improve their efficiency.

2.0 Strategies to enhance effectiveness of microbiological attenuation

2.1 Bioaugmentation

Monitored natural attenuation (MNA) and enhanced *in situ* bioremediation (EISB) remedies hold the promise of reducing the costs associated with cleanup of DOE and DoD sites impacted by chlorinated solvents. However, there are many DOE and DoD sites where tetrachloroethene (PCE) and trichloroethene (TCE) are only undergoing partial dechlorination to cis-1,2-dichloroethene (cis-DCE), even when sufficient electron donor is present/added. The partial dechlorination tends to occur because microorganisms that halo-respire PCE and TCE, including *Dehalobacter*, *Desulfitobacterium, Dehalospirillum, Desulfonomile, Desulfuromonas, Enterobacter* are found widely in the environment, but are incapable of further dechlorinating cis-DCE to VC or ethene. As a result, there are a significant number of plumes at DOE, DoD and related sites where PCE and TCE have been dechlorinated to cis-DCE, but where the cis-DCE persists and migrates uncontrolled in groundwater rather than undergoing further dechlorination to ethene (the desired end product in MNA and EISB remedies).

Research has shown that bacteria from the group *Dehalococcoides* are the only known group of microorganisms that can dechlorinate cis-DCE via VC to ethene. While *Dehalococcoides* are present at many sites, they are not ubiquitous in the environment. Field demonstrations conducted by Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) have shown that it is possible to “engineer” MNA and improve EISB applications through bioaugmentation using cultures containing *Dehalococcoides* and allowing these microorganisms to slowly disperse and populate the aquifer, provided that a suitable electron donor and reduced conditions exist within the plume (Major et al, 2002, Ellis et al., 2001)

However, anaerobic bioremediation/bioaugmentation may not be the best remediation strategy at sites with large cis-DCE plumes in aerobic aquifers. Instead, aerobic biotreatment of the cis-DCE may be more cost-effective, provided that this process can be induced to occur over the target treatment area. Until recently, aerobic biodegradation of cis-DCE was thought to require addition of an appropriate cometabolite such as methane, propane or toluene, to stimulate the co-oxidation of the cis-DCE, and this process was generally determined to have limited feasibility for large scale field application. Recent research conducted under SERDP sponsorship (CU-1168) has isolated and described a novel aerobic bacterium (JS666) that uses cis-DCE as sole carbon and energy source (Coleman et al., 2002a,b). This organism was found in only one of 37 sample-types screened for ability to aerobically oxidize cis-DCE. Thus, while not necessarily *unique*, it appears at least to be relatively rare. Since it requires no exotic growth factors, JS666 is a promising bioaugmentation agent for aerobic sites where cis-DCE is recalcitrant. In essence, this microorganism can be used to achieve MNA, without any further intervention other than adding it to groundwater because the microorganism will grow and thrive when oxygen and cis-DCE are combined. Though cisDCE is the only chloroethene known (thus far) to serve as growth substrate for JS666, the organism transforms several other chloroethenes (trichloroethene, 1,2-dichloroethane, trans-dichloroethene, and vinyl chloride), suggesting that it may be effective in mixed-contaminant systems.

3.0 Strategies to enhance effectiveness of phytoremediation

Lines of Inquiry are derived from the predominant mechanisms of phytoremediation, with the goal being to enhance natural processes that are already active, while promoting potentially productive avenues that may now not be operating at high rates, but can be enhanced by engineering approaches (e.g., use of transgenics). To a large extent the utility of phytoremediation is dependent on plant root interaction with the contaminant.

Processes that increase the surface area of contact are likely to enhance phytoremediation. For example, the main pathway for uptake of TCE is passive via the plant transpiration stream. Over 50% of the [C-14] recovered label of TCE in a wetland microcosm containing broad-leaved cattail (*Typha latifolia*) and eastern cottonwood (*Populus deltoides*) was volatilized (Bankston et al. 2002), suggesting a critical role for plant transpiration. Another key role of plants may be in modifying the rhizosphere to promote microbial degradation of the contaminant, primarily through the production and release of organic acids and water-soluble carbohydrates. Therefore, goals associated with enhancing phytoremediation are to 1) increase our fundamental understanding of the biochemical basis for phytoremediation, 2) deploy available plants that maximize chlorinated volatile organic compound (cVOC) uptake microbial destruction, and 3) enhance phytoremediation by genetic transformation to produce larger root mass. Enhancing root surface area increases contaminant contact and contaminant uptake and can promote exudate production and thereby increase in situ microbial degradation of the contaminant.

3.1 Criteria and characteristics of selection of alternate species

Ideal plant species for phytoremediation 1) are widely adapted and fast-growing perennials (required for long-term phytoremediation of contaminated sites), 2) allocate a large fraction of assimilated carbon to root production and maintenance (required to occupy and affect large soil volumes), 3) produce and exude high concentrations of organic acids and water-soluble carbohydrates that can sustain the plant-microbe interactions, and 4) continue to function (as described in 1-3 even under stresses, such as drought. A wide range of plant species has demonstrated varying degrees of phytoremediation capability, either directly on TCE or indirectly via stimulating rhizosphere interactions (Anderson et al. 1995).

Of the tree species evaluated at a site in the southeastern US contaminated with TCE and *cis*-DCE, bald cypress (*Taxodium distichum*), tupelo (*Nyssa aquatica*), and loblolly pine (*Pinus taeda*) contained the highest concentrations of TCE, particularly in the lower trunk (Vroblesky et al. 1999). Several recent studies highlight the physiological and morphological characteristics that set poplar species and their hybrids apart as ideal candidates for phytoremediation in temperate climates (Newman et al. 1997, Gordon et al. 1998, Shang et al. 2001, Bankston et al. 2002). For tropical and subtropical climates, the capability of a tropical leguminous tree (*Leuceana leucophala*) recently was demonstrated to take up and metabolize ethylene dibromide and TCE (without its symbiont – i.e. with the nitrogen fixing bacteria removed to avoid confusion of the mechanism) (Doty et al. 2003). Therefore, one obvious research need includes matching species with high phytoremediation potential with environmental constraints (above and below ground) prevailing at the contaminated site.

Members of the genus *Populus* in general are fast-growing, woody perennials ideally suited for phytoremediation. Most taxa within the genus are cross-fertile, thus allowing numerous, broadly adapted hybrids to be created (Stettler *et al.* 1980, Dickmann and Stuart 1983). Hybrids currently exist that are tolerant of drought, high salt concentrations in soils, or periodic flooding (Tuskan 1998). A further advantage of *Populus* is that once selected, individual hybrids can be easily cloned, permitting a superior genotype to be propagated and utilized across a large number of sites. Most hybrid poplars display hybrid vigor in their growth rates and basic physiology (Heilman and Stettler 1990). Under optimum conditions, hybrids can achieve above ground growth rates of 10 dry tons per acre per year (Heilman and Stettler 1985). Below ground growth is equally high, with structural root dry weights representing ca. 33% of the above-ground dry weight and fine root turnover occurring at ca. 0.5 dry tons per acre per year (Dickmann *et al.* 1996). Fine root turnover is important because it ultimately increases soil carbon content (Hansen 1993) and may alter soil pH, both of which are factors in sustaining soil microbial populations. Furthermore, DOE is sponsoring a large research effort that will elucidate the genome of *Populus* within the next year. This milestone will open new opportunities for selecting clones and generating transgenics that express key genes that will enhance phytoremediation capabilities.

Structural root systems of many hybrids occupy and affect a large volume of soil, penetrating to depths of 6 to 12 feet depending upon the soil texture and depth to water table. Besides their capacity to exploit large soil volumes and their high water use, poplar trees are capable of taking up TCE and metabolizing it into trichloroethanol, trichloroacetic acid, and dichloroacetic acid (Newman et al. 1997). Furthermore, trichoroethanol was glycolysated and was detectable in all tissues in concentrations 10x greater than free trichloroethanol (Shang et al. 2001). Research is needed that establishes the phytoremediation potential of the different poplar species and their hybrids and the main modes of TCE degradation.

3.2 Transpiration as a contaminant removal mechanism

Beyond actual uptake and metabolism of contaminants such as TCE, plants also can translocate contaminants from the soil and groundwater to the atmosphere through transpiration. Laboratory research has shown that poplar trees have a promising ability to uptake and transpire TCE, atrazine (Burken and Schnoor, 1996) and other organic contaminants. For some species (e.g., alfalfa), much of the phytoremediation of TCE is accomplished via plant transpiration, although some degree of microbially-mediated anaerobic biodegradation is also evident (Narayanan et al. 1995, 1999).

High transpiration rates facilitate high consumptive water use, which provides a vehicle for the uptake and movement of soil-bound compounds into and through the vascular cambium. Judicious selection of plant species or clones or cultivars that maximize water use by maintaining active production of leaves and/or high leaf area index can be achieved. Field data indicate that some hybrid poplars consume 30-54 inches of water per acre per year during the growing season (Hansen 1992). Some clones allocate a considerable amount of carbon below ground in the form of an extensive root system, but there is a balance in the amount of roots (and their ability to cover a large soil volume) and the amount of leaf area that is required to support an extensive root system. Determination of water balance to estimate evapotranspiration from vegetative cover types is needed, including leaf measurements of transpiration and whole-plant measurements of water use, to evaluate in more detail the diurnal and seasonal patterns of whole-plant water use.

In summary, plants can be used as sustainable solar-driven pump-and-treat systems. However, research is needed to fully exploit clonal variability in water use to maximize this component of phytoremediation potential.

3.3 Transpiration as a hydrologic control mechanism

A second potential benefit of high transpiration rates is the ability of trees to alter water infiltration fluxes and to manipulate the shape of the water table that can result in changes in the location and geometry of contaminant plumes. Consumption of 30-54 inches of water per acre/year by some hybrid poplars may be sufficient to have a significant affect on subsurface soil moisture and to modify groundwater flow and contaminant migration in predictable ways.

One approach is to use plants to control the flux of infiltrating recharge through the vadose zone. This has been suggested as a method for reducing the dissolution rate and associated flux of contaminants from a cVOC source in the unsaturated zone. In principle it is a methodology for controlling (i.e. reducing) the mass flux of contaminants from the source to enable the natural attenuation capacity of the aquifer to become effective.

A second approach is to use the high transpiration rates of trees such as poplars to modify the shape of the water table. It may be feasible to use this strategy to create hydrologic barriers to influence contaminant migration pathways in desirable ways. For example, it may be possible to use this strategy to reduce the zone of discharge to surface streams or wetlands and to optimize placement of other treatment and monitoring facilities.

At the present time there have been few, if any, field studies to demonstrate that these approaches are viable. Measurements of transpiration rates, water uptake, and localized impacts to the water table as a result of trees have been made. Likewise, modeling studies have been conducted that support the potential value of these strategies. However, confirmatory field evidence for the specific purposes of modifying contaminant migration and attenuation are lacking.

3.4 Enhancements to improve plant-rhizosphere interactions

3.4.1 Enhancements to natural capacity

Plants can also be used as sources of soil carbon to enhance plant-rhizosphere interactions. There is a need to better understand what rhizosphere mechanisms allow plants and microbes to effectively process contaminants in soils. Carbon inputs to soils improve the environment for degradation of TCE by bacteria. The carbon input occurs both from the microbial-driven breakdown of plant tissues (decay of abscised roots and leaves), and from the direct exudation of organic solutes from living tissues. There is a need to determine the constitution of organic solutes in fine roots that are likely to be important in phytoremediation. Specifically, tricarboxylic organic acids, phenolic acids and water-soluble carbohydrates can support soil microbes. It is well known that plants exude large amounts of organic acids, carbohydrates, phenolics, etc. upon exposure to stress, such as excessive metal availability levels (Lee *et al.*, 1977; Thurman and Rankin, 1982).

Populus species and hybrid clones display great variability in the organic acids produced from root exudates. Examples include citric acid, malic acid, oxalic acid, salicylic acid, and their higher-order phenolic glucosides that are complexed with caffeic acid and benzoic acid (populin, tremuloiden, tremulacin, salireposide, salidroside, etc.) (Tschaplinski and Tuskan 1994, Tschaplinski and Blake 1994, Tschaplinski and Blake 1989a,b). The function of hybrid poplar in phytoremediation has been largely attributed to the production of these organic acids and phenolics released as root exudates when roots are exposed to contaminated environments, but details of which clones and which specific compounds are most stimulatory of plant-microbial interactions that foster TCE breakdown are not well known. Prudent clone selection can be used to maximize production of those organic acids, water-soluble carbohydrates and phenolic compounds that will enhance microbe availability and TCE metabolism.

3.4.2 Fertilization – what and how applied

Fertilization can be used to promote plant growth and microbial degradation. There are tradeoffs though as excessive fertilization can depress phenolic concentrations (e.g., salicylates) in plant tissues, as most of the soluble organic solutes are required for biomass production and a lower proportion of the fixed carbon is partitioned into secondary carbon (phenolic) metabolism. However, increased dry matter production that occur following fertilization increases carbon input from the turnover of fine roots. This increases carbon availability as well as the potential for increased organic acid exudation from roots. Nitrogen (N) fertilization has a profound effect on increasing the flux in organic acid production, where the organic acids produced in the tricarboxylic acid cycle (Krebs cycle) are used as carbon skeletons to assimilate the applied N into amino acids. Fertilizer application needs to be timed to when it is most beneficial for plant-microbial interactions. Excessive addition of ammonia can lead to damage of the fine roots, especially under flooded conditions during which the plants have a limited capacity to assimilate the N that has been applied. Different plant species and clones also have different requirements for nitrate versus ammonia-N as well as other macro and micronutrients that have to be optimized, before a fertilization strategy is deployed.

3.5 Layered construction to establish or enhance plant communities

Layered construction can be used to enhance the phytoremediation capability of a plant community. However, the long-term phytoremediation potential and modes are complicated by the prevailing redox conditions and how that changes over time with ecological succession. For example, the mix of plant species can increase the interaction with the contaminant by ensuring both shallow and deep-rooted species are established at a site. If the site is a wetland, direct degradation will likely occur under reducing conditions as dictated by the redox conditions prevalent in soils (Williams 2002). Planting tree species (e.g., poplar) that can survive under such conditions will over time modify the soils (via increased transpiration) to oxidizing conditions, with the degree and modes of phytoremediation changing over time. Little is known of the diverse microbial populations that would shift over time as the plant associations and soil conditions change, and how those changes alter the communities' capacity to remediate the site.

3.6 Genetic transformation of higher plants for enhanced phytoremediation

Genetic transformation offers the potential to improve a plant's ability to detoxify, sequester or isolate contaminants by modifying plant morphology or physiology. Generally, two genetic engineering approaches to enhance remediation by higher plants are through two *Agrobacterium* species, *A. rhizogenes* and *A. tumefaciens,* by 1) engineering roots with larger root biomass and 2) insertion of genes for direct remediation functions. *A. rhizogenes* causes hairy root symptoms in plants via genetic transformation by infection of wounding sites and transferring hairy root gene from the Ri plasmid of the bacteria into the host genome (Tepfer 1989). An increase in large root masses by using *A. rhizogenes* potentially increases water uptake relative to non-transformed plants, with a larger amount of soil contaminants moved to plants, where they can be degraded (Stomp *et al*., 1993) or transported to the leaves and transpired to the atmosphere. Additionally, the increased rhizosphere surface contact with contaminated soils and enhanced root exudation can increase rhizosphere microbial activities. Increased root mass in genetically transformed plants enhances the production (quantity and quality) of secondary carbon metabolites and microbial activity in the rhizosphere, thus increasing the capacity of vegetation to translocate TCE and other VOCs from soils to aboveground plant components.

Genes responsible for detoxification of several organic contaminants have been identified. Phytoremediation using genetically-transformed plant materials currently includes the breakdown of trichloroethylene and other chlorinated halogens via naphthalene (NAL) degradation genes. The NAL degradation genes can be included in the Ri plasmid, and placed under a constitutive promoter to allow continuous expression of the introduced genes. Transformation using the NAL gene construct will result in novel enzyme synthesis for the detoxification of TCE and other chlorinated halogens. Profound increases (640x) in the metabolism of TCE have been accomplished by the introduction of the mammalian cytochrome P450 2E1, with the enzyme oxidizing TCE, ethylene dibromide, carbon tetrachloride, chloroform and vinyl chloride (Doty et al. 2000). Other enzyme systems that result in TCE degradation can be identified in effective organisms, with the genes then similarly transferred into poplar clones to further enhance TCE degradation capability.

4.0 Large scale hydrologic modifications to enhance natural attenuation

Most of the concepts for EPR rely on increasing the attenuation capacity of the system so that it is sustainable and exceeds the contaminant loading. An alternative concept is to reduce the contaminant loading so that the natural attenuation capacity of the site is sufficient. There are a variety of different approaches that are possible to achieve this goal. Most of these approaches rely on reconfiguring the site to permanently modify the large-scale hydrology. Because "loading" is the product of concentration and flow, this term can be directly modified by altering and reducing the flow of water. Further, setting up permanent, sustainable, and easily documented changes in large-scale hydrology is relatively straightforward. Flow controls will be in place as long as the hydraulic controls are in place.

This concept uses large-scale modification of the hydrologic system to reduce flow and minimize contaminant loading. Hydraulic controls attempt to prevent contaminated water from reaching certain regions of the aquifer or to prevent clean water from contacting contaminated sources. Hydraulic controls alone are often not considered in evaluating options because they do not destroy or immobilize contaminants. When considered in the context of MNA and EPR where the goal is to maximize capacity and minimize loading, this concept appears promising. Implementation can take many forms including the obvious variants that have been periodically considered and implemented: "capping near the source" and "building a dam." These concepts may provide some improvements, but as described below, there are other viable concepts that may perform even better. A dam installed on a gaining stream, for example, provides a transient benefit, but over time, the plume discharge shifts to a location just below the dam. After a new steady state is established, the loading, the flow rates and total flow times are often similar to the pre-dam conditions. Alternative concepts to dams and caps include: "passive collection and bypass of clean up-gradient water", and "increasing runoff and evapotranspiration throughout the plume area". While not yet widely implemented, these approaches are receiving increasing attention as DOE is developing strategies for sites that are contaminated with chlorinated and radioactive contaminants. Recent examples include technical recommendations for plumes at the DOE Kansas City Plant (KCP), the Ashtabula Closure Project (ACP), and the Savannah River Site (e.g., DOE, 2002).

The DOE KCP is underlain by a low permeability material characterized by low groundwater flow rates and a stable plume of chlorinated solvents and polychlorinated biphenyls (PCBs). The site is bounded by rivers that receive the relatively limited quantity of groundwater flow and which are subject to periodic flooding from stormwater surges (Figure 2). KCP managers are developing a comprehensive strategy to address both short term issues, such as trace contamination appearing in storm sewers that traverse the plume, and long-term issues, such as implementing technically based and protective actions for the whole site.

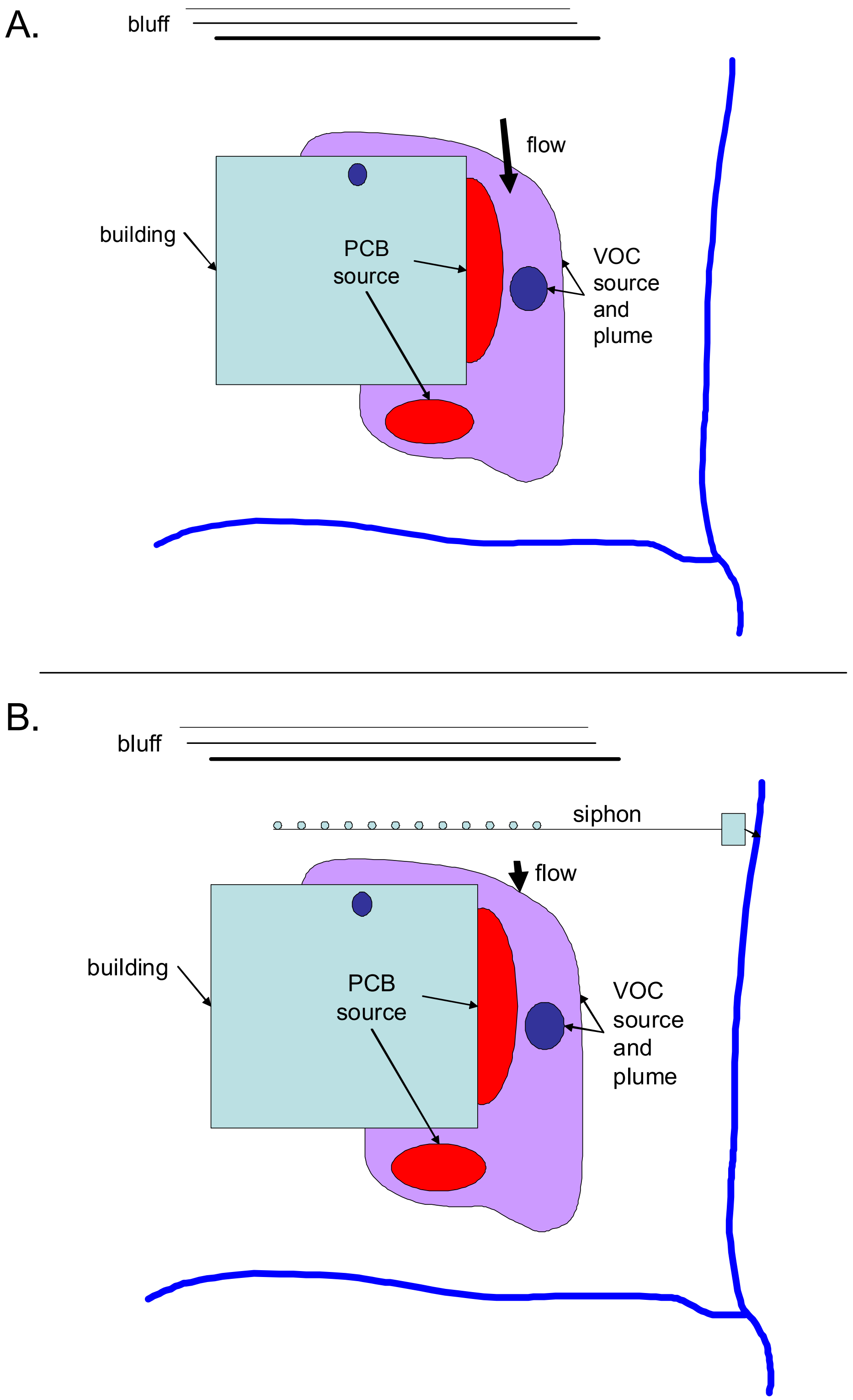


Figure 2. Simplified diagram of Geosiphon concept as evaluated for Kansas City Plant; a) baseline, b) with controls

One of the potential long-term actions recommended by an independent technical team was up-gradient water collection and control. This simple concept collects clean water up-gradient of the source and sends it down-gradient using an engineered system. This further reduces flow though the system and the potential contaminant loading. Every gallon of water that is bypassed is a gallon of water that is not available to leach and move the chlorinated solvent. Up-gradient water control management, especially if the water is clean, is low cost, moderately low risk and easily implemented. The team concluded:

> "If data and risk assessment show that the residual sources are relatively stable and only limited supplementary methods would assure risk reduction performance, a passive version of this technology might be applied. In this configuration, up-gradient "geosiphon" wells (such as those developed at the Savannah River Site) or high evapotranspiration plantings (such as have been applied at Portsmouth and other sites) would extract water. The system would target clean water entering the system from the bluffs to the north along with infiltration north of the major site plume(s). For the geosiphon, the difference in elevation between the water level in the wells and the receiving Blue River provides the motive force for water flow from the wells via a siphon. The result would be a reduction in the driving force through the groundwater system minimizing flow through PCB and VOC source zones. The system would need to be carefully designed to pump an appropriate quantity of water to flatten the gradient without inducing flow toward the siphon. More modeling (or addition of appropriate scenarios to existing models) would be useful to properly design and document a geosiphon system…. A geosiphon/phytoextraction may be viable at this site." (DOE 2002)

A passive up-gradient collection and bypass system is a particularly attractive option, but all forms of large-scale hydraulic control should be examined. In addition to the geosiphon concept described above, various DOE sites are considering horizontal drain wells, maximizing evapotranspiration and runoff, using capillary barriers, and low permeability caps to reduce up-gradient flow into plumes and dams and down-gradient infiltration system to slow the plume migration rate. In clean up-gradient areas, creative systems for controlling water levels using engineered wells that connect two aquifers that have different water levels have been proposed (Figure 3). Finally, systems that combine hydrologic control with creation of a sustainable reaction zone have been proposed (Figure 4). Few of these systems have been selected and implemented so the practicality and utility within the framework of disciplined and documentable MNA is uncertain. Most of the efforts to data have been qualitative rather than quantitative. Additional quantitative evaluation of the potential of such systems will be needed to support inclusion of this class of enhancement in the next generation MNA/EPR protocols.

The major advantage of this concept is that it approaches the challenge if MNA and EPR from a different perspective and provides process control that is distinct from the generally recognized concepts of manipulating attenuation capacity. Moreover, large-scale hydrology modification is relatively straightforward to model and document and monitoring is likely to be inexpensive. Simply stated, differences in hydraulic head are robust and will operate without detailed knowledge of underlying processes.

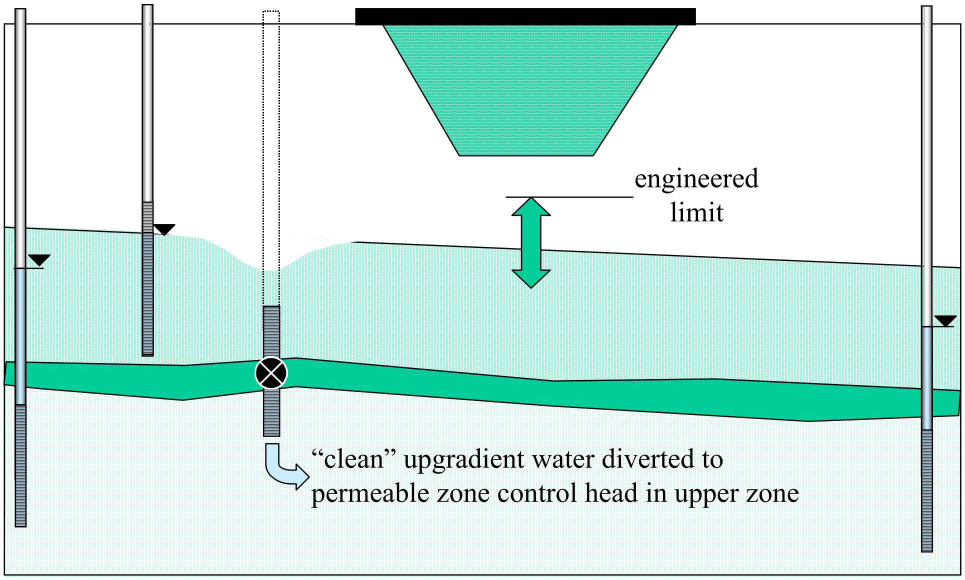
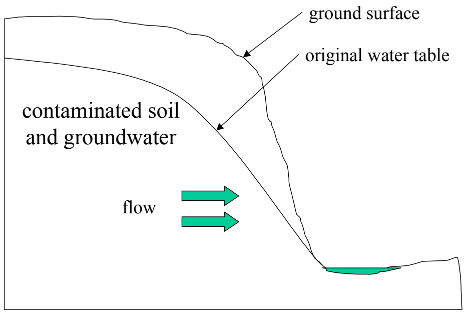


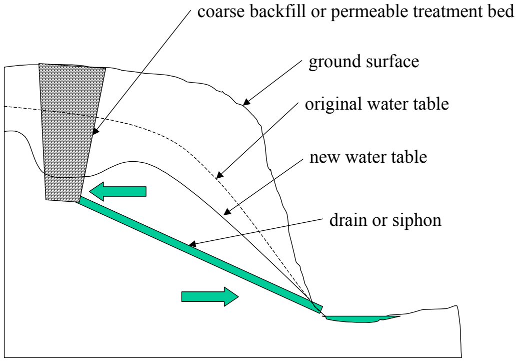
Figure 3. Control well system to reduce flow of water, hydraulic driving force for plume migration, and contaminant loading. Various designs for the well control system have been evaluated.

a)



Baseline Conditions

b)



Basic GeoDrain
(see text for description of options)

c)

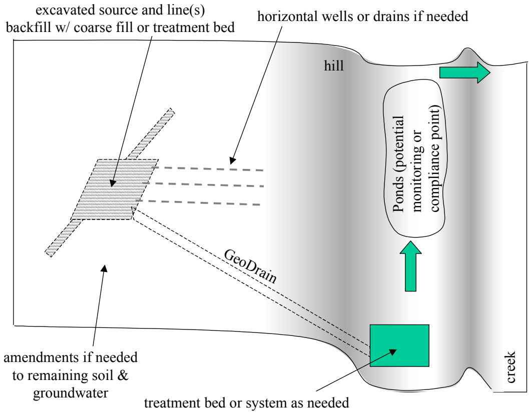


Figure 4. Simplified Schematic Diagrams of Options developed for the Waste Management Unit at the DOE ACP - a) baseline conditions, b) cross section with controls, c) site configuration options.

References

Anderson, T.A., and B.T. Walton. 1995. "Comparative fate of [C-14] trichoroethylene in the root-zone of plants from a former solvent disposal site". *Env. Tox. and Chem*. 14:2041-2047.

Bankston, J.L., D.L. Sola, A.T. Komor, and D.F. Dwyer. 2002. "Degradation of trichloroethylene in wetland microcosms containing broad-leaved cattails and eastern cottonwood". *Water Res*. 36:1539-1546.

Burken, J.G., and J.L. Schnoor. 1996. "Phytoremediation: Plant uptake of atrazine and role of root exudates". *J. Env. Eng*. 122:958-963

Dickmann, D.I., and K.W. Stuart. 1983. *The Culture of Poplars in Eastern North America*. Hickory Hollow Associates, Dansville, MI.

Dickmann, D.I., P.V. Nguyen, and K.S. Pregitzer. 1996. "Effects of irrigation and coppicing on above-ground growth, physiology, and fine-root dynamics of two field-grown hybrid poplar". *For. Ecol. and Manage*. 80:163-174.

DOE, 2002. *Technical Assistance to Kansas City Plant: Mitigation of Polychlorinated Biphenyl Discharges*, WSRC-RP-2003-00276, DOE Office of Environmental Management, available from the DOE Office of Science and Technology Information, Oak Ridge TN.

Doty, S.L., T.Q. Shang, A.M. Wilson, A.L. Moore, L.A. Newman, S.E. Strand, and M.P. Gordon. 2003. "Metabolism of the soil and groundwater contaminants, ethylene dibromide and trichloroethylene, by the tropical leguminous tree, *Leuceana leucephala*". *Water Res*. 37:441-449.

Doty, S.L., T.Q. Shang, A.M. Wilson, J. Tangen, A.D. Westergreen, L.A. Newman, S.E. Strand, and M.P. Gordon. 2000. *Proc. Nat. Acad. Sci*. 97:6287-6291.

Ellis, D.E., E.J. Lutz, J.M. Odom, R.J.J. Buchanan, C.L. Bartlett, M.D. Lee, M.R. Harkness, and K.A. Deweerd, 2000. "Bioaugmentation for accelerated in situ anaerobic bioremediation," *Environmental Science and Technology* 34:2254-2260.

Gordon, M.P., N. Choe, J. Duffy, G. Ekuan, P. Heilman, P. Muiznieck, M. Ruszaj, B.B. Shurtleff, S. Strand, J. Wilmoth, and L.A. Newman. 1998. "Phytoremediation of trichloroethylene with hybrid poplars". *Env. Health Pers*. 106:1001-1004.

Hansen, E.A. 1993. "Soil carbon sequestration beneath hybrid poplar plantations in the north central United States". *Biomass and Bioenergy* 5:431-436.

Hansen, E.A. 1992. "Mid-rotation yields of biomass plantations in the north central United States". U.S.D.A. Forest Service Res. Pap. NC-309. 8 p.

Heilman, P.E., and R.F. Stettler. 1985. "Genetic variation and productivity of *Populus trichocarpa* and its hybrids. II. Biomass production in a 4-year plantation". *Can. J. For. Res*. 15:382-388.

Heilman, P.E., and R.F. Stettler. 1990. "Genetic variation and productivity of *Populus trichocarpa* and its hybrids. IV. Performance in short-rotation coppice". *Can. J. For. Res*. 20:1257-1264.

Lee J., K.D. Reeves, R.R. Brooks, and T. Jaffre. 1977. "Isolation and identification of a citrato-complex of nickel from nickel-accumulating plants". *Phytochem*. 16:1503-1505.

Major, D.W., M.L. McMaster, E.E. Cox, E.A. Edwards, S.M. Dworatzek, E.R. Hendrickson, M.G. Starr, J.A. Payne, and L.W. Buonamici, 2002. "Field demonstration of successful bioaugmentation to achieve dechlorination of tetrachloroethene to ethane," *Environ. Sci. Technol*. 36(23):5106-5116.

Narayanan, M., L.E. Erickson, and L.C. Davis. 1999. "Simple plant-based design strategies for volatile organic pollutants". *Env. Prog*. 18:231-242.

Narayanan, M., L.C. Davis, and L.E. Erickson. 1995. "Fate of volatile chlorinated organic-compounds in a laboratory chamber with alfalfa". *Environmental Science and Technology* 29:2437-2444.

Newman, L.A., S.E. Strand, N. Choe, J. Duffy, G. Ekuan, M. Ruszaj, B.B. Shurtleff, J. Wilmoth, P. Heilman, and M.P. Gordon. 1997. "Uptake and biotransformation of trichloroethylene by hybrid poplars". *Environmental Science and Technology* 31:1062-1067.

Shang, T.Q., S.L. Doty, A.M. Wilson, W.N. Howald, and M.P. Gordon. 2001. "Trichloroethylene oxidative metabolism in plants: the trichloroethanol pathway". *Phytochem*. 58:1055-1065.

Stettler, R.F., R. Koster, and V. Steenackers. 1980. "Interspecific crossability studies in poplars". *Theor. Appl. Genet*. 58:273-282.

Stomp, A.M., K.H. Han, S. Wilbert, and M.P. Gordon. 1993. "Genetic improvement of tree species for remediation of hazardous wastes". *In vitro Cell Dev. Biol*. 29:227-232.

Tepfer, D. 1989. "Ri T-DNA from *Agrobacterium rhizogenes*: a source of genes having applications in rhizosphere biology and plant development, ecology and evolution". In: T. Kosuge and E.W. Nester, eds. *Plant-microbe interactions, molecular and genetic perspectives*, vol. 3, pp. 294-342.

Thurman D.A., and A.J. Rankin. 1982. "The role of organic acids in zinc tolerance in *Deschampsia caespitosa"*. *New Phytol*. 91:629-635.

Tschaplinski, T.J., and T.J. Blake. 1994. "Carbohydrate mobilization following shoot defoliation and decapitation in hybrid poplar". *Tree Physiol*. 14:141-151.

Tschaplinski, T.J., and T.J. Blake. 1989a. "Correlation between early root production, carbohydrate metabolism, and biomass production in hybrid poplar". *Can. J. Bot*. 67:2168-2174.

Tschaplinski, T.J., and T.J. Blake. 1989b. "Water stress tolerance and late-season organic solute accumulation in hybrid poplar". *Can. J. Bot*. 67:1681-1689.

Tschaplinski, T.J., and G.A. Tuskan. 1994. "Water-stress tolerance of black cottonwood and eastern cottonwood clones and four of their hybrid progeny. II. Metabolites and inorganic ions that constitute osmotic adjustment". *Can. J. For. Res*. 24:681-687.

Tuskan, G.A. 1998. "Short-rotation woody crop supply systems: We do we know and what do we need to know?" *Biomass and Bioenergy* 14:307-315.

Vroblesky, D.A., C.T. Nietch, and J.T. Morris. 1999. "Chlorinated ethenes from groundwater in tree trunks". *Environmental Science and Technology* 33:510-515.

Williams, J.B. 2002. "Phytoremediation in wetland ecosystems: Progress, problems, and potential". *Crit. Rev. Plant Sci*. 21:607-635.