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Phytoremediation of Trichloroethylene (TCE)

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Introduction

Trichloroethylene (TCE) is a chlorinated hydrocarbon used as a solvent in many degreasing and dry-cleaning operations. TCE is one of the most widespread contaminants of soil and groundwater in the United States. It can be found at 50% of the Superfund National Priority List cleanup sites managed by the United State Environmental Protection Agency (USEPA). According to the USEPA, TCE is also above action levels in 17% of the groundwater and 16% of the soil at Resource Conservation and Recovery Act sites (Cooke 1999; Schmiedeskamp 1997; Chappell 1998).

Remediation of trichloroethylene is a priority because it is a suspected carcinogen. Known as a mutagen from laboratory studies, chronic inhalation exposure has been found to cause liver, kidney, and neural reactions in animals. Vinyl chloride, a breakdown product of TCE, is considered even more toxic. The USEPA estimates that drinking 1 part per million (ppm) TCE in water over a lifetime will cause cancer cases in 32 persons in 100,000, while drinking 1 ppm vinyl chloride will cause 9,570 cases in 100,000 (Chappell 1998).

TCE tends to enter soil in relatively small areas--from leaking drums, pipes or landfills--and to diffuse outward through unsaturated zones in the soil. As it continues to move through the soil, it reaches downward to underlying aquifers. Because TCE is denser than water, it then "collects in small pools of contaminant" at the bottom of aquifers. Consequently, TCE is difficult to locate and bring to the surface (Cunningham *et al.* 1996; Cooke 1999).

In the past, TCE has been remediated in soil by removing the contaminated soil and transporting it to incinerators where it was burned. TCE has been removed from groundwater by pumping contaminated water to the surface and passing it through carbon adsorption/absorption filters. In situ groundwater treatments have involved the stimulation of microbial activity in aquifers, a bioremediation technique whereby microbes break down TCE (Newman *et al.* 1997).

More recently, phytoremediation has been suggested as a strategy for treating TCE contamination. Phytoremediation uses plants to remove, degrade and stabilize contaminants in soil and water. Researcher S.D. Cunningham has described phytoremediation as the use of plants for "solar-driven pumping and filtering systems" (though plants don't actively transport TCE). Their roots have been described as "exploratory, liquid phase extractors that can find, alter, and/or translocate elements and compounds" (Cunningham *et al.* 1996).

In the case of TCE contamination, hybrid poplars (*Populus trichocarpa x Populus deltoides*) and Eastern cottonwoods (*Populus deltoides*) have received most of the attention. These are phreatophytic species, meaning that their deep roots draw water from the water table. In addition, poplars and cottonwoods have a fast growth rate, and have demonstrated an ability to take up TCE from both soil and water.

A number of mechanisms have been suggested to explain why phreatophytes may be useful in clean-up of TCE, and to predict the fate of TCE during phytoremediation:

- Phreatophyte roots may break down TCE in soil through the effect of the enzyme dehalogenase, a root exudate which transforms or mineralizes TCE.
- Phreatophytes and other plants may assist in TCE breakdown in soil through enhancement of microbial activity in the rhizosphere. Plant roots provide passive aeration, serve as a nutrient source for microbes, and draw water to the surface.
- Plant tissues may accumulate TCE. Poplars have demonstrated the ability to uptake and store heavy metals in intracellular root spaces, and to translocate these compounds to shoots and leaves (Hinchman 1994). Some researchers believe that the same mechanism may be effective in removing organic compounds such as TCE.
- Phreatophytes may remove TCE through metabolism, converting it all the way to normal end points such as carbon dioxides and salts.
- Poplars may provide a hydraulic control of TCE, containing subsurface water through uptake, thus decreasing the tendency of surface contaminants to move toward groundwater. Poplars have been shown to transpire from 50 to 300 gallons of water per day under some conditions (Technology Innovation Office 1998).

Recent Research

Recent research has been able to illuminate some of the predicted mechanisms for TCE phytoremediation. Early studies focused on the degradation of TCE by *ex planta* enzymes (those released by the plant into the root zone). Dehalogenases have been identified as enzymes that degrade TCE, but their degradation capacities are not fully understood. Degradation capacity depends not only on the production of dehalogenases and their ability to degrade TCE, but also on their rate of release, the nature of the soil, and the concentration of TCE, areas that have not yet been addressed (Cunningham *et al.* 1996).

Rhizosphere interactions among soil, microbes, plants, and TCE have also been studied. Excretion of root exudates contributes to an increase in the density of microorganisms in the rhizosphere, and the metabolic activity of these microorganisms is greater than that in soil without exudates. Accelerated degradation of TCE has been documented in slurries of rhizosphere soil collected from four plant species at a former solvent disposal site; these same soil samples also showed significant mineralization of TCE (Walton and Anderson, in Cunningham *et al.*, 1996). Reseachers speculate that these lab cultured rhizosphere samples gave conservative estimates of degradation and mineralization, and that if living plants were growing in the samples, degradation would have increased. However, this was not confirmed.

In planta studies at the University of Washington have been conducted in the laboratory, the greenhouse, and in a controlled field setting (Newman *et al.* 1998). Axenic (sterile, homogenous) cell cultures have been studied to examine the metabolic capabilities of hybrid poplar (*P. trichocarpa x P. deltoides* line H 11-11) in the absence of soil, mycorrhizal flora, or microbial activity. Axenic poplar cells were incubated with TCE, and methyl-*t*-butyl ether was used to extract metabolites from the cells for analysis by gas chromatography using an electron capture detector. Chloral, trichloroacetate, dichloroacetate, and trichloroethanol compounds were identified in extracts of plant cells exposed to TCE. These compounds have been previously identified in mammals and bacteria as oxidative metabolites of TCE; thus, researchers suspect that similar oxygenase activities exist in poplar cells (Newman *et al.* 1997).

The axenic poplar cell cultures were also incubated with ^{14}C radiolabeled TCE in a sealed system for various time lengths. In a careful mass balance, the radiolabel incorporated into the cells was traced and quantified, as was the amount remaining in the media, CO_2 produced by mineralization, and untransformed TCE that volatilized from the system. Nearly 100% of the total radiolabel was recovered. The poplar cells transformed approximately 2% of the TCE in one day, and another 6-8% in four days. The cells produced up to 1% of the total radiolabel as ^{14}C labeled CO_2. This showed that the H11-11 poplar hybrid has the ability to mineralize TCE to CO_2 (Newman *et al.* 1997; Newman *et al.* 1998).

Initial whole plant experiments at the University of Washington involved growing hybrid poplars (*P. trichocarpa x P. deltoides* and *P trichocarpa x P. maximowiczii*) in the greenhouse in PVC pipes. In one study, 12 dormant 1-year-old stem cuttings were placed in 1.1 m long PVC pipes, which had been filled with 30 cm of sand and 60 cm of Sultan silt loam. Nine days after planting, six of the plants were dosed with water containing 50 ppm TCE; the other six plants received water without TCE.

Plants were watered in this way for eight months. During that time, monitoring showed that the plants were transpiring TCE, though the experiment was not able to provide a mass balance, quantitative measure of the amount transpired. At the end of eight months, the plants were harvested and analyzed for TCE and possible metabolites. In the TCE-treated plants, significant levels of TCE were detected in the stems, though little was found in the leaves. Roots showed concentrations of di- and trichloroacetic acid metabolites as expected. This study demonstrated that hybrid poplars were capable of TCE uptake, storage, mineralization, and transpiration (Newman *et al.*1997).

A more in-depth whole plant study has taken place over the past three years at the University of Washington (Newman 1999). In this study, hybrid poplars (*P. trichocarpa x P. deltoides* H 11-11) were planted in large containers built to simulate an artificial aquifer. The containers were constructed of 3m x 6m x 1.5m "cells" with 60-gauge polyethylene liners. The cells were filled with a bottom layer of sand overlaid with Sultan silty clay loam topsoil from the site. An irrigation system in the bottom sand layer provided water at a constant rate. Two cells were planted with freshly rooted cuttings of hybrid poplar H11-11; these cells were irrigated during the study with TCE-contaminated water. A third cell was not planted, but was watered with TCE-contaminated water; while a fourth cell was planted, but was treated with TCE-free water.

In the unplanted cell treated with TCE-contaminated water, 68% of the added TCE was recovered at the end of the second year from the cell's effluent well. The 32% loss of TCE was attributed to soil adsorption and other soil interactions.

In the planted cells treated with TCE-contaminated water, researchers found that the trees were able to grow at significant TCE levels (approximately 15 ppm, much higher than the levels considered safe for drinking water). These cells were able to remove 99% of the added TCE during the growing seasons. Less than 9% of the TCE was transpired to the atmosphere during the second and third years. Examination of plant tissue showed the same metabolites found in the earlier studies, but at low levels. Chloride ion significantly accumulated in the soil, suggesting that dechlorination is another fate of TCE. Researchers concluded that "treatment of TCE-contaminated groundwater with this poplar clone can result in efficient destruction of TCE" (Newman *et al.* 1999).

Based on the promising findings from laboratory, greenhouse and controlled field studies, a number of pilot-scale field studies have been undertaken. The United States military is currently testing TCE phytoremediation in the field at the Edward Sears Site in New Jersey and at the Aberdeen Proving Grounds in Maryland; hybrid poplars are being used on these sites to treat TCE contamination at depths of approximately 2.5 m (8 ft.). At the Aberdeen site, the poplars have been planted as hydraulic pumps, in a pattern designed to try to prevent TCE from moving to a nearby marsh (Cooke, 1999).

The largest military demonstration site is at the Naval Air Station in Ft. Worth, Texas (USA), formerly Carswell Air Force Base. Eastern cottonwoods (*Populus deltoides*) have been planted at the Ft. Worth site to treat TCE contamination in a groundwater plume at depths of 1.2 to 2.5 m (4 to 8 ft.). Site selection and characterization was completed in January 1996; site development, including planting of trees and installation of an irrigation system, was completed in April 1996. Trees were planted in overlapping rows perpendicular to the groundwater flow to maximize root to aquifer contact, with careful spacing to maximize root densities. Baseline sampling began in June 1996, and researchers believe that roots penetrated to the capillary fringe of the aquifer as early as the summer of 1997. Transpiration data collected in the summer of 1997 showed that the larger trees were pumping approximately 3.75 gallons of water per day. Demonstration sampling is expected to continue until 2000, when remediation data will become available (Rock 1997; Cooke 1999).

Promises and Problems

Phytoremediation of TCE is an attractive strategy for several reasons. First, it is considered less costly than conventional methods. The Environmental Protection Agency estimates that costs for TCE phytoremediation may vary from 10% to 50% of other methods, such as pumping and treating groundwater. The cost savings can be attributed to the fact that initial costs are often limited to some basic site preparation, planting of foot-long cuttings, and occasional maintenance, usually irrigation. Installations can use standard or slightly modified agricultural practices and equipment. Ongoing operation and maintenance costs can be much lower than those for in situ microbial bioremediation (Rock and Freeman 1999; Boyajian 1997). Plants are considered easier to monitor than microbes.

Secondly, phytoremediation of TCE is considered an environmentally sensitive strategy. Vegetation is a "natural" part of ecosystems; trees provide shade, habitat, and windbreaks. Implementation of phytoremediation may be less invasive than soil stripping or installation of pumping systems. Unlike some conventional pump-and-air-strip systems, phytoremediation does not appear to release appreciable amounts of TCE into the air; thus, it may be more appropriate in densely populated areas (Schmiedeskamp 1997).

Finally, phytoremediation of TCE meets with high public acceptance. Tree plantations have a park-like aesthetic, while on the other hand "biofilms are notoriously unphotogenic and regular engineering remediation activities can look like lunar mining expeditions" (Cunningham *et al.* 1996). There is an intuitive sense that a site covered in thriving vegetation is less hazardous than a bare lot. In successful phytoremediation strategies, trees do present a direct, visual bioassay of the natural system's ability to sustain life and restore itself, at least to some extent (Newman *et al.* 1998).

However, because phytoremediation of TCE is a new strategy, it is still controversial. Research in the laboratory and greenhouse has not yet been met by research in the field. The rate and extent of phytoremediation in different ecosystems has not yet been established. The fate of TCE in plants is not completely confirmed. This leaves regulators, managers, and researchers with many questions.

Clean-up rates are limited to the rate of plant growth, uptake and metabolism. These rates may prove slower than conventional methods--too slow, perhaps, for use on sites posing acute risks to humans and other parts of ecosystems. In addition, plants may not be able to remove TCE to an extent that meets regulatory treatment goals at various target levels (Rock and Sayre, 1999; Rock 1997).

There are concerns that plants may not be able to grow or to remain healthy over the long term, especially at higher concentrations of TCE contamination, or on sites with additional contaminants such as salts and heavy metals. Poplars in greenhouse studies were noted to be 15% smaller than controls not treated with TCE. Fine-roots of TCE-treated plants had less biomass and did not extend into sand layers at the bottom of greenhouse pots, though they supported the crown of the plants (Newman *et al.* 1997). These findings raise questions about the ability of plants to grow and take up TCE in contaminated soils, since the structure and function of these soils is often significantly compromised (Fuller *et al.* 1997).

In addition, because root density decreases with depth, and because TCE moves outward and downward, roots may not be able to reach the contaminant. Current research suggests that TCE contamination as deep as 10 meters can be drawn up by poplars, through a combination of root presence and hydraulic gradient induced by transpiration. However, since TCE tends to settle at the bottom of aquifers, 10 meters may not be deep enough. Also, since the zone of contamination is much wider at the bottom of an aquifer than at the surface of the soil, poplars may not reach all of the TCE, despite their more than 100 million miles of roots per acre (Cunningham *et al.* 1996). On some sites, particularly in urban areas, it may not be possible to plant the number of trees needed to reach the broad base of contamination.

Regulators express concerns that lack of adequate information about phytoremediation of TCE may have unforeseen environmental impacts. Should hybrid poplars or other non-native species be introduced in already stressed areas? If TCE is metabolized and/or stored in poplars, will it enter the food chain as insects and small rodents feed on plants containing contaminants? Will TCE stored in plants re-enter the ecosystem through leaf fall, use of mulch, or burning of firewood from trees containing the compound (Technology Innovation Office 1998)? What will happen to TCE transpired into the atmosphere? Though researchers so far believe that TCE is transpired in innocuous end-products which degrade in a matter of days, regulators are still concerned that phytoremediation may simply transfer TCE from the subsurface level to the air (Compton *et al.* 1998).

Finally, there are concerns that costs may not be as low as predicted for phytoremediation of TCE. Not all sites are ideal settings for tree plantations. Abandoned manufacturing sites, military installations, or parking lots could have prohibitive site preparation costs. Use of plowing, rototilling, ripping and planting equipment could be very difficult. Irrigation, fertilization, and application of herbicides could be more costly than predicted if sites have to be maintained for many years because of slow clean-up rates. Estimates would also need to consider the costs of obtaining valuable land, such as urban property, and keeping it planted in trees over a long period. Some have even stated that realistic cost estimates must include lawyer hours needed to convince regulators of the effectiveness and safety of a new strategy (Cunningham *et al.* 1996).

Future Research

Because phytoremediation of TCE does not have a long track record of successful use, there is a need for more basic research, field study, and innovation. Laboratory, greenhouse and pilot scale studies can be used as proof of concept, but regulators, owners and commercial interests will want to see completed cleanups or site closures before phytoremediation is fully accepted as a strategy (Boyajian 1997).

Exploration of uptake, metabolism, storage and transpiration of TCE must continue. Exploration into the phytoremediation of xenobiotics began about 20 years ago with research involving pesticide remediation, but studies of organic compounds such as TCE comprise only 3% of current phytoremediation literature (Newman *et al.* 1998).

Field research will need to assess short-term effectiveness of TCE phytoremediation in reducing immediate risks, as well as permanence and reliability of the strategy over time. The use of phytoremediation needs to be studied in different ecosystems, to demonstrate effectiveness under different matrixes of soil, climate, vegetation and contamination. Field research will also need to answer questions about broader environmental concerns such as food chain impacts and use of byproducts.

Currently, no standardized performance parameters exist for phytoremediation of organics. Plant scientists, engineers and regulators must work together to develop standards for sampling, analyzing, managing and monitoring TCE phytoremediation. Realistic systems models need to be developed to include: input parameters such as contaminant concentration, bioavailibility, and plant uptake and degradation; output parameters such as metabolic end points, rate and extent of remediation; events within the soil/plant/air/water matrix such as diffusion, mass balance, mass flow; and costs, including true capital and operating expenses (Cunningham *et al.* 1996).

More research will focus on plant selection and development. Plants to be chosen for TCE phytoremediation must develop substantial biomass quickly, take up water at significant rates, and elongate roots to deep levels. Plants other than poplars and cottonwoods must be found to match ecosystems with varying growing seasons, average temperatures, rainfall, soil types and nutrient levels. Willows (*Salix spp*.), eucalyptus (*Eucalyptus spp*.), black locust (*Robinia pseudoacacia*), Russian olive (*Elaeagnus angustifolia*), and Hawaiian koa (*Acacia koa*) are some species being considered (Schmiedeskamp 1997). In Washington, species other than poplar are being studied in order to find plants more resistant to coastal fungal diseases; while in the Rockies, aspen (*Populus tremuloides*) and alder (*Alnus spp*.) are being considered because of cold tolerance. Native species must be considered for areas where introduction of non-natives is undesirable. In addition, genetic engineering is seen as a promising area for plant research, as genetic tools may enable researchers to design plants better equipped to locate and metabolize TCE in particular ecosystems (Newman 1998).

Hybrid technologies are seen as another area of promising research. These technologies combine the most effective aspects of two or more strategies. In the case of TCE, for example, the contaminated soil might be treated initially in an anaerobic bioreactor, and then plants would be grown in the soil as a "finishing" step to remove any residual TCE. Contaminated groundwater that is beyond the reach of plant roots might be pumped to the surface and applied to a tree plantation as irrigation; the plants would then remove the TCE. This strategy is currently being used with poplars near Medford, Oregon, to remediate trichloroethane (TCA) from a truck spill. Such a system has to be designed and monitored to ensure that contaminated water doesn't go beyond the root zone, and that water is pumped from downgradient and does not spread beyond the original plume (Schmiedeskamp 1997).

According to Lee Newman, a key researcher at the University of Washington, if the positive prospects of TCE phytoremediation are exagerrated, it will be doomed to fail, leaving some site owners to simply plant trees and walk away (Compton *et al.* 1998). But if phytoremediation's limitations are acknowledged, and if sound research continues, phytoremediation of TCE and other organics may prove to be cost-effective, user-friendly, and environmentally sensitive on some contaminated sites.

Literature Cited

Boyajian, G. E. and L. H. Carreira. 1997. Phytoremediation: a clean transition from laboratory to marketplace? Nature Biotechnology 15: 127-128.

Chappell. 1998. Phytoremediation of TCE in Groundwater using Populus. Washington, D.C.: Technology Innovation Office, Office of Solid Waste and Emergency Response.

Compton, H., L. Erickson, L. Newman, P. Cichy, and C. Hartnett. Summary of the Remediation Technologies Development Forum, Phytoremediation of Organics

Action Team, TCE in Ground Water Subgroup. Conference Call. <http://www.rtdf.org/public/phyto/minutes/tce/tce106.htm> 6 October 1998.

Cooke, M.T. 1999. Phytoremediation: Using Plants to Remediate Groundwater Contaminated with Trichloroethylene (TCE). State College, PA: Pennsylvania State University.

Cunningham, S. D., T. A. Anderson, A. P. Schwab, and F. C. Hsu. 1996. Phytoremediation of soils contaminated with organic pollutants. Advances in Agronomy 56: 55-107.

Fox, J. L. 1997. US military takes up phytoremediation. Nature Biotechnology 15: 612.

Fuller, M. E., K. M. Scow, S. Lau, and H. Ferris. 1997. TCE and toluene effects on the structure and function of the soil community. Soil Biology and Biochemistry 29: 75-89.

Hinchman, R. and C. Negri. 1994. The grass can be cleaner on the other side of the fence. Logos 12: 8.

Newman, L. A., S. L. Doty, K. Gery, P. E. Heilman, I. A. Muiznieks, T. Q. Shang, S. T. Siemieniec, S. E. Strand, X. Wang, A. M. Wilson, and M. P. Gordon. 1998. Phytoremediation of organic contaminants: a review of phytoremediation ressearch at the University of Washington. Journal of Soil Contamination 7: 531-542.

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

Newman, L. A., X. Wang, I. A. Muiznieks, G. Ekuan, M. Ruzaj, R. Cortelucci, D. Domroes, G. Karscig. T. Newman, R. S. Crampton, R. A. Hasmonay, M. Yost, P. E. Heilman, J. Duffy, M. P. Gordon, and S. E. Strand. 1999. Remediation of trichloroethylene in an artificial aquifer with trees: a controlled field study. Environmental Science and Technology 33: 2257-2265.

Rock, S. A. 1997. Phytoremediation. The Standard Handbook of HazardousWaste Treatment and Disposal. 2nd ed. H. Freeman, ed. New York: McGraw Hill.

Rock, S. A. and A. Ferro. Phytoremediation of petroleum in soil and groundwater. <http://www.epa.gov/ordntrnt/ORD/NRMRL/rcb/phytopet.htm> 16 September 1999.

Rock, S. A. and G. Harvey. Phytoremediation of TCE-contaminated shallow groundwater. <http://www.epa.gov/ordntrnt/ORD/NRMRL/rcb/phytoce.htm> 16 September 1999.

Rock, S. A. and P. G. Sayre. Phytoremediation of hazardous wastes: potential regulator acceptability. <http://www.epa.gov/ordntrnt/ORD/NRMRL/rcb/phytohaz.htm>16 September 1999.

Schmiedeskamp, M. 1997. Pollution-purging poplars. Scientific American 277: 46.

Technology Innovation Office. 1998. A Citizen's Guide to Phytoremediation. Washington, D. C.: United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. EPA 542-F-98-011.