CASE STUDIES OF PHYTOREMEDIATION OF PETROCHEMICALS AND CHLORINATED SOLVENTS IN SOIL AND GROUNDWATER

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Abstract. The use of plants and the microbes associated with their growth to cleanup contaminated soils and water (phytoremediation) is an innovative technique approved by state and federal regulators for use in full-scale restoration of hazardous waste sites. Three case studies on the use of phytoremediation technologies for remediation of volatile organic contaminants (VOCs) in soil and groundwater are discussed. In Case Study #1 willow tress were planted over a petroleum spill and used to clean-up residual contamination in soils and the contaminated groundwater below. After three growing seasons 90% of the contamination was removed from the site. In Case Study #2, a combination of poplar and willows trees was used as a polishing step for a chlorinated solvent plume while in-situ chemical oxidation with potassium permanganate was used for source control. The parent chlorinated ethenes and chloroacetic acids (oxidative transformation products) were detected in the tree tissues at the end of the first growing season, confirming the uptake and phytodegradation of the contaminants. Case Study #3 focused on the assessment of the contribution of plants in the attenuation of a mixed-contaminant plume of hydrocarbons and chlorinated solvents at a hydrocarbon burn facility at the Kennedy Space Center in Florida. Analysis of the geochemical and hydrogeological data confirmed the attenuation of the plume in the natural wetland at the site.

INTRODUCTION

Historically, remediation of soil and groundwater has focused on microbes or physical treatment (air stripping, dig-and-treat, or adsorption) techniques to perform the cleanup work. However, there are multitudes of plants that have the ability to metabolize or sequester many classes of contaminants. The use of plants and the microbes associated with their growth (phytoremediation) to cleanup contaminated soils and water is an innovative technique approved by state and federal regulators for use in full-scale restoration of hazardous waste sites. Phytoremediation is an emerging remediation technology that has promise as a means of treating contaminated ground and surface water and soils at sites where spills and releases have occurred. Phytoremediation systems have shown great promise in the treatment of municipal wastewater prior to discharge into streams and rivers, for the treatment of chlorinated organic contaminants, pesticides, munitions, hydrocarbons and for sequestration of metals.

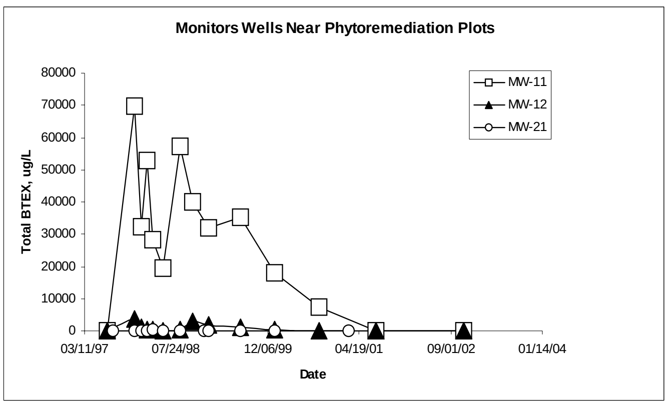
Basic research has provided us with a better understanding of phytoremediation processes (McCutcheon and Schnoor 2003). Information from our laboratory research and published materials suggest that there are five (5) processes that make phytoremediation work. In the rhizosphere of some plants, released plant exudates and enzymes that stimulate biochemical activity may enhance the biodegradation of environmental contaminants (rhizodegradation). Plants may take up and assimilate contaminants (phytoaccumulation), volatilize the contaminants into the atmosphere (phytovolatilization), or degrade the contaminants within plant tissues using enzymes (phytodegradation). For metals, plants may be used to absorb and precipitate large quantities of toxic metals in soils, thus reducing their bioavailability and preventing their entry into groundwater and food chains (phytostabilization). State and Federal regulators are interested in phytoremediation case studies to improve their understanding and evaluation of the various applications of this cost-effective innovative technology.

CASE STUDIES

Case Study #1

The site was subject to an accidental release of gasoline in 1998, and has since been under remediation using soil vapor extraction and phytoremediation techniques. Pilot testing of phytoremediation was conducted during the 1999 and 2000 growing seasons. The specific objective of the pilot test was to screen local plant species that will survive in the gasoline-contaminated soils and evaluate phytoremediation as an effective corrective action. The plants species that were screened included: black willows, cottonwoods, cattail, burreed, native sedge, arrowhead and bulrush. Black willow and cottonwood were planted along the edge of the drainage areas while sedge, rush, burreed, and cattail were planted in the wettest areas of the ravine because the latter can tolerate standing water. The control plots had no vegetative cover.

At the end of the 2000 growing season the results of the pilot phytoremediation project was evaluated. Herbaceous plants were found to be effective in treating shallow soils (0–1 ft) when compared to the unvegetated control plots. Native sedge was distinctively effective in treating shallow soils because of their extensive shallow root system. Shallow planted willow cuttings were not effective in the remediation of deeper soils, thus deep-planted bare root trees (willows and cottonwood) were recommended for full-scale implementation of phytoremediation in the ravine.



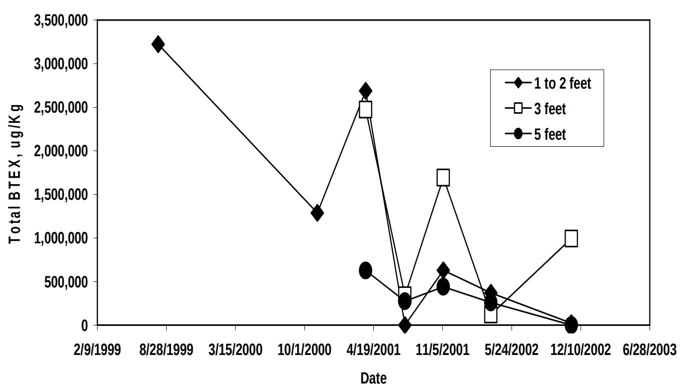


Figure 1. Change in concentration of COCs in groundwater wells (above) and soils (below).

At the beginning of the 2001 growing season a full-scale phytoremediation system was installed at the site. A total of 290 bare root white willow trees (4-6 ft) were planted during the first week in April 2001. This was in addition to the existing black willows planted as cuttings during the pilot study phase in 2000. The new willow trees were planted in the control plots and areas in the old plots that had no trees. Deep root planting of the bare root trees was adopted to increase rhizodegradation in the contaminated soils and shallow aquifer. A planting distance of 4 ft between willow trees was adopted with natural or manual methods used to thin the trees. Plots that had established a healthy grass or tree growth were simply enhanced by planting additional plants where none existed.

Trees growing on the side of the ravine were pruned or removed to improve the penetration of sunlight into the site. A 6 ft fence was installed to prevent deer and beaver from grazing on the planted vegetation and to keep out people and other trespassers. The contaminated soil, groundwater and plant tissue are monitored to assess the performance of phytoremediation of petrochemicals at this site (Figure 1). After three growing seasons (three years) 90% of the initial petrochemicals at the site had been removed. The areas remediated with soil vapor extraction continued to show here concentrations of the spilled petrochemicals in soil.

Case Study #2

Ground water investigations in 1996 and 1997 revealed concentrations of chlorinated ethenes above Florida Environmental Protection Department maximum contaminant levels (MCLs) at this site. The chlorinated volatile organic compounds (CVOCs) in groundwater originated from improper handling of perchloroethylene (PCE) used at the base laundry. The CVOC plume extends from 4 to 45 ft below land surface. It originated near a building and flowed toward a nearby lake with anaerobic degradation products of PCE, such as TCE, cis- 1,2-Dichloroethene (cDCE), and vinyl chloride (VC) present within the plume.

In January 1999 and December 2000, treatability studies conducted at the USEPA National Exposure Laboratory and the University of Georgia in Athens demonstrated the efficacy of coupling natural attenuation and phytoremediation (Figure 2) as polishing steps to treat the residual contamination in the “northern” and “southern” plume areas following source removal by in-situ chemical oxidation.

Design. The phytoremediation treatment system was installed in March, 2002. A dense plantation was installed on the 3 acre site and consisted of 2,000 Eastern cottonwoods, 2,000 hybrid poplars (DN-34), and 600 willows in four plantation zones surrounding the plume. To establish successful growth before the summer rains, an irrigation system was installed. The system was designed so each plantation zone would receive the equivalence of 1.5 to 2 inches of rain per week using 0.37 gallons per minute (gpm) emitters. The irrigation system utilized potable water for two zones and groundwater treated by an air stripper unit for the remaining two zones.

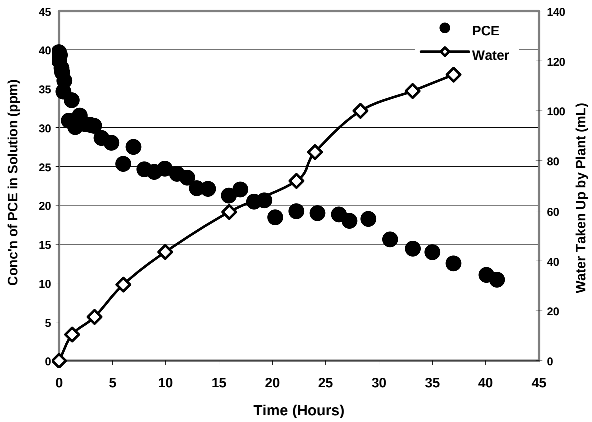


Figure 2. Results of bench scale treatability tests to confirm uptake of chlorinated solvents from groundwater by the trees used in Case Study #2.

Phytoremediation O&M activities included mowing between all tree rows and applying pesticides to the weeds and grasses near each tree, particularly in the wetland area. The plantation began producing new foliage in mid-March and has full coverage by May. Pesticide treatment of the cottonwood leaf beetle was required mostly in spring months. Grass and other weedy plant growth among the poplars and cottonwoods in each zone are a source of nutrient and moisture competition. Senescence (foliage begins to fall from some trees) sets in mid- to late September each year.

Monitoring Results. The data first collected from the April 2003 tissue sample event established that uptake of DCE, TCE, and PCE was occurring in the poplar and willow trees located in areas above the historically highest concentrations of PCE and TCE onsite. The haloaceticacids (HAA) results for analyzed tree leaves indicated that considerable metabolic activity has occurred in virtually all trees sampled during this summer event. The metabolic degradation of VOCs into HAAs has occurred primarily in the leaf tissues, which is in agreement of treatability studies data. The dominant constituents detected were chloroacetic acid, trichloroacetic acid, and dibromoacetic acid with multiple estimated detections of trichloroethanol (TCEOH). Low levels of TCEOH in leaf tissues were expected since it volatilizes readily. Detections of TCEOH from leaf and root tissue correspond well with the respective detection of PCE in root tissues.

The decrease in PCE concentration and increase in reductive dechlorination products – TCE, DCEs and VC confirmed that rhizodegradation is occurring. Results of multiple sampling events have shown that the range in microbial biomass has been consistent throughout the study period, and the microbial community structures of the majority of samples are diverse and primarily composed of gram negative Proteobacteria (Spriggs et al., 2003). PLFA profiles of the July 2004 samples showed that the microbial community structures of the majority of samples were diverse and primarily composed of gram negative Proteobacteria, as shown by the proportion of monoenoic PLFA. Quantitative Real-time polymerase chain reaction (PCR) detected *Dehalococcoides* spp. at low concentrations in two wells. Both of these samples had large proportions of total anaerobes approximately 22 percent and 30 percent, respectively), which suggests the presence of anaerobic conditions suitable for reductive dechlorination.

In the July 2004 event, estimates of viable biomass ranged from 10^3 to 10^5 cells per mL of sample. This range in biomass was consistent with what has been seen throughout the study period (since March 2002). The frequency of NA sampling will be increased once contaminant concentrations are significantly reduced across the site by operating the selected source area remediation system.

Case Study 3

Plant tissue samples were collected from selected benchmark plants for the purpose of detecting chemical uptake. All plant tissue samples were collected from the Hydrocarbon Burn Facility wetland at the Kennedy Space Center, Florida. The plant tissue sampling was conducted as close as possible to the cluster of monitoring wells installed in the wetland area. The criteria for selecting plant species for analysis of the contaminants of concern (COCs) were as follows: the predominance of the plant species at the site, its location within the plume, and the likelihood that the plant roots may be impacted the contaminated groundwater. In the collection of specific plant tissue samples, the following factors were considered: 1) the concentration of the parent VOC in leaf tissue depends on the location of the leaves on the trees, and 2) the concentration of the VOCs in roots is determined by its location within the path of the plume. The COCs included specific hydrocarbon and chlorinated organic compounds that were monitored because they have been identified in surface and ground water at the HBF wetland.

The most abundant species of each Taxa was sampled. From trees and shrubs were harvested roots, trunk, branches and Leaves while only leaves and roots were harvested from grasses. Each tissue harvested from 3 or more plants and combined to form one composite. Samples for VOC analysis were harvested, weighed and stored in purge-and-trap grade methanol in screw top glass vials sealed with aluminum faced septa. Samples for metabolites analysis treated similarly, but received no methanol. The plant tissue samples, trip blanks and controls were shipped to the laboratory overnight in a 4^{o}C cooler. Plant tissue samples used for controls were harvested 20 ft away from the edge of wetland on either side of the road leading to HBF and the adjacent natural wetland. The control location was not contaminated by the COC.

The VOCs of concern (benzene, toluene, ethylbenzene, xylene(s), perchloroethylene (PCE), trichloroethylene (TCE), dichlorothene(s) (DCE), and vinyl chloride (VC) were analyzed using EPA Method 524.2 and the metabolites using modified EPA Method 552.2. The chlorinated solvent metabolites (Trichloroethanol (TCEtoh); Trichloacetic acid (TCAA); Dichloroacetic acid (DCAA); and Monochloroacetic acid (MCAA)) in plant tissue were analyzed using methods (534.2 and 552.2. It should be noted that there is currently no specific EPA approved method for the quantitative analysis of VOCs and their metabolites in plant tissues.

Monitoring Results. Willows and Brazillian peppers were the dominant plant species at the wetland locations that were sampled. Overall BTEXs was detected at higher concentrations than CVOCs in the plant tissues, which is in agreement with the higher BTEX concentrations measured in the site groundwater. Plants tissues harvested in Summer contained relatively higher concentrations of VOCs than in the Winter plants of similar species. This can be attributed to a greater uptake and evapotranspiration by the wetland plants during the Summer growing season. One or more BTEXs was detected in 99% of the plants sampled in Summer while CVOCs were detected only in 50% of plant samples.

Metabolites of CVOCs were measured in plant tissues at a higher concentration than the parent compounds. This suggests that the CVOCs were mostly metabolized and possibly evapotranspired, rather than phytoaccumulated. The highest concentration of metabolites was observed in the leaves of willow trees with no detectable concentrations of the metabolites identified in willow roots. The occurrence of the CVOC transformation products mostly in the leaves is in agreement with results in the published phytoremediation literature (Nzengung et al., 1999). Comaparison of the average concentrations of the identified metabolites of the CVOCs indicated that MCAA > TCAA > DCAA > TCEtoh. The predominance of monochloroacetic acid in the plant samples corresponds with a higher concentration of vinyl chloride in the groundwater at the HBF wetland.

This is attributed to the selective and high rate of metabolism of benzene in the organic rich wetland sediments. Toluene and Xylenes detected at relatively higher concentrations in plant tissues than benzene, which was mostly BDL. Except for Toluene, 90% of plant tissues collected in Winter had no detectable concentrations of the parent VOCs, suggesting a strong seasonal influence on the uptake of the contaminants. BTEXs detected mostly in Brazilian peppers.

Role of Plants at HBF. The data collected during one growing season suggested that plant-mediated attenuation of the COCs in the natural wetland at the HBF at the Kennedy Space Center may be attributed to the following phytoprocesses:

1. Rhizosphere Biodegradation (Rhizodegradation)

Plants can enhance natural attenuation through mineralization of the parent VOCs and BTEX by root zone microorganisms and plant exudates. However, it is very difficult to distinguish between plant and microbial catalyzed biodegradation reactions in the root zone (rhizosphere).

2. Uptake and Phytodegradation was established using metabolites identified in plant tissues and the high concentration of chloroacetic acids measured in plant leaves.

3. Uptake and Volatilization (Phytovolatilization)

Uptake mass estimated as >5 mg VOCs/m^2-year (conservative). Estimation of Uptake Mass: Uptake Mass = (TSCF)(C_{solute})(T)(f). Where TSCF is transpiration stream concentration factor (a constant) that is compound specific. Value of 0.12 was used in this study. C_{solute} is average groundwater concentration of a contaminant (mg/L). T is cumulative volume of water transpired per unit area per year (L/m^2-yr): 1,220 L/m^2-yr realistic for KSC wetland, and f is the fraction of plant water needs met by contaminated groundwater (0.1 – 0.5 reasonable range).

Total VOCs Mass Removal = $\sum$(Individual VOC Mass Removed)

CONCLUSION

It is evident from the results of these case studies that phytoremediation is an effective technology for restoration of VOCs contaminated soils and groundwater. For groundwater plumes upwelling into natural wetland, plants contribute significantly in the attenuation of the COCs. The use of suitable soil amendments to enhance rhizodegradation process tends to minimize fertilization needs and increases the rate of phytoremediation.

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