DRIP IRRIGATION AIDED PHYTOREMEDIATION FOR REMOVAL OF TCE FROM GROUNDWATER

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ABSTRACT: Groundwater in D-Area at the Savannah River Site (SRS) is contaminated with trichloroethylene (TCE) and by-products resulting from discharges of this organic solvent during past disposal practices. This contaminated groundwater occurs primarily at depths of 9 m to 15 m below ground surface, well below the depths that are typically penetrated by plant roots. The process investigated in this study involved pumping water from the contaminated aquifer and discharging the water into overlying test plots two inches below the surface using drip irrigation. The field treatability study was conducted from 8/31/00 to 4/18/02 using six 0.08 ha test plots, two each containing pines, cottonwoods, and no vegetation (controls). The primary objective was to determine the overall effectiveness of the process for TCE removal and to determine the principal biotic and abiotic pathways for its removal. Results demonstrated that the process provides a viable method to remove TCE-contaminated groundwater. The data clearly showed that the presence of trees reduced volatilization of TCE from the drip irrigation system to the atmosphere. Influent groundwater TCE concentrations averaging 89 µg/L were reduced to non-detectable levels (<5 µg/L) within the upper two feet of soil (rhizosphere).

INTRODUCTION

Phytoremediation is an emerging technology that utilizes plants and associated microbes to remediate contaminated media. Previous studies at the Savannah River Site (SRS) demonstrated degradation of low concentrations of chlorinated solvents by plants and associated rhizosphere microorganisms (Anderson et. al., 1993). D-Area at SRS has a large dilute groundwater plume of TCE (mostly <100 µg/L) that is close to the Savannah River. Most of the TCE-contaminated groundwater occurs near the bottom of an approximately 9-15 m thick aquifer, well below the depth of typical tree root penetration. Thus, the drip irrigation component of the proposed process provided a means to allow plant and associated microbial communities an opportunity to remediate contaminated groundwater from depths otherwise unavailable to plant systems. The overall objective of this project was to evaluate a novel drip irrigation-phytoremediation process (Figure1) for remediating volatile organic contaminants (VOCs), primarily trichloroethylene (TCE), from this contaminated groundwater. The process has the potential to be less expensive and more beneficial to the environment than traditional TCE remediation technologies. It could safely reduce plumes of TCE in D-Area groundwater to below drinking water standards (<5 µg/L), while facilitating the growth of plants that can be used in timber production. The removal of TCE is effectuated by both abiotic (adsorption, absorption, volatilization) and biotic (phytoremediation) pathways. The phytoremediation pathways involve three mechanisms: (1) rhizodegradation, or the breakdown of organic contaminants by microbial activity enhanced by the presence of plant roots, (2) phytodegradation, the breakdown of contaminants by plant metabolic processes, and (3) transrespiration, physical processes including volatilization and transpiration. The project

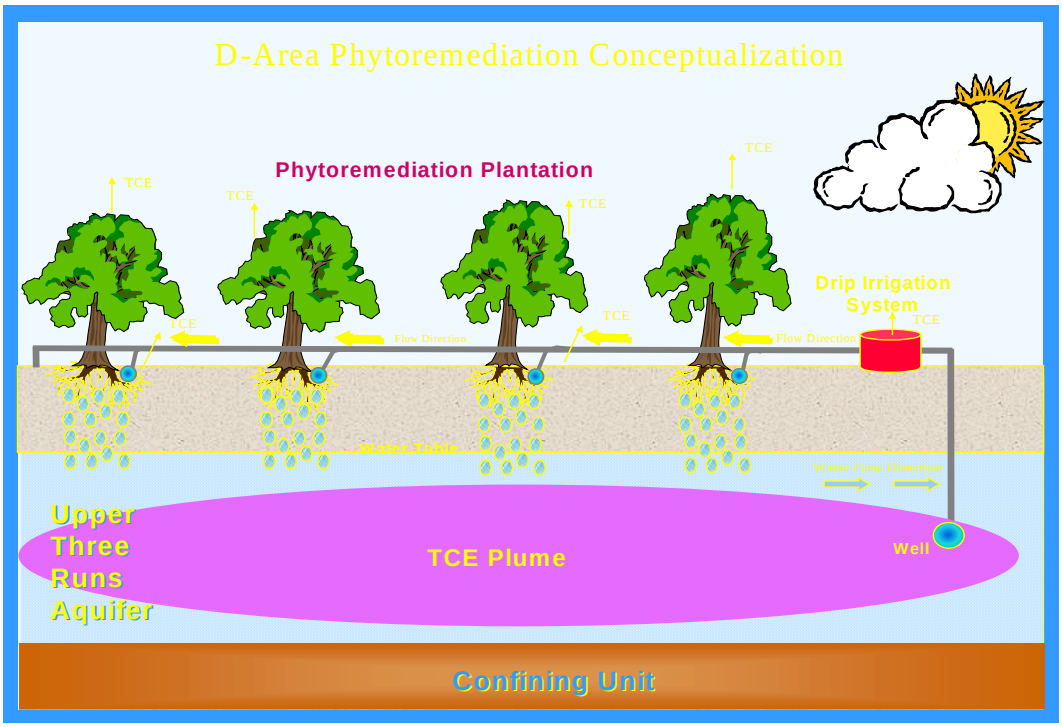

Figure 1. Conceptual design of drip irrigation/phytoremediation process

was conducted in two phases. Phase 1 involved setup and evaluation of the system while Phase 2 involved process development and proof of principal experimentation.

MATERIALS AND METHODS

Description of Drip System. Drip irrigation lines were installed in four 0.24 ha test blocks above the TCE-contaminated groundwater in D-Area. Each test block consisted of three adjacent 0.08 ha test plots that were randomly assigned to receive one of three treatments: Pine, cottonwoods or no vegetation. The plots were prepared by removing all vegetation in two of the plots and all vegetation except mature pine trees in the third plot. One of the two completely cleared plots in each block served as non-vegetated control and the other was planted with cottonwood trees in the spring of 2001. Each treatment plot was 28.7 m X 28.7 m. Although each entire plot was plumbed for irrigation, sampling was restricted to the interior 20.1 m X 20.1 m (0.04 ha) region, thus providing an 8.5 m buffer zone along the exterior portion of each plot. The irrigation design for each plot consisted of 23 irrigation feed lines spaced 1.2 m apart and running the entire distance of the plot. During Phase 1, water was pumped from a monitoring well to a 9464 liter stainless steel holding tank. The water was then pumped, at timed intervals from the tank to the irrigation system of the plots via a 2.54 cm diameter manifold line. Irrigation feed lines branched from the manifold line. Each feed line was attached to a drip line consisting of emitters spaced at 0.6m intervals. The emitter lines were buried approximately 5 cm below the surface. There were four connections between each feed line and emitter line and these were equipped with pulsators, which helped regulate flow among emitters. During Phase 1, flow was restricted to a maximum of 488 l per day to only four of the 12 plots because of limitations on the single well in

operation. Two new wells were installed for Phase2 and produced flows of > 2650 l per day.

Initial Soil Characterization. Prior to the initiation of flow to the system, baseline measurements of TCE/PCE levels, anion concentrations and microbial densities were conducted from soil samples at depths of 0.6 m and 2.4 m. Soil pH was also measured (Forster, 1995). Field and analytical methods for the study were as follows:

Water sampling. Water sampling was conducted on 13 occasions during Phase 1(June 2000 – May 2001) and 24 occasions during Phase 2 (April 2001-April 2002). Various plots were sampled on various dates to facilitate a timed rotating irrigation schedule that was controlled electronically. Field methods for water sampling involved collecting duplicate 10 mL samples during irrigation and placing them in 22 mL headspace vials for measurements of TCE and by-products in the lab using EPA Procedure 8260B.

Soil Sampling. Soil samples were collected on four dates in Phase 1 and 10 dates in Phase 2. These samples were collected using a hand auger at 15.2 cm depth intervals from the surface to a depth of 2.4 m. Each soil sample (2.5 - 5 mL) was collected with a modified plastic syringe and placed directly into a 22 mL glass headspace vial with 5 mL deionized water and immediately sealed for subsequent VOC analysis. TCE and PCE analyses were performed on samples in sealed glass vials using headspace gas chromatography in accordance with EPA Procedure 5021. Chloride, nitrite, nitrate, phosphate, and sulfate concentrations were measured using ion chromatography.

The methodology for determining microbiological densities involved collecting approximately 100 g soil in sterile whirl-pack bags, keeping the samples refrigerated in the field, and transporting them to the lab within hours for immediate microbiological processing. Total microbial population densities (Hobbie et al., 1977) and plate counts (Balkwill, 1989) were conducted.

Lysimeter Sampling. Duplicate lysimeters were installed prior to irrigation at two depths (2 ft and 8 ft) at two randomly selected locations in each of the six test plots utilized in Phase 2 of the study. Sampling was conducted in November 2001 and April 2002. During sampling, the existing cap of the lysimeter was replaced with a cap containing a self-sealing quick disconnect fitting and tubing attached to a vacuum pump powered by a portable generator. Samples were collected in Tedlar air bags and refrigerated in the field. Aliquots were analyzed by GC/MS within 24 hr of collection.

Volatilization Sampling. Volatilization sampling was conducted during November 2001 and April 2002. Flux chambers (Figure 2) were used to sample volatilization to the atmosphere during irrigation. These 28.3 l stainless steel chambers (2 per plot) were placed on the soil surface over emitters at least two days prior to the scheduled sampling period. After irrigation had been in operation for at least one hour, a vacuum pump was analyzed by GC/MS within 24 hr of collection.

FIGURE 2. Flux chamber used to measure volatilization

Plant Tissue Sampling. Tree tissue samples included leaf, stem and trunk cores. Leaf and stem samples were not taken from the pines due to the height of the trees. Core samples were not taken from the cottonwoods due to their young age and trunk diameter (<10 cm). All tissue samples were stored at -80°C prior to being analyzed for TCE, PCE, and trichloroethanol (TCEOH), as previously described (Newman et al. 1999).

Modeling. In addition to the field sampling during Phase 1, a multiphase numerical model was developed to simulate future phytoremediation experiments at the D Area site. The model was designed to capture the basic equilibrium partitioning behavior of aqueous phase TCE in the soil as it is applied by drip irrigation to experimental plots with different vegetation treatments. An isothermal model (19°C) with no advective components other than those associated with the drip irrigation was used. Three irrigation application rates were simulated covering a range of application rates and using a TCE concentration that was assumed to be approximately the maximum available from nearby wells. The numerical simulations were therefore set up as optimal scenarios for transferring aqueous TCE to the root zone of the phytoremediation system. No biological degradation and minimal sorption loss was assumed in these simulations. A total of 65 grid blocks were used to describe the soil column from ground surface to the water table (depth of 3.75 m) for the simulations with 1-cm resolution for the uppermost half meter where the emitters were located. The upper boundary condition was a very large grid block (30 m) to simulate unlimited capacity for TCE that volatilized from the soil column. Two different types of sediments were included in the model using soil property data from actual SRS soils that are similar to those in the experimental area.
The simulations were started with soil moisture contents at gravity drainage values. Simulations were run with the emitter at 5 cm and 30.5 cm below ground surface (bgs) to study the effects of varying the depth of the emitter. (The actual placement of the emitters was 5 cm deep.). The volume of water supplied to the system was scaled to the one

dimensional to coincide with three flow rates; 488, 2044, and 4542 liters per day per plot. The concentration of aqueous phase TCE was set at 200 ug/L for all of the simulations.

RESULTS AND DISCUSSION

The initial sampling (Phase 1) identified the need for several modifications to the process. For example, with the original design, substantial quantities of TCE were being lost by volatilization to the atmosphere from a holding tank. The initial TCE/PCE monitoring data, along with initial modeling data strongly suggested that even with decreased volatilization from the holding tank, TCE input to the system with the original well (a monitoring well) was not sufficient to facilitate the delivery of measurable quantities of TCE to the rhizosphere zone of the test plots. Several corrective actions were initiated in response to this issue. Two wells were drilled in areas with higher TCE concentrations. This permitted the application of much higher water flows with water containing much higher TCE levels in Phase 2.

Baseline Soil Characterization and Modeling. Baseline characterization prior to irrigation showed that TCE and PCE levels in the soil were <1 mg/Kg in all plots. The pH of the soil ranged from 4.2 - 5.0 in the 4 plots sampled for pH and studied in Phase 1. Measurements of pH in the six plots (Plots 4-9) sampled in Phase 2 ranged from 3.2-5.4. There was no discernable relationship between soil pH and plot vegetation treatment.

Modeling. Results showed how concentrations decreased with depth and time from the point of injection (emitter location) with various application scenarios. The TCE concentration ranged between 15 and 20 ug/L at depths between 0.35 and 0.62 m bgs for application rates of 2044 l/day after one month. When the simulated application rate was increased to 4542 l/day, concentrations were between 35 and 45 ug/L at the same depths. These simulations were run using an assumed fraction of organic carbon (FOC) of 0.0001. When the concentration profiles were compared with emitter depths of 5 cm or 30.5 cm below ground and an application rate of 4542 l/day per plot, there was substantially less loss to the atmosphere with the emitter located deeper in the subsurface. In a simulation comparing two application rates (488 and 4542 l/day per plot) and two different FOCs, it was clear that lower FOC corresponds to higher TCE concentrations in the aqueous phase. Simulations comparing the concentration profile developing through time showed that concentrations begin to reach a steady state after one year. The application rate for these plots was 488 l/day. A simulation comparing continuous injection through the emitter and pulsed injection where the maximum allowable volume per day is injected in one hour with a daily application rate of 4542 l per plot showed that the pulsed application produces slightly higher aqueous concentrations at depth than the continuous application.

Water sampling. Average TCE concentrations applied to the plots during Phase 2 are shown in Figure 3. Statistical analyses of water sampling data in phase 2 showed that there was no significant differences (95% confidence) between TCE concentrations at the Well, (DRW-1) and the six study plots that were sampled. Likewise, there was no discernable pattern in TCE concentrations at sampling ports in study plots relative to their proximity to the well. However, there was a significant loss of TCE within the plots between the header side of the plots and the non-header side of the plots when samples

from all plots were compared. Dripline TCE concentrations averaged 14.1 µg/L more on header sides than on non-header sides of the test plots.

Soil Sampling. TCE was virtually absent from all samples at all depths prior to irrigation and was present only at depths of 0.6 m or less after the irrigation system became operational in Phase 2. Results of the statistical analyses indicated that there was no consistent pattern of TCE buildup in the soil over the course of the study and there were no significant differences in soil concentrations of TCE, PCE or cis-DCE in relation to plot treatment (pine, cottonwood, non-vegetated).

Total bacteria quantities did not show any significant trends relative to irrigation or plot vegetation treatment. However, quantities of viable bacteria (colony forming units) were substantially higher following irrigation relative to the baseline measurements

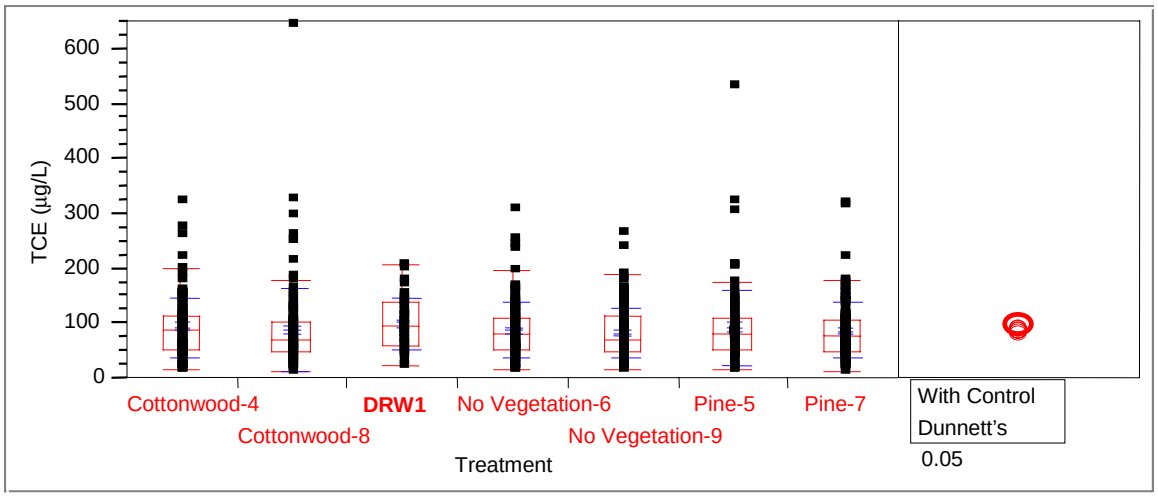

Figure 3. Mean concentrations (µg/L) of TCE at Well DRW-1 and Plots 4-9

performed prior to irrigation. The Ion Chromatograph (IC) analyses of anions in soil did not show discernable patterns other than a tendency for the sulfate levels to be lower at 2.4 m than at 0.6 m. This may be indicative of sulfate-reducing bacteria at the greater depth. Soil and groundwater chloride levels ranged from <1.0 to 41.4 mg/kg and were not indicative of aerobic TCE transformation because of the relatively low (µg/L) TCE concentrations being applied to the soil.

Plant tissue Sampling. The November 2001 tissue sampling revealed the presence of TCE (1.6 ppb – 283 ppb) in three pine core samples. However subsequent sampling in April 2002 did not indicate TCE in pine cores. No TCE or TCEOH were detected in cottonwood samples. Thus, it was not clear whether the November results represent tree uptake, analytical error or sample contamination. The low concentrations in the groundwater and soil made it difficult to detect TCE or its metabolites, despite use of detection limits in the ng/L range. Other studies at SRS (Brigmon et.al., 2001) and at the University of Washington (Newman, et. al. 1999) have proven that trees do uptake, metabolize and degrade TCE.

Lysimeter Sampling. Lysimeters were not sampled in Phase 1 because the soil cores revealed no significant TCE penetration below the surface. Results from the lysimeter sampling conducted in Phase 2 corroborated the soil core sampling results in terms of confirming that TCE is virtually absent at a depth of 2.4 m. There were no obvious differences in the lysimeter measurements relative to plot treatment.

Volatilization Sampling. Volatilization sampling utilizing flux chambers was conducted in November 2001 and April 2002. Volatilization showed a strong tendency to be related to the vegetation treatments. Average gas v/v ppb concentrations of TCE were 313, 234 and 80 for no vegetation, cottonwood, and pine, respectively. Thus, the presence of trees retarded volatilization and pines with their shallower root system appeared the most effective species for preventing TCE volatilization to the atmosphere with drip irrigation.

CONCLUSIONS

The results suggest that the drip irrigation/phytoremediation process that was tested in D-Area provides a viable alternative to remove TCE-contaminated groundwater and simultaneously grow trees (i.e. Cottonwoods) that would not otherwise be able to survive. The data clearly show that TCE was reduced to non-detectable levels within the upper 0.6 m of soil in all test plots utilized. It appears that the presence of trees retards volatilization. However, a definitive understanding of the pathways being utilized for TCE dissipation and the relative importance of each has not been achieved at this point nor has the maximum loading of TCE to the system without breakthrough (TCE penetrating >2.4 m in the soil column) been determined.

Initial attempts at describing degradation rates and mass balance calculations were inconclusive and indicative of a need for more testing. A pie chart (Figure 4) was prepared showing percent of water TCE (from dripline measurements) that can be accounted for by TCE in soil samples and volatilization (converted flux chamber measurement). The mass balance illustration shows that at least 92% of TCE was unaccounted for, degraded or possibly metabolized in plants.

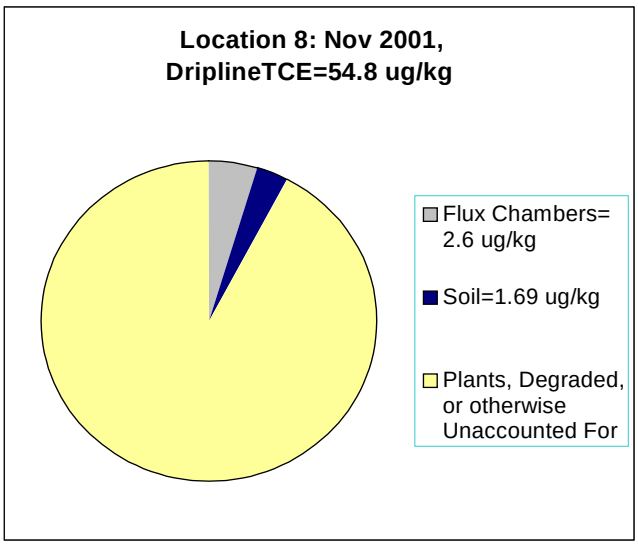

Figure 4. Preliminary mass balance for TCE dissipation

Overall, the results of the study suggested that the process provides a viable method to remove TCE-contaminated groundwater. The data clearly show that TCE was reduced to non-detectable levels within the upper two feet of soil (rhizosphere) in all test plots with the flow rates that were tested. Further system operation, plant and microbial analyses, soil column testing, and evapotranspiration measurements would be needed to complete the evaluation of the D-Area drip irrigation-phytoremediation process and determine the optimal use of this technology.

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