This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

Moving Beyond Pump and Treat Toward Enhanced Attenuation and Combined Remedies: T-Area, Savannah River Site

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ABSTRACT: Groundwater beneath T-Area, a former laboratory and semiworks operation at the Department of Energy (DOE) Savannah River Site, is contaminated by chlorinated solvents (cVOCs). Since the contamination was detected in the 1980s, the cVOCs at T-Area have been treated by a combination of soil vapor extraction and groundwater pump and treat. The site has received approval to discontinue the active treatments and implement a full scale test of *enhanced attenuation* – an engineering and regulatory strategy that has recently been developed by DOE and the Interstate Technology and Regulatory Council. Enhanced attenuation uses active engineering solutions to alter the target site in such a way that the contaminant plume will passively stabilize and shrink and to document that the action will be effective, timely, and sustainable. The paradigm recognizes that attenuation remedies are fundamentally based on a mass balance. Thus, long-term plume dynamics can be altered either by reducing the contaminant loading from the source or by increasing the rate of natural attenuation processes within all, or part of, the plume volume. The combination of technologies that emerged for T-Area included: 1) neat (pure) vegetable oil deployment in the deep vadose zone in the former source area, 2) emulsified vegetable oil deployment within the footprint of the groundwater plume, and 3) identification of attenuation mechanisms and rates for the distal portion of the plume. In the first part, neat oil spreads laterally forming a thin layer on the water table to intercept and reduce future cVOC loading (via partitioning) and reduce oxygen inputs (via biostimulation). In the second and third parts, emulsified oil forms active bioremediation reactor zones within the plume footprint to degrade existing groundwater contamination (via reductive dechlorination) and stimulates long-term attenuation capacity in the distal plume (via cometabolism). For T-Area, the enhanced attenuation development process proved to be a powerful tool in developing a defensible strategy that provides a high degree of performance while minimizing adverse collateral impacts of remediation (e.g., energy use and wetland damage) and minimizing life-cycle costs.

INTRODUCTION

T-Area is a former laboratory and semiworks operation at the DOE Savannah River Site in South Carolina. T-Area is located near the Savannah River and groundwater flows through Southeastern Coastal Plain sediments. Groundwater flow at this site is relatively simple, driven by recharge through the vadose zone and discharge into the river and associated wetlands. T-Area operation began in 1951 and historical discharges and spills from those operations resulted in the release of cVOCs to soil and groundwater. This contamination was identified in the 1980s and treatment of cVOCs was initiated at that time; treatment consisted of a combination of active soil vapor extraction (SVE) and groundwater pump and treat. The former process removed the bulk of the residual vadose zone contamination while the latter contained and reduced the size of the groundwater plume consistent with interim action goals.

Through the years, the site has worked with regulators to optimize and properly match technology to the evolving site needs and site conditions. For example, when the SVE contaminant removal rates declined to low "tailed" values after seven years of operation, the large-scale centralized active SVE system was replaced by smaller-modular solar powered units targeted to specific wells. This transition resulted in lower overall costs while meeting treatment objectives. Subsequently all of the buildings have been removed and the site is currently covered by a cap that reduces and controls infiltration; during the capping, the infrastructure was preserved for continued pump and treat operation. The baseline plan for this site was to continue pump and treat and SVE operations for an extended period until final remedial goals are achieved.

Based on the current state of T-Area, deployment of edible oil was selected as a promising alternative approach to accelerate the progress toward remedial goals and to transition the site into a passive enhanced attenuation condition. In this case, the deployment would allow discontinuing the active (groundwater pump and treat and SVE) operations, would reduce concentrations, and would facilitate transitioning to a protective condition in which the groundwater plume stabilizes and shrinks passively.

Use of edible oils at sites with relatively low contaminant concentrations has proven to be a cost-effective alternative for treatment of residual contamination in the saturated zone (DOD, 2004). As depicted in Figure 1, Edible oil deployment serves to decrease chlorinated compound concentrations in two ways: 1) physical sequestration, which reduces effective aqueous concentration and mobility; and 2) stimulation of anaerobic, abiotic and cometabolic degradation processes. In the central deployment area, contaminant initially partitions into the added oil phase. Biodegradation of the added organic substrate depletes the aquifer of oxygen and other terminal electron acceptors and creates conditions conducive to anaerobic degradation processes. The organic substrate is fermented to produce hydrogen, which is used as an electron donor for anaerobic dechlorination by organisms such as *Dehalococcoides*. Daughter products leaving the central treatment zone are amenable to aerobic oxidation. Further, the organic compounds leaving the central deployment zone (e.g., methane and propane) stimulate and enhance downgradient aerobic cometabolism which degrades both daughter compounds and several parent cVOCs. Figure 1 depicts TCE concentration reduction processes (labeled in green) along with their corresponding breakdown products.

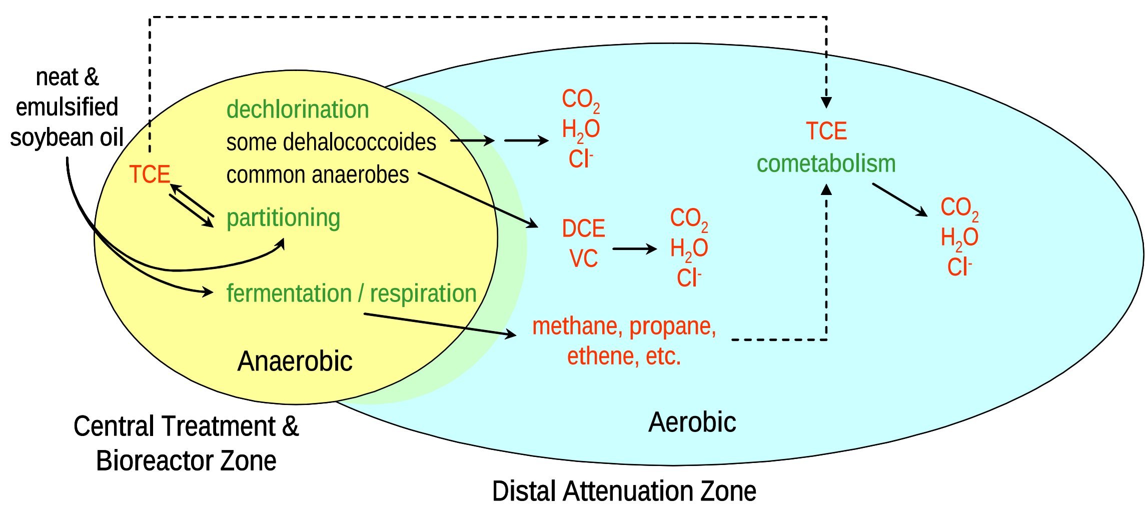


FIGURE 1. Schematic of TCE Concentration Reduction Processes

DESIGN APPROACH AND FIELD IMPLEMENTATION

The design for this combined remedy to transition the remediation of cVOCs in the soil and groundwater of T-Area at the Savannah River Site to passive attenuation based remedy derives from two mechanisms, partitioning and degradation, combined with standard hydrology and engineering calculations. The current configuration of T-Area influences the assumptions used in developing this design. Notably, the design utilizes existing wells and piezometers for access and eliminates additional penetration of the cap as requested by the site owners and regulators. This required creative application of treatment reagents to exploit site features and characteristics such as the water table and lithology to generate a deployment zone that has the correct geometry to intercept contaminants and effectively treat the groundwater plume.

The result of the design process was a two part deployment: 1) neat (pure) vegetable oil at the water table in the residual source area, and 2) emulsified vegetable oil in the core of the groundwater cVOC plume. In the first part, neat oil spreads laterally forming a thin layer on the water table to intercept and reduce future cVOC input from the vadose zone (Figure 2). In the second part, emulsified oil serves to stimulate formation of an active bioremediation "reactor" within the active plume footprint to degrade existing groundwater contamination and any future inputs (Figure 3). For this design, pure soybean oil was assumed for the neat oil and a commercially available remediation product (EOS® 5998 B42) was assumed for the emulsified oil. The enhanced oil substrate (EOS®) has properties suitable to deployment and distribution using existing wells (Kovacich et al, 2006) and this amendment includes nutrients (e.g., lactate and vitamin B12) that are beneficial for the biodegradation of cVOCs. Additional reagents (e.g., to stabilize pH near 7) and nutrients were also specified. The locations and quantities of reagents and chase water were all calculated using standard engineering approaches along with lab measurements of oil distributions in cores.

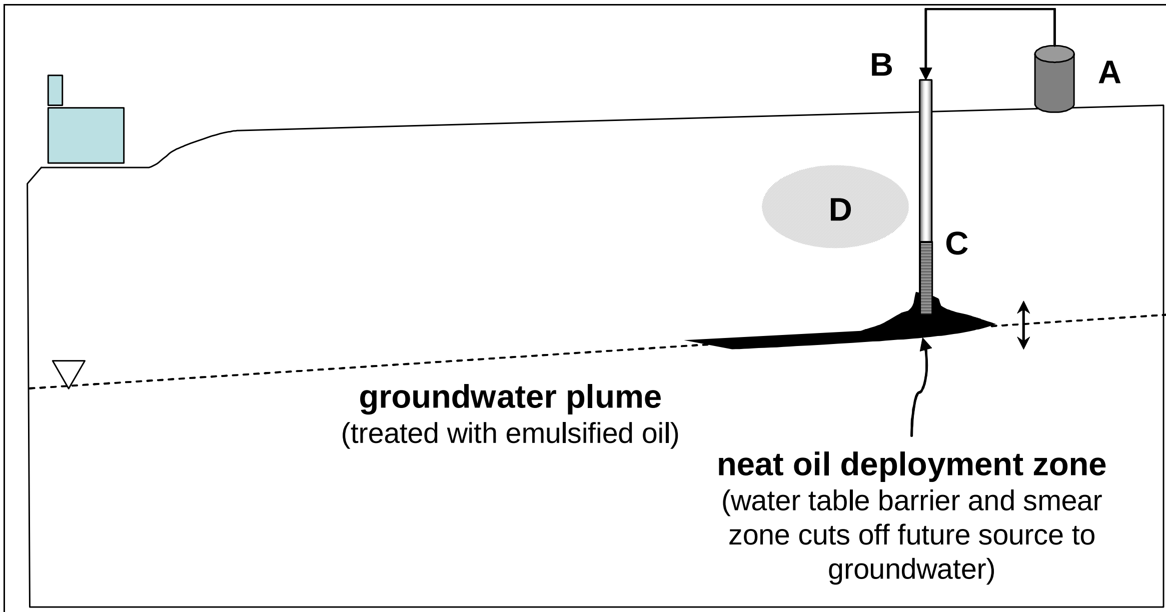
Plan view maps of the proposed deployments are shown in Figures 4 and 5, for the neat oil deployment and the emulsified oil deployment, respectively. Key summary parameters from the design are as follows:

Neat Oil at the Water Table

- Description of deployment: Emplace a thin sheet of oil at the water table beneath residual vadose sources using selected deep vadose wells or groundwater wells with dry screen just above the water table. The deployment relies on the characteristics of the oil (density and transport properties) to move it into the desired configuration.
- Quantity of oil: approximately 10,600 L (approximately 2,800 gallons)
- Existing wells used in deployment: TVX3L, TVX5L, and either TVX6L or TBG5
- Approximate field time needed for deployment: One to Two weeks.

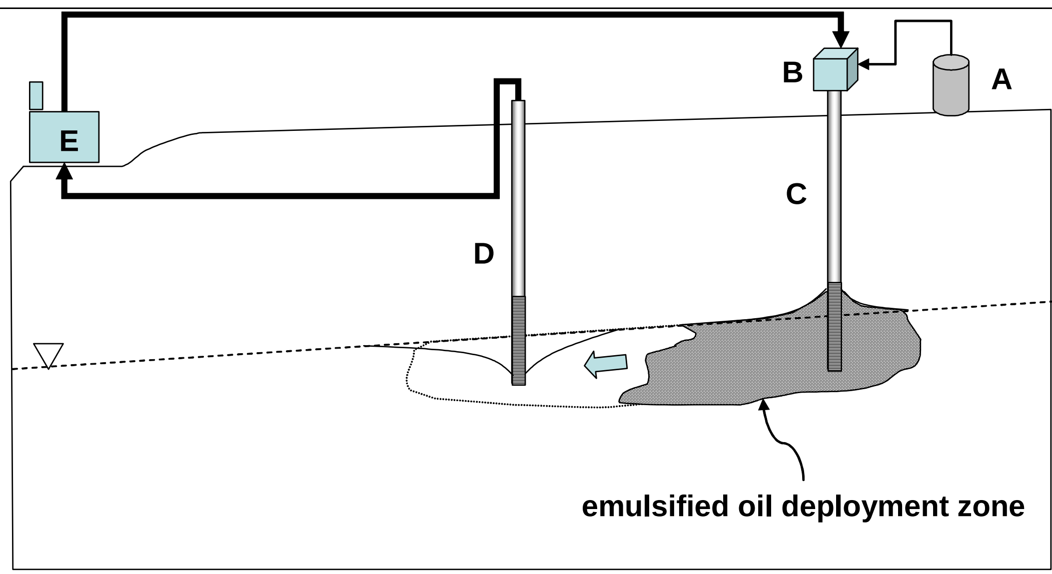
Emulsified Oil Substrate in the Groundwater Plume

- Description of deployment: Water would be extracted from a down gradient well, treated with an air stripper and reinjected in an up gradient well fitted with an EOS® metering system. In each injection-extraction pair, the operation would continue until the desired EOS® is injected along with sufficient water to distribute the EOS® throughout the entire volume between the wells.
- Quantity of EOS®: 14,600 L (approximately 30,000 lbs or 3,850 gallons of emulsion)
- Total quantity of blend/chase water: 760,000 L (approximately 200,000 gallons)
- Existing wells used in deployment: Deployed sequentially using injection extraction pairs when possible (TBG5 → TRW-4R, TRW-4R → TBG4, TRW-4R → TNX3D)
- Approximate field time needed for deployment: 30 to 60 days



A = neat (pure) vegetable oil
B = injection, metering and flow monitoring system
C = deep vadose / water table oil injection well
D = residual vadose source

FIGURE 2. Schematic diagram of neat oil deployment



A = concentrated emulsified food grade vegetable oil, nutrients and buffer/base
B = metering and flow monitoring system
C = emulsified oil injection well
D = extraction well to control oil zone geometry
E = air stripper – VOC water treatment system (equipped with tank/pump for recirculation)

FIGURE 3. Schematic diagram of emulsified oil deployment

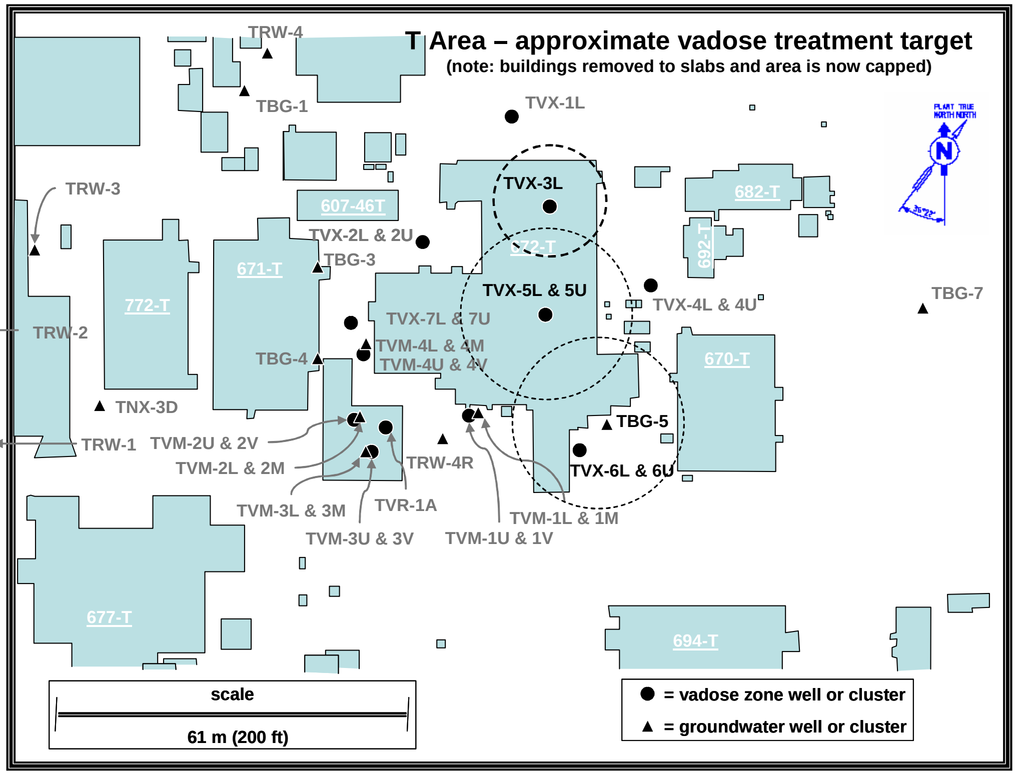


FIGURE 4. Plan view map for neat oil deployment in vadose zone

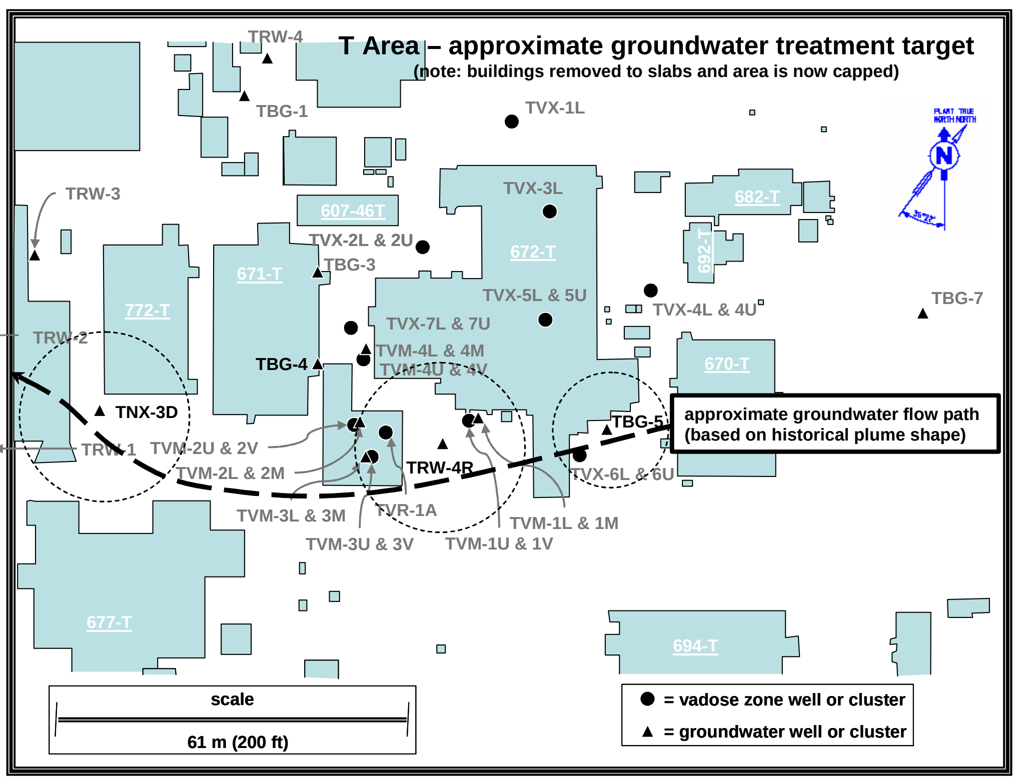


FIGURE 5. Plan view map for emulsified oil deployment in the groundwater

MONITORING

The goals, metrics and methods for monitoring the performance of the enhanced attenuation remedy are listed in Table 1. The sampling strategy is designed to optimize data collected to meet the study objectives, while minimizing analytical costs. Measurements are being made in a representative set of wells within the treatment zone and in an up-gradient well (for background information) and in representative downgradient wells (to evaluate the aerobic treatment zone).

TABLE 1. Strategy for sampling and analysis

Test Goal	Metric	Method
Evaluate neat oil distribution	Measure oil presence and thickness in existing wells	oil/water interface probe, bailing
Evaluate emulsified oil distribution	Measure oil presence and approximate concentration in the treated zone using existing wells	Visual identification in water samples. TOC analysis
Assess the extent and rate of change from aerobic to anaerobic	Measure temporal dissolved oxygen (DO) in existing wells	Field sensors and test kits
Determine TCE degradation and degradation rates	Measure temporal TCE and daughter product concentrations	SRNL modified method 5021 headspace analyses
	Measure TCE destruction	Stable C isotope enrichment analyses
Assess daughter products and their subsequent degradation	Measure temporal cVOC concentrations	SRNL modified method 5021 headspace analyses
Assess degradation pathways	dechlorination: measure cVOC daughter products	SRNL modified method 5021 headspace analyses
	cometabolism: measure activity dependent enzymes	Activity-dependent enzyme probes, North Wind Inc.; Stable C isotope ratios
	abiotic: TBD	Stable C isotope ratios
Assess the recruitment of appropriate bacteria and sufficient amount of biomass	Measure temporal type and abundance of the microbial community (fermentative, dechlorinating, and cometabolic)	Quantitative polymerase chain reaction (qPCR) by SRNL and/or commercial laboratory
Determine if additional means are needed to stimulate and/or maintain attenuation	Measure geochemistry and chemistry parameters for maintenance of appropriate attenuation conditions: DO, ORP, TOC, pH, alkalinity, ammonia, sulfate, phosphate, nitrate	Field sensors and test kits
	Measure co-metabolites: methane, propane, butane, ethene, ammonia (breakdown products of soybean oil)	SRNL sample method and GC analysis.

STATUS & PRELIMINARY RESULTS

The field deployment of the amendments was initiated in February 2008 and is scheduled for completion in April 2008. Flow rates for diluted emulsion injection and groundwater extraction in the first well pair were below the design assumptions (approximately half of the assumed values) but subsequent well pairs are operating at higher design basis flow rates. Data collected in the field indicate that the injected fluids are distributing in the subsurface as expected. The data indicate that the buffer added to the injection (trisodium phosphate and bicarbonate) has increased the pH from approximately 5 (typical for the Southeastern Coastal Plain) to values above 7 within the treatment zone. Modeling results suggest that the most significant early observation will be a partitioning effect associated with the deployment of the neat oil in the deep vadose zone. These predictions indicate near source cVOC concentrations decreasing from about 50 µg/L down to about 10 µg/L within the first few months. As the vadose source equilibrates with the deployed neat oil (over about 4 years) the near source concentration is predicted to rebound up to about 33 µg/L. Field data and case studies from other emulsified oil deployments indicate that the conditions needed for anaerobic degradation in the T-Area central bioreactor zones may several months to develop. These model results and case studies suggest that the partitioning benefit and the biogeochemistry/degradation should properly synchronize. Thus, early monitoring is focusing on amendment distribution, observation of the partitioning effect, the development of central zone biogeochemistry, and documentation of baseline cometabolism rates in the downgradient zone to allow future assessment of any increased rates associated with the deployment.

ENHANCED ATTENUATION & COMBINED REMEDIES

The engineers and scientists responsible for soil and groundwater activities at T-Area initiated a technical evaluation process to determine if continued pump and treat operations are advantageous. Importantly, the evaluation did not presume that the site needed to transition directly to monitored natural attenuation. Instead, the team considered a range of options and examined *enhanced attenuation* – a concept that has recently been explored by the Interstate Technology and Regulatory Council (ITRC, 2007). The basis of the enhanced attenuation paradigm is to implement up-front active engineering solutions that alter the target site in such a way that the contaminant plume will passively stabilize and shrink and to document that the action will be effective, timely, and sustainable. The paradigm encourages combining remedial technologies so that each is matched to the target conditions and contaminant concentrations throughout the life of the site (until achieving regulatory goals).

Understanding and documenting contaminant mass balance, and the mass balance of important nutrients or inhibitors, are the keys to developing and documenting enhanced attenuation remedies and determining sustainability. Thus, the long-term plume dynamics can be altered by either reducing the contaminant loading from the source or by increasing the rate of natural attenuation processes within all, or part of, the plume volume. A significant fraction of the contamination has been removed from the groundwater underlying T-Area using SVE and groundwater pump and treat. A preferred combination of technologies that emerged for finalizing the remediation of T-Area included: 1) neat (pure) vegetable oil deployment in the deep vadose zone in the former source area, 2) emulsified vegetable oil deployment within the footprint of the groundwater plume, and 3) stimulation and documentation of aerobic attenuation for the distal portion of the plume.

For T-Area, the enhanced attenuation development process proved to be a powerful tool in developing a defensible strategy that provides a high degree of performance while minimizing adverse collateral impacts of remediation (e.g., energy use and wetland damage) and minimizing life-cycle costs.

ACKNOWLEDGEMENTS

This work was sponsored by the U. S. Department of Energy Environmental Management Program and funded under Contract No. DE-AC09-96SR18500. Reference herein to any specific commercial product, process, or service by trademark, name, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring of same by the United States Government or any agency; thereof.

REFERENCES

DOD. 2004. *Principles and Practices of Enhanced Anaerobic Biodegradation of Chlorinated Solvents*, U. S. Department of Defense, Air Force Center for Environmental Excellence, San Antonio TX.

ITRC. 2007. *A Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes*. Interstate Technology and Regulatory Council, Enhanced Attenuation Chlorinated Organics Team, document available at: http://www.itrcweb.org/Documents/EACODecisionFlowchart_v1.pdf (accessed 03/14/2008).

Kovacich, M. S., D. R. Beck, P. Rich, M. Zack and M. Cannaert. 2006. Direct-Push Injection and Circulation Biobarrier to Remediate a TCE Groundwater Plume, *Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, May 22, 2006, Monterey CA.