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Enhanced Anaerobic Bioremediation Using CAP18™ as a Polishing Application for CVOC Impacted Groundwater

TECHNICAL PAPER

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ABSTRACT

An in-situ pilot study was conducted in 2006 by Environmental Chemical Corporation (ECC)/Burns & McDonnell Engineering Co. Inc. at the former dry cleaning facility (DCF) at Fort Riley, Kan., to determine if groundwater contamination identified during previous field investigations could be treated with in-situ remedial technologies.

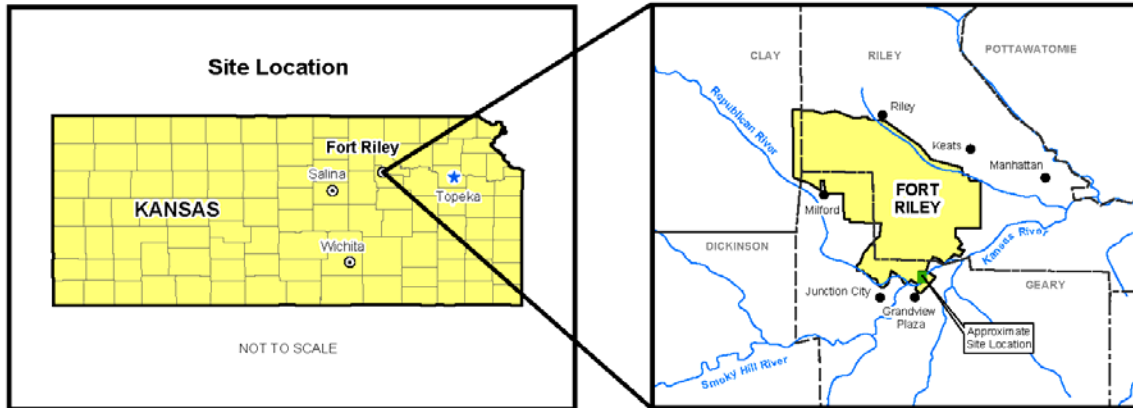
An alluvial terrace dominates the topography across the DCF pilot study area. The specific area of concern (AOC) addressed during the in-situ pilot study was AOC 2, which contained groundwater contaminated with tetrachloroethylene (PCE) located beneath the former building footprint in a buried bedrock erosional channel. PCE, trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-1,2-DCE) were detected at levels greater than the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) in groundwater. The suspected sources of contamination were broken and cracked sanitary sewer lines and manholes that handled process wastewater during dry cleaning operations. The AOC 2 pilot study objectives were to determine the feasibility of in-situ treatment of groundwater contamination in the terrace aquifer using enhanced anaerobic bioremediation (EAB) to accelerate the biodegradation of chlorinated compounds to levels below the cleanup criteria, and to serve as a final stage remedial polishing agent to decrease the overall AOC 2 monitoring timeframe and cost.

Enhanced bioremediation of the contaminants in the terrace aquifer was selected due to the relatively high levels of PCE daughter products in the downgradient alluvial wells as compared to the PCE-dominated terrace wells. CAP18™, a non-emulsified (or neat) vegetable oil product offered by DBI Products (now Carus Corp.) was selected for this study because it is a cost effective, long-lasting substrate that is proven to facilitate biodegradation of chlorinated compounds at concentrations similar to, and greater than those found in the pilot study area. The size of the treatment area was approximately 75 feet by 230 feet. CAP18™ was applied through direct-push rods at 2 to 3-foot depth intervals, at 73 locations spaced on 18-foot centers. Based on performance monitoring data collected from down gradient monitoring wells, very positive trends in key parameters such as volatile organic compounds (VOC) concentrations, dissolved oxygen (DO), oxidation-reduction potential (ORP), and methane indicate that an enhanced reducing environment has been established and that EAB via the injection of CAP18™ can be used as a final stage polishing amendment for the reduction of chlorinated solvents.

INTRODUCTION

An in-situ pilot study was conducted at the DCF at Fort Riley, Kan., to determine if groundwater contamination identified during previous field investigations could be treated with in-situ remedial technologies. This pilot study was developed and conducted by ECC/Burns & McDonnell in support of the Fort Riley Directorate of Public Works-Environmental Division (PWE) Installation Restoration Program (IRP).

Fort Riley is located in north-central Kansas (Figure 1) between Salina and Topeka. The DCF pilot study site is on the Main Post portion of Fort Riley, just north of the Kansas River.



A former dry cleaning facility at this site was demolished and removed approximately two years before the pilot study. PCE was used as a cleaning solution from 1966 until dry cleaning operations ceased in 1983. PCE is present in groundwater at concentrations above the USEPA MCLs and the Kansas Department of Health and Environment (KDHE) Risk-based (RSKs) level of 5 micrograms per liter ($\mu\text{g}/\text{l}$). There were two specific, co-located AOCs identified for the former DCF location. The first AOC (AOC 1) contained soil contaminated with PCE above the KDHE RSKs (KDHE, 2007) of 180 milligram per liter (mg/l). AOC 1 was excavated to a depth of 12 feet below ground surface and the soil was transported off-site to a landfarm treatment cell. The groundwater beneath AOC 1 was designated as AOC 2. This AOC contained PCE impacted groundwater located beneath the former DCF building footprint in a buried bedrock erosional channel.

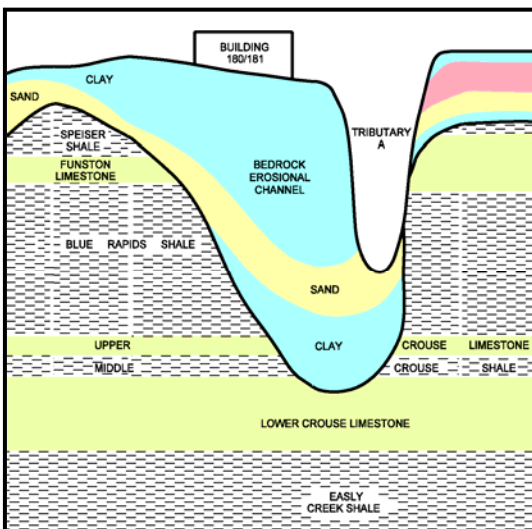


FIGURE 2. General Subsurface Conditions

Site Geology and Hydrogeology. An alluvial terrace dominates the topography of the AOC 2 pilot study area. The DCF is adjacent to the Kansas River, which flows in a general west to east direction. The DCF area is composed of two alluvial terraces. These terraced areas are composed of material deposited during flooding of the Kansas River, erosion of upland areas north of DCF, or placement of fill material (anthropogenic) along the boundaries of the DCF. Geology of the alluvial terraces consists of clays, sands, and silts overlying Permian age sedimentary rock which is composed of alternating sequences of shale and limestone (Figure 2). A bedrock erosional channel underlies the AOC 2 pilot study area. The axis of the channel runs from northeast to southwest and extends into the Kansas River alluvium.

The aquifers beneath the DCF pilot study area consist of unconfined terrace aquifer overlying semi-confined bedrock aquifers. The unconfined terrace aquifer transitions into the alluvial aquifer toward the southern portion of the site adjacent to the Kansas River. Current groundwater flow conditions for the DCF show a south, southeast direction of flow toward the Kansas River. Groundwater flow within the Kansas River alluvium is controlled by the Kansas River and generally conforms to the direction of river flow.

Site Analytical Constituents. PCE, TCE, cis-1,2-DCE and vinyl chloride (VC) have historically been detected in groundwater at levels greater than MCLs. The suspected sources of PCE are broken and cracked sanitary sewer lines and manholes that handled process wastewater during dry cleaning operations (Figure 3). PCE degradation products including TCE and cis-1,2-DCE were detected in monitoring wells downgradient of the source area (Monitoring Wells DCF93-13 and DCF02-41). The groundwater contamination at the AOC 2 pilot study area extended into the Kansas River alluvium. Based on VOC concentrations and groundwater geochemical conditions, including DO, ORP and methane, the groundwater contamination was degrading naturally, but not to levels below the cleanup objectives.

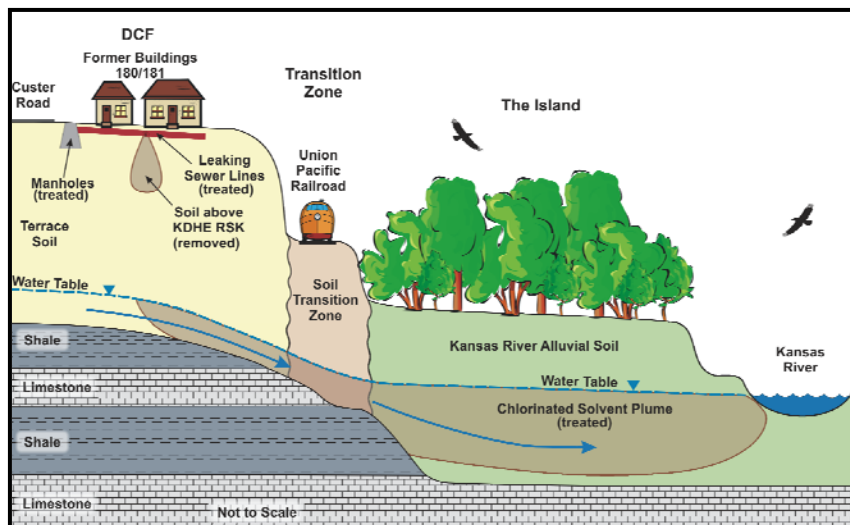


FIGURE 3. Contaminant Location and Movement

Pilot Study Objectives. The AOC 2 pilot study project objectives were to determine the feasibility of in-situ treatment of groundwater contamination in the terrace aquifer using EAB to accelerate the biodegradation of chlorinated compounds to levels below the cleanup criteria, and to serve as a final stage remedial polishing agent to decrease the overall AOC 2 monitoring time and cost. Enhanced bioremediation of the contaminants in the terrace aquifer was selected due to the relatively high levels of PCE daughter products in the downgradient alluvial wells, as compared to the PCE-dominated terrace wells. CAP18™, a non-emulsified (or neat) vegetable oil product offered by DBI Products (now Carus Corporation) was selected for this study because it is a cost effective, long-lasting substrate that is proven to facilitate biodegradation of chlorinated compounds at concentrations similar to, and greater than, those in this area.

PILOT STUDY DESIGN

EAB Amendment Selection. In recent years, vegetable oil substrates have gained wide acceptance for groundwater remediation of VOCs by EAB. Burns & McDonnell selected CAP18™ for this study because it is a cost-effective substrate that is proven to facilitate biodegradation of chlorinated compounds existing at concentrations similar to those in AOC 2. In addition, the neat oil is more likely to remain within the treatment area under the potentially high groundwater flow rate conditions that exist at AOC 2. Additional advantages identified for this type of EAB amendment included the following:

- Viscosity is similar to vegetable oil allowing injection using standard direct-push equipment into soils with varying degrees of permeability.
- Dissolves slowly to provide a long-term hydrogen source that lasts for months. Unlike more soluble/less viscous amendments, frequent re-injection or recirculation systems are not necessary, thus decreasing costs.
- Is a metabolically diverse substrate composed of C18 fatty acids producing a wide range of compounds for microbial hydrogen production, ideal for diverse aquifer conditions.
- Is a concentrated hydrogen source, providing fuel to establish optimal groundwater conditions and overcome competitive demand.

Treatment Area. The groundwater treatment area is located within the bedrock erosional channel that underlies the eastern portion of the former dry cleaning building (Figure 4). Monitoring wells installed in this channel include Monitoring Wells DCF92-05, DCF93-13, DCF06-40, and DCF02-41. Based on analytical data collected from these monitoring wells, as the groundwater flows down the axis of the channel toward the Kansas River, the chlorinated solvent contamination is naturally attenuated. To increase the effectiveness of the natural attenuation in the bedrock erosional channel, a pilot study involving the injection of CAP18™ down the axis of the bedrock erosional channel was conducted. The size of the treatment area was approximately 75 feet by 230 feet.

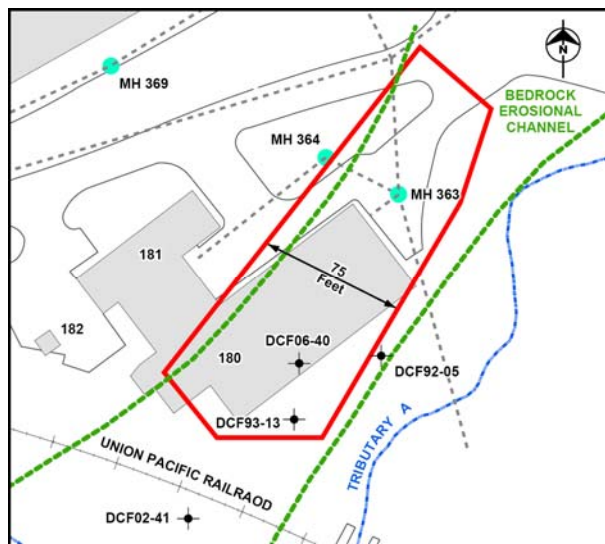


FIGURE 4. AOC 2 Treatment Area

Groundwater Analytical Baseline. Groundwater data from the AOC 2 monitoring wells were collected in 2005 to provide a groundwater analytical baseline for chlorinated solvent concentrations. The VOC results for this event are presented as follows:

Wells	PCE	TCE	cis-1,2-DCE
92-05	8.4	ND	ND
06-40	80.2	ND	ND
93-13	26.5	20.6	9.9
02-41*	ND	5.3	74.3

All results are reported in micrograms per Liter (µg/L). **26.5** Indicates above MCL and RSK.

* Well located down gradient of treatment area. ND = Nondetect.

The groundwater analytical baseline data indicated that some degree of bioremediation was occurring down gradient of the source area located near Monitoring Wells DCF 92-05 and DCF 06-40. At the source area, only PCE concentrations were detected for Monitoring Wells DCF 92-05 and DCF 06-40 at 8.4 and 80.2 ug/l, respectively. As the plume travels south along the bedrock erosional channel, down gradient monitoring wells DCF 93-13 and 02-41 show decreasing concentrations of PCE and increasing concentrations of TCE and cis-1,2-DCE.

The groundwater geochemical baseline data also indicated that bioremediation was occurring down gradient of the source based on decreasing DO and ORP concentrations as groundwater travels south along the bedrock erosional channel.

Wells	DO (mg/L)	ORP (mV)	Ferrous Iron (mg/L)	Methane (µg/L)
92-05	7.58	134	0.0	ND
06-40	5.72	146	0.03	ND
93-13	5.25	75	0.02	ND
02-41	0.51	-167	1.69	ND

mg/L = Milligrams per Liter
DO = Dissolved Oxygen

mV = Milli-Volt
ORP = Oxidation Reduction Potential

ND = Nondetect

Wells were purged using USEPA Low Flow Protocols Version 1.3.

-167 Indicates favorable conditions for reductive dechlorination (USEPA, 1988).

Subsurface Amendment Demand. The EAB amendment demand for site-specific VOCs was calculated using the highest concentration detected in the AOC 2 monitoring wells. For DO and nitrate, an average of the concentrations recorded in the monitoring wells was used in the demand calculation. The sulfate and ferrous iron concentrations for the demand calculation were estimated by averaging the concentrations recorded in the monitoring wells. Hardness was estimated using alkalinity (as calcium carbonate) concentrations. An average of the alkalinity concentrations recorded in the monitoring wells was used in the CAP18™ demand calculation.

EAB PILOT STUDY APPLICATION

In May 2006, CAP18™ was applied in and around the former dry cleaning building foot print (Figures 4 & 5). The vertical treatment interval extended from the water table at approximately 35 feet below ground surface (bgs) to the bedrock surface at approximately 43 feet bgs. The treatment zone varied in thickness from approximately one to seven ft. The soil within the treatment zone consists of sand with minor amounts of clay. CAP18™ was applied through direct-push rods at 2- to 3-foot depth intervals, at 73 locations spaced on 18-foot centers. Approximately 8,250 pounds (or approximately 1,080 gallons) of CAP18™ was applied to the treatment area. The total dosage was divided among the 73 injection points. In general, the target dose for each location was between 15 and 20 gallons per point, spread between the three depth intervals. This amounted to approximately 115 to 155 pounds of CAP18™ per location, or approximately 16 to 22 pounds of CAP18™ per vertical foot of the treatment interval.

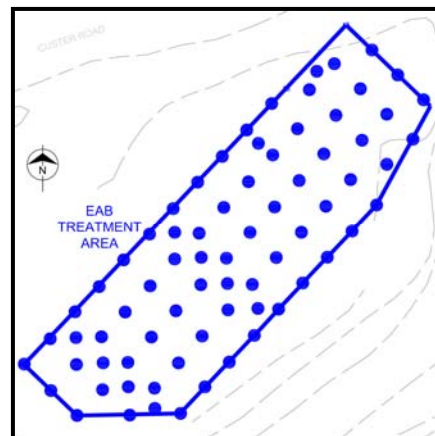


FIGURE 5. EAB Injection Locations

Injection was accomplished at each injection location through direct-push rods using an injection pump and delivery hose. CAP18™ was fed by gravity to the injection pump. The injection pump was connected to direct-push rods using a high-pressure hose and the rods were equipped with an injection probe tip. Injection at each location was accomplished using a “top-down” direct-push injection method (Figure 6).

PILOT STUDY RESULTS

The post performance monitoring program consisted of groundwater sampling at Monitoring Wells DCF92-05, DCF06-40, DCF93-13, and DCF02-41 (Figure 2).

Parameters that were measured during post-performance monitoring included VOCs, nitrate, sulfate, methane, pH, DO, ORP, total iron and ferrous iron. These parameters were measured using a low-flow, multi-channel meter, a flow cell and dedicated bladder pumps. Groundwater was purged from each monitoring well using carbon dioxide carrier gas for several measurement cycles and performance parameters were recorded until the wells stabilized, based on low-flow purging protocols established by the USEPA. The final post-performance monitoring results conducted in 2008 are presented below.

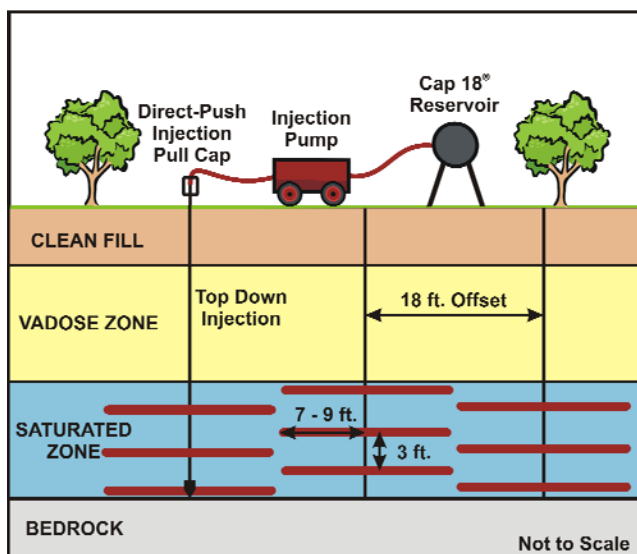


FIGURE 6. Delivery Method

Wells	PCE	TCE	cis-1,2-DCE
92-05	ND	0.7	2.6
06-40	22.1	0.6	2.0
93-13	ND	3.4	3.4
02-41*	ND	ND	92.1

All results are reported in micrograms per Liter (µg/L). **22.1** Indicates above MCL and RSK. * Well downgradient of treatment area. ND = Nondetect.

Wells	DO (mg/L)	ORP (mV)	Ferrous Iron (mg/L)	Methane (µg/L)
92-05	1.11	-287	10	3,230
06-40	0.23	-303	0	2,810
93-13	0.50	-338	1.0	4,000
02-41	0.50	-344	7.0	ND

mg/L = Milligrams per Liter mV = MilliVolt ND = Nondetect.

Wells were purged using USEPA Low Flow Protocols Version 1.3.

-167 Indicates favorable conditions for reductive dechlorination (USEPA, 1988).

Monitoring data collected to evaluate the effectiveness of EAB for PCE reduction is summarized in Figure 7. The figure includes pre-injection data back to 2004 to aid in trend analysis.

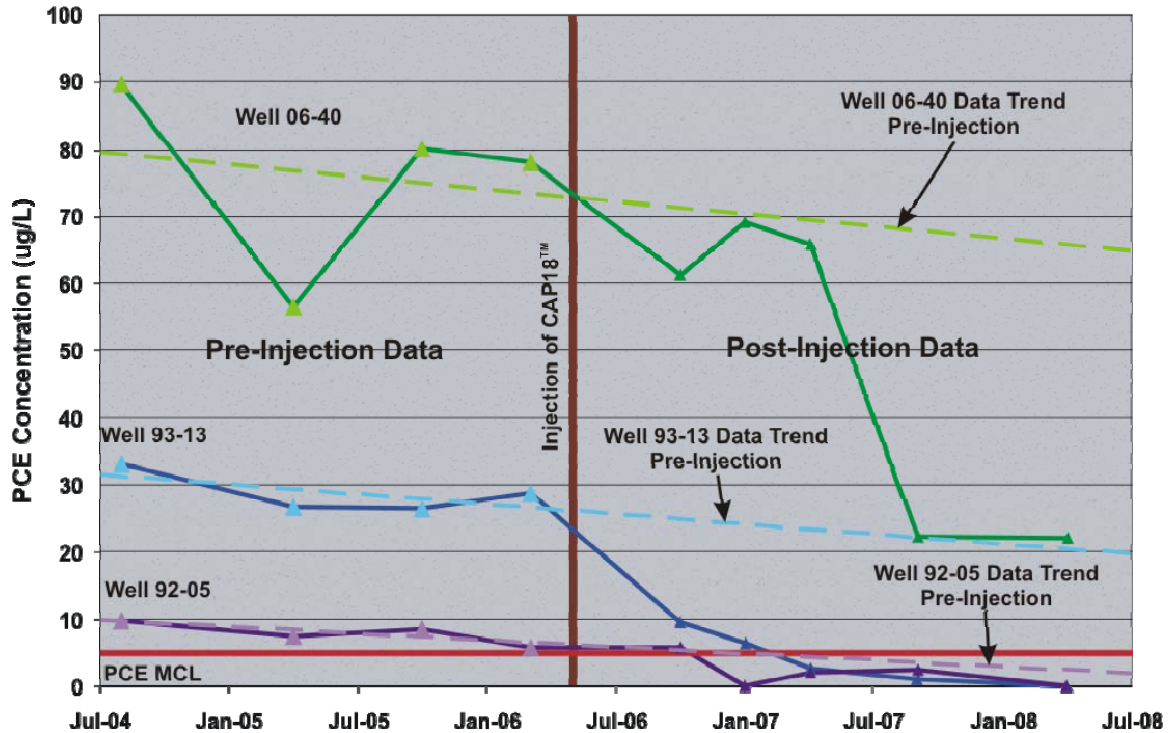


FIGURE 7. PCE Results, Pre- and Post-Treatment

For all three monitoring wells in the immediate area of injection (DCF92-05, DCF 93-13, and DCF06-40), the post-injection data trends were very positive for PCE, DO, and ORP. For these three wells, there is a reduction of PCE concentrations and concentrations of PCE daughter products TCE and cis-1,2-DCE are now evident at the source area. DO levels have reduced, and ORP is significantly negative (approximately -200 mV or lower). Significant increases in concentrations of methane were also recorded for these three wells. The results for ferrous iron and sulfate levels vary. Data from DCF02-41 was not included in the figure because of its significant distance from the injection area. Data from this well was collected to aid in the analysis of the overall AOC 2 groundwater conditions, but impacts from injection were not expected during the course of this pilot study.

CONCLUSIONS

Based on performance monitoring data collected for Monitoring Wells DCF92-05, DCF93-13 and DCF06-40, very positive trends in key parameters such as VOC concentrations, DO, ORP and methane indicate an enhanced reducing environment has been established. Based on these results and data collected regarding the injection process, the following conclusions were reached for the EAB pilot study:

- EAB is a viable remedial option for groundwater at this site.
- EAB via vegetable oil substrate injection was effective in enhancing the natural attenuation of PCE, TCE, and cis-1,2-DCE in groundwater at AOC 2.
- EAB has reduced contaminant concentrations in AOC 2 below the KDHE RSKs and MCLs as demonstrated by the results for Monitoring Wells DCF92-05 and DCF93-13. A substantial reduction in PCE concentration was also demonstrated by the Monitoring Well DCF06-40 results.
- Based on data trends established during post performance monitoring, the breakdown products TCE and cis-1,2-DCE are now being detected at low levels in Monitoring Well DCF06-40, which has historically exhibited only PCE concentrations.
- The long-term monitoring timeframe and cost for AOC 2 was reduced due to the enhanced natural attenuation of PCE, TCE, and cis-1,2-DCE in groundwater.
- EAB can be used as a final stage polishing amendment for groundwater impacted with chlorinated compounds.

REFERENCES

- Burns & McDonnell (BMcD). 2007. *Proposed Plan for the DCF Study Area, Operable Unit 003, Fort Riley, Kansas*, October 11, 2007.
- BMcD. 2003. *Remedial Investigation Addendum for the DCF Study Area, Operable Unit 003, Fort Riley, Kansas*, April 30, 2004.
- Environmental Chemical Corporation (ECC)/BMcD. 2008. *Pilot Study Report for the DCF Study Area, Operable Unit 003, Fort Riley, Kansas*, January 3, 2008.
- Kansas Department of Health and Environment (KDHE). 2007. *Risk-Based Standards for Kansas, RSK Manual — 4th Version*.