Groundwater
Monitoring&Remediation

Long-Term Evaluation of Mulch Biowall Performance to Treat Chlorinated Solvents

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Abstract

Permeable reactive barriers (PRBs), such as mulch biowalls, have been installed at numerous groundwater cleanup sites, and laboratory and field studies have demonstrated biotic and abiotic processes that degrade chlorinated volatile organic compounds (CVOCs) in groundwater passing through these engineered remedies. However, the longevity of mulch biowalls remains a fundamental research question. Soil and groundwater sampling at seven mulch biowalls at Altus Air Force Base (AFB) approximately 10 years after installation demonstrated the ongoing degradation of CVOCs. Trichloroethene was not detected in five of seven groundwater samples collected from the biowall despite upgradient detections above federal drinking water standards. Microbial sampling established the presence of key dechlorinating bacteria and the abundance of genes encoding specific enzymes for degradation, high methane concentrations, low sulfate concentrations, and negative oxidation-reduction potential, all indicative of highly reducing conditions within the biowalls and favorable conditions for CVOC destruction via microbial reductive dechlorination. High cellulose content (>79%) of the mulch, elevated total organic carbon (TOC) content in groundwater, and elevated potentially bioavailable organic carbon (PBOC) measurements in soil samples further supports an ongoing, long-lived source of carbon. These results demonstrate the ongoing and long-term efficacy of the mulch biowalls at Altus AFB. In addition, concentrations of bacteria, TOC, PBOC, and other geochemical parameters suggest a modest impact of the biowalls downgradient. The continued presence of CVOCs downgradient may be attributable to back diffusion from low-permeability shale. However, the biowalls continue to provide benefits by removing CVOCs in groundwater, thus reducing further CVOC loading to the downgradient, low-permeability strata.

Introduction

A permeable reactive barrier (PRB) is a passive, in situ remedial technology that treats contaminated groundwater via natural and engineered biotic and abiotic processes (e.g., AFCEE 2008). PRB installation typically involves reactive material (e.g., mulch) mixed with a permeable matrix (e.g., sand and gravel) installed in trenches oriented perpendicular to the flow of groundwater. One common PRB reactive material consists of organic materials such as mulch and bark; these PRBs are typically called biowalls. Conceptually, a biowall intercepts impacted groundwater flow, and the constituents of concern are degraded via biological and biogeochemical transformation reactions induced by the reactive material within the biowall (e.g., AFCEE 2008; Whiting et al. 2014). After flowing through the biowall, the treated groundwater mixes with native groundwater, thereby lowering chlorinated volatile organic compound (CVOC) concentrations. Depending on site-specific conditions, this treated groundwater may promote further degradation of CVOCs in downgradient groundwater through the transport of reactive substrates.

When mulch biowalls were initially installed in the 1990s and 2000s, there was substantial uncertainty as to the longevity and sustainability of this technology (AFCEE 2008; ITRC 2011; Obiri-Nyarko et al. 2014). For example, the United States Air Force 2008 technical protocol for mulch biowalls suggested that while the mulch fraction may last 10 to 15 years or longer, the biowalls may need to be replenished with additional organic substrate if the primary reactive media becomes depleted (AFCEE 2008). In addition, the long-term sustainability of biowall performance was identified as a key regulatory issue by AFCEE (2008) and others (ITRC 2011; Obiri-Nyarko et al. 2014). Lu et al. (2007) demonstrated field performance at the OU-1 biowall at Altus Air Force Base (AFB) based on 4 years of monitoring data. Longer term predictions of biowall longevity have typically been based on laboratory studies rather than field data collected from actual biowall sites. For example, Shen et al. (2010) estimated that the mulch in the SS-17 biowall at Altus AFB is expected to support microbial activity for 10 years, but their results were based on laboratory studies rather than the evaluation of performance data collected in the field.

Sustained treatment encompasses the ongoing, long-term performance of in situ remedial technologies years after initial installation. Adamson et al. (2011) introduced the concept of sustained treatment to describe enhancements

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to the attenuation capacity after the conclusion of the active treatment period. Mechanisms that contribute to contaminant removal over long timeframes may include endogenous biomass decay (Suthersan et al. 2013), slow diffusion of remedial amendments from low-permeability zones, and the formation of reactive mineral species (e.g., He et al. 2015). Enhanced bioremediation was identified as a technology that lends itself to sustained treatment (Adamson et al. 2011).

This paper evaluates the sustained treatment of mulch biowalls at Altus AFB approximately 10 years after biowall installation. We hypothesize that sustained treatment processes remain active within the biowalls and contribute to the ongoing attenuation of CVOCs within and downgradient of the biowalls. Altus AFB was selected as a test candidate due to the scale of the mulch biowalls (approximately one mile in total length) and the availability of extensive historical data collected as part of the ongoing site investigation and monitoring program, which was provided by the Remedial Project Manager at the AFB. Additional field data were collected in 2015 to assess the performance of the biowalls in terms of the degree of ongoing CVOC degradation, the geochemical environment present within the biowalls, and the processes that may be contributing to degradation of CVOCs in groundwater flowing through the biowalls. The data were also analyzed to evaluate the effects of the biowalls on downgradient groundwater quality.

Background

Site Description and History

Altus AFB is located in Jackson County in southwestern Oklahoma (Figure 1). Biowalls have been installed at two areas of the Altus AFB complex: at Operable Unit 1 (OU-1) and at Spill Site 17 (SS-17). The OU-1 biowall was installed in the eastern portion of the base in June 2002 and has been the subject of several field and laboratory studies (Kennedy and Everett 2003; Lu et al. 2007; He et al. 2008; USEPA 2009; Lebrón et al. 2010; Shen et al. 2012; Whiting et al. 2014). One focus of this prior research at the OU-1 biowall was evaluating the potential for abiotic reactions. The prior research at OU-1 documented favorable biogeochemical conditions for the abiotic degradation of CVOCs flowing through this biowall, as well as a biological degradation component based on accumulation of vinyl chloride (Whiting et al. 2014).

The research presented herein focuses on the six SS-17 series of biowalls (biowall segments A-F), which are generally located along the southern property boundary of the base (Figure 1). In 2005, six mulch biowall segments (identified as biowalls A through F), totaling approximately 5300 linear feet (1615 m), were installed to a depth of 35 feet (10.7 m) below ground surface (bgs) to treat CVOCs in groundwater. The thickness of the biowalls is approximately two feet (0.6 m) in the direction of groundwater flow. The biowalls were constructed of 42% mulch and 11% cotton burrs as the reactive media, and 32% sand and 15% rock as the permeable matrix (Parsons 2006). Whiting et al. (2014) estimated the residence time of groundwater within the biowall to range from 2 to 50 days; this wide range is based on varying estimates of groundwater flow velocities in the portion of the shallow aquifer where the biowall was installed (described below), and it has been suggested that the residence time of CVOCs may be longer within biowalls due to sorption within the biowall matrix (AFCEE 2008).

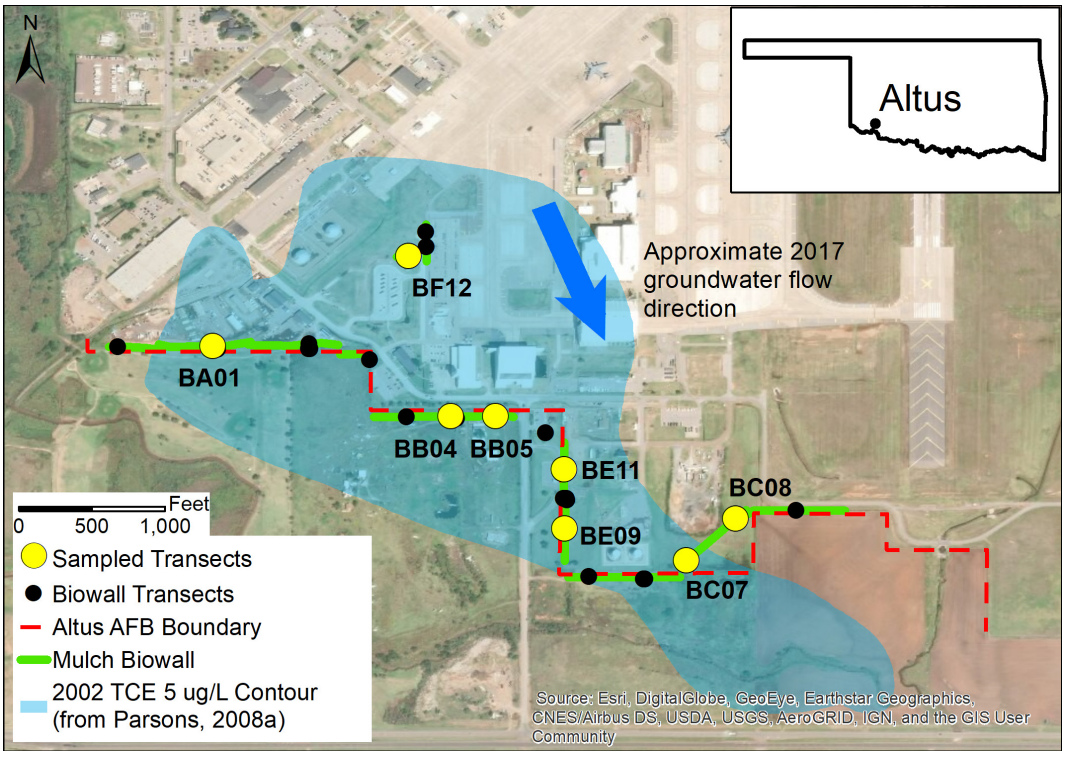

Figure 1. Site layout showing the SS-17 biowall segments at Altus Air Force Base and the estimated TCE plume in 2002 prior to biowall installation.

A 180-foot (55 m) portion of biowall B (centered around monitoring well transect BB04) was spiked with magnetite during biowall construction in 2005 to increase the iron content of the sand from 1600 mg per kilogram (mg/kg) to 118,000 mg/kg to promote biogeochemical CVOC degradation (Parsons 2006). In 2008, approximately 685,000 pounds of soybean oil were injected into each of the six SS-17 biowall segments (A through F) based on a recommendation to enhance biowall effectiveness even though data did not indicate decreasing effectiveness of the biowall for treatment of CVOCs (Parsons 2008a, 2008b).

Multiple studies have evaluated the SS-17 biowall transects at the laboratory and field scale, primarily to investigate the biogeochemical transformation processes and rates acting within the mulch biowall (Shen and Wilson 2007; Lebrón et al. 2010; Evans et al. 2014; Whiting et al. 2014). These studies of the SS-17 biowalls have documented the efficacy of CVOC removal within the biowall, as well as the presence of biogeochemical transformation and abiotic patterns of contaminant degradation. However, these studies did not evaluate the long-term performance of the mulch biowall to treat parent and daughter CVOCs. The study presented in this manuscript focuses on the long-term performance of the SS-17 mulch biowall at Altus AFB by evaluating historical data and current conditions approximately 10 years after biowall installation.

Site Geology/Hydrogeology

As described extensively in other site documents (Waterstone 2007; Parsons 2008a), Altus AFB is underlain primarily by the Permian Hennessey Group, which consists of reddish-brown shale with interbedded siltstone and sandstone (Parsons 2008a). The site geology near the biowall consists of surface alluvium and residual soil cover from surface to approximately 10 to 15 feet (3.0 to 4.6 m) bgs. Beneath the surface alluvium, weathered red shale extends from approximately 15 to 40 feet (6.1 to 12.2 m) bgs, followed by a more competent, consolidated shale below 40 feet (12.2 m) bgs. The shale contains natural gypsum and anhydrite, contributing to naturally elevated sulfate concentrations in groundwater around 1500 to 2000 mg/L. Zones of fracturing and weak/crumbly bedding in the Hennessey Shale below approximately 10 to 15 feet (3.0 to 4.6 m) bgs appear to be preferential pathways for groundwater and CVOC migration, with higher permeability fractures surrounded by lower permeability shale. Thus, fracture flow, rather than flow through a continuous porous medium, contributes to the flow regime in the deeper portions of the shallow aquifer, and there is some potential for impacted groundwater to flow underneath the biowalls or around the ends of the biowalls. However, based on historical site investigation activities and groundwater flow patterns measured during routine monitoring events, the biowalls appear to intercept the impacted groundwater through their maximum installed depths.

Groundwater near the SS-17 biowalls generally flows to the southeast. Hydraulic conductivities of the shallow aquifer have been reported in a variety of studies and range from approximately 2 to 30 feet/d (0.6 to 9 m/d; $7x10^{-4}$ to $1x10^{-2}$ cm/s); Parsons (2008a) reported a geometric mean conductivity value of 4 feet/d (1.2 m/d; $1x10^{-3}$ cm/s) based on slug tests performed in the upgradient and downgradient biowall monitoring wells, with groundwater seepage velocities ranging from approximately 2 to 400 feet per year (0.002–0.3 m/d).

Based on groundwater flow data and patterns in July 2005 and October 2006, Parsons (2008b) concluded that the biowall system had not impacted the groundwater flow system on a site-wide basis. Our review of groundwater elevation data collected in 2017 and 2018 also does not indicate significant changes in the overall groundwater flow regime at the site as a result of the biowalls, nor do they indicate observable permeability reductions in the vicinity of the biowalls (e.g., no groundwater mounding has been observed upgradient of the biowalls). In addition, we are not aware of any studies that have evaluated the biowall permeability over time, but field inspection of the biowall material during sampling in 2015 indicated loose mulch material consistent with a highly permeable zone that would not impede groundwater flow.

Nature and Extent of CVOC Impacts

This study focuses on the CVOC plumes within groundwater originating from spill sites SS-17, SS-18, and SS-23 intersected by the SS-17 mulch biowall. This combined plume contains CVOCs from multiple assumed sources. The primary CVOC is trichloroethene (TCE). The extent of the groundwater plume in 2002, prior to biowall installation, is estimated in Figure 1 as the extent of the USEPA maximum contaminant level (MCL) for TCE concentrations (0.005 mg/L TCE); the extent of this plume was estimated from isoconcentration contours in the upper and lower zones of the shallow groundwater unit, as shown in Parsons (2008a).

Methods

Historical Sampling Data

Historical analytical data were provided by the Air Force from the Environmental Resources Program Info Management System (ERPIMS) database for the CVOCs (i.e., tetrachloroethene [PCE], TCE, cis-1,2-dichloroethene [cis-DCE], and vinyl chloride) at the groundwater monitoring wells associated with the SS-17 biowalls.

Field Sampling and Analytical Program

In order to evaluate the long-term sustainability of the mulch biowalls, an extensive field sampling program was undertaken in May and June 2015.

Groundwater samples were collected from existing monitoring wells installed at eight transects based on historical CVOC concentrations (see Figure 1): BA-01, BB-04, BB-05, BC-07, BC-08, BE-09, BE-11, and BF-12. Groundwater monitoring wells were installed within the biowall and approximately 20 feet (6.1 m) upgradient and downgradient of the biowall. These wells were installed to depths of approximately 35 feet bgs (10.7 m), with the screened interval extending from approximately 5 feet bgs (1.5 m) to the total depth at approximately 35 feet bgs (10.7 m). The screened intervals are thus consistent with the depth of the biowalls and are expected to represent flow conditions flowing through the biowall.

Groundwater samples were collected using low-flow sampling techniques. The samples were shipped overnight to National Environmental Laboratory Accreditation Program (NELAP)-accredited commercial laboratories using standard USEPA methodologies for analysis of: CVOCs by gas chromatography/mass spectrometry (USEPA SW-846 Method 8260B); chloride, nitrate, and sulfate by ion chromatography (USEPA SW-846 Method 9056); dissolved calcium, iron, magnesium, potassium, and sodium by inductively coupled plasma-atomic emission spectrometry (USEPA SW-846 Method 6010B); alkalinity by the titration method (USEPA Method 2320B) (field-filtered with a 0.45 µm filter); biological oxygen demand (BOD) by USEPA Method 5210B; chemical oxygen demand (COD) by semi-automated chlorimetry (USEPA Method 410.4); total organic carbon (TOC) by carbonaceous analyzer (USEPA SW-846 Method 9060A); and dissolved gases methane, ethane, and ethene by gas chromatography (USEPA Method RSK175). Microbial biological analyses were performed on groundwater samples by Microbial Insights. Specifically, results were obtained using their proprietary QuantArray-Chlor approach, which utilizes quantitative polymerase chain reaction (qPCR) techniques to quantify the abundance of genes encoding specific enzymes for degradation.

The following groundwater field parameters were measured using a hand-held flow-through cell and meter (Horiba model U-52, Horiba Instruments Incorporated, Irvine, California): temperature (thermistor method), pH (glass electrode method), specific conductivity (4 AC electrode method), turbidity (light emitting diode [LED] light source and 30° scattering method), dissolved oxygen (DO) (polarographic method), and oxidation–reduction potential (ORP) (platinum electrode method; Ag/AgCl reference electrode). Ferrous iron was also measured in the field using a portable Hach colorimeter (Model 850, Hach Company, Loveland, Colorado) by Hach Method 8146 (1,10 Phenanthroline Method).

During the 2015 field investigation, 21 soil borings were advanced to approximately 35 feet (10.7 m) bgs with a sonic drill at locations adjacent to each of the upgradient, biowall, and downgradient groundwater monitoring wells at seven of the eight transects sampled for groundwater; soil borings were not advanced at transect BE-09 due to conflicts with existing utilities. Potentially bioavailable organic carbon (PBOC) from each of the 21 soil borings was analyzed at the laboratory of Dr. Mark Widdowson at the Virginia Polytechnic Institute and State University (Virginia Tech) by the PBOC methodology documented in Rectanus et al. (2007), Chapelle et al. (2012), Thomas et al. (2013), and Lebrón et al. (2013).

Mulch samples were collected from three different depths from within the saturated zone of the biowalls and shipped to the Soil and Forage Analysis Laboratory at the University of Wisconsin, Madison Extension for forage analysis and analyzed for the percent of dry matter, percent moisture, total nitrogen, total phosphorus, total potassium, sulfur, NH_4-N, pH, total carbon, acid detergent fiber (ADF), neutral detergent fiber (NDF), lignin, and silica ash. The cellulose content was calculated as the difference between ADF and lignin. The hemicellulose content was calculated as the difference between NDF and ADF.

An in situ bioreactor was installed upgradient of transect BF-12 in 2007 and organic vegetable oil was injected into the bioreactor in 2008. Evidence of the vegetable oil was noted in the field, and data from this transect were excluded from further analyses in this paper to avoid confounding impacts of the mulch biowall with those from the bioreactor. This bioreactor with vegetable oil injections is separate from the 2008 vegetable oil injections that were injected directly into the six biowall segments.

Data Analyses

Differences in upgradient, biowall, and downgradient concentrations collected in 2015 were compared with the Wilcoxon signed-rank test, which is a nonparametric version of the paired *t*-test, where the samples were paired by transect.

Concentration trends were calculated with the Mann-Kendall nonparametric trend test, which is frequently used for analyzing long-term trends in groundwater monitoring data (Connor et al. 2014).

To provide a single metric for expressing the extent of CVOC degradation at each location, the chlorine number was calculated (AFCEE 2007). The equation for the chlorine number is as follows, where the concentration of each analyte is a molar concentration:

$$\text{Chlorine Number} = \frac{4[\text{PCE}]+3[\text{TCE}]+2[\text{DCE}]+[\text{VC}]}{[\text{PCE}]+[\text{TCE}]+[\text{DCE}]+[\text{VC}]+[\text{ethene}]+[\text{ethane}]}.$$

When calculating the chlorine number, nondetect measurements were assumed to be zero, and it was assumed that ethane and ethene are stable under reducing conditions (AFCEE 2007).

To illustrate temporal trends, a site-wide chlorine number was calculated for each year. After computation of the chlorine number for each sample event, the mean annual chlorine number was calculated for each groundwater monitoring well for each year. The median chlorine number for each of the seven upgradient, biowall, and downgradient transects was then calculated annually.

First-order decay rates at individual locations (k_{point}) were calculated for each location as the negative slope of the best-fit line on the natural log of concentration vs. time plot (Newell et al. 2002), which were calculated based on historical monitoring data and the data collected from the May-June 2015 field program. These k_{point} decay rates can be translated to half-lives by dividing 0.693 by the k_{point} rate constant.

Results and Discussion

The ongoing efficacy of the mulch biowalls approximately 10 years after biowall installation is demonstrated by five primary lines of evidence from data collected in 2015:

- CVOC concentration patterns and decay rates;
- Biowall geochemical environment;

- Biowall mulch composition;
- Microbial environment; and
- Downgradient effects.

CVOC Concentration Patterns and Decay Rates

Boxplots of TCE, cis-DCE, and VC concentrations measured in 2015 at the upgradient, biowall, and downgradient locations for each of the seven sampled transects are shown in Figure 2, with the actual concentrations depicted as dots. TCE was detected in only two of seven biowall monitoring wells, and detected concentrations were below the USEPA MCL (Table SI-1). TCE concentrations were statistically different between the upgradient and biowall locations (Wilcoxon p value = 0.02) and the biowall and downgradient locations (Wilcoxon p value = 0.03). These results show that the mulch biowalls remain effective at degrading TCE approximately 10 years after biowall installation to below regulatory limits.

The presence of cis-DCE and VC at the upgradient locations demonstrates that there is some natural anaerobic biodegradation of TCE to daughter products within the aquifer matrix. Spatial patterns of cis-DCE concentrations show a similar pattern to TCE, indicating that the biowall is capable of further breakdown of cis-DCE to vinyl chloride. cis-DCE concentrations were statistically different between the upgradient and biowall locations (Wilcoxon p value = 0.03) and the biowall and downgradient locations (Wilcoxon p value = 0.02). The vinyl chloride data demonstrate comparable concentrations between upgradient locations and the biowall (Wilcoxon p value = 0.69), with slightly elevated but not statistically significant vinyl chloride concentrations downgradient compared to upgradient (Wilcoxon p value = 0.09) and biowall concentrations (Wilcoxon p value = 0.18), suggesting that vinyl chloride is being produced within the biowall faster than it is being degraded (Figure 2c).

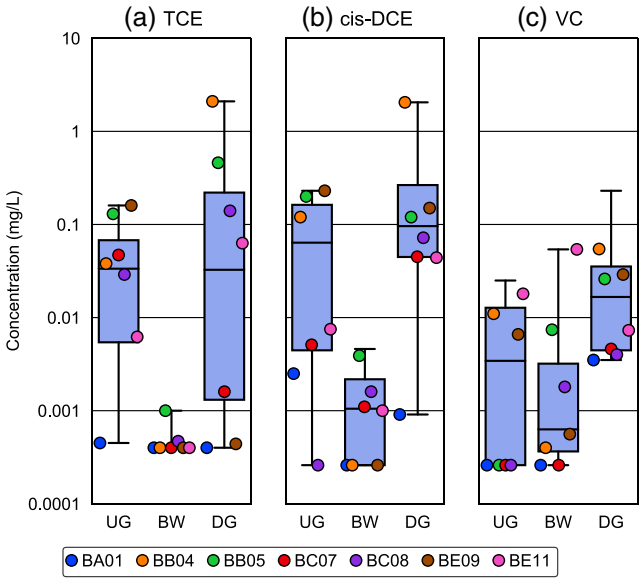

Figure 2. Boxplots of 2015 concentrations of groundwater collected from upgradient (UG), biowall (BW), and downgradient (DG) groundwater monitoring wells at seven transects. The dots show the individual sampling results for each transect. The box shows the 25-75th percentile range of the data, the whiskers represent the maximum and minimum, and the horizontal line within the box is the median.

Downgradient concentrations of TCE and cis-DCE remain consistent with upgradient concentrations despite their removal within the biowall (Figure 2a and 2b; Wilcoxon p values of 0.31 and 0.73, respectively). These results are consistent with the results that Whiting et al. (2014) reported for samples collected in 2007–2008 at transects BB04 and BB05. The dissolved groundwater plume historically extended downgradient of the biowalls prior to biowall installation, suggesting the potential for CVOC mass to have diffused from the higher permeability fractures into low permeability strata (i.e., shale) downgradient of the biowall. Since TCE and cis-DCE concentrations within the biowall are substantially lower than the upgradient locations, flushing of this cleaner water would be expected to reduce downgradient concentrations over time. Thus, the fact that TCE and cis-DCE concentrations remain elevated implies that matrix diffusion out of a lower-permeability matrix into the higher-permeability fracture zones may be a partial explanation of these elevated CVOC concentrations downgradient. The potential for impacted groundwater bypassing the biowall underneath may also contribute but is unlikely to fully explain the patterns observed here due to the fracture patterns observed in the field.

To evaluate the efficacy of the biowall over time, a plot of median annual chlorine number (solid lines) in the upgradient, biowall, and downgradient locations is shown on Figure 3, and a plot of median annual concentrations of each of the primary CVOCs are shown on Figure 4. Data collected in 2004 (prior to biowall installation) at upgradient and downgradient locations indicate that the overall CVOC groundwater plume was dominated by a CVOC composition consistent with a source composition composed almost entirely of TCE (i.e., a chlorine number of 3), consistent with relative concentrations of the individual CVOCs (Figure 4). The upgradient data indicate a decreasing trend (Mann-Kendall S = −32, confidence factor > 0.99) in the chlorine number, suggesting that natural attenuation processes are slowly removing chlorine from the source material (as characterized by a chlorine number of 3), with partial but incomplete dechlorination to daughter products, consistent with a reduction in chlorine number. This is consistent with concentrations of TCE, cis-1,2-DCE, and vinyl chloride at the upgradient locations (Figure 4).

In contrast, the biowall data show a rapid decrease in chlorine number from greater than 2 to approximately 1 between 2005 and 2011 as the TCE is converted to cis-1,2-DCE, vinyl chloride, and ethene. Compared to the upgradient locations, the biowall has resulted in more complete degradation of TCE to lower-chlorine daughter products and stable end products, thus demonstrating the influence of active treatment via the mulch biowalls, even if degradation to nonchlorinated end products is incomplete. After approximately 2011, the overall CVOC composition of groundwater within the biowall is consistent with vinyl chloride (average chlorine number = 1) and has not materially increased since 2011. Since 2008, the chlorine number trend within

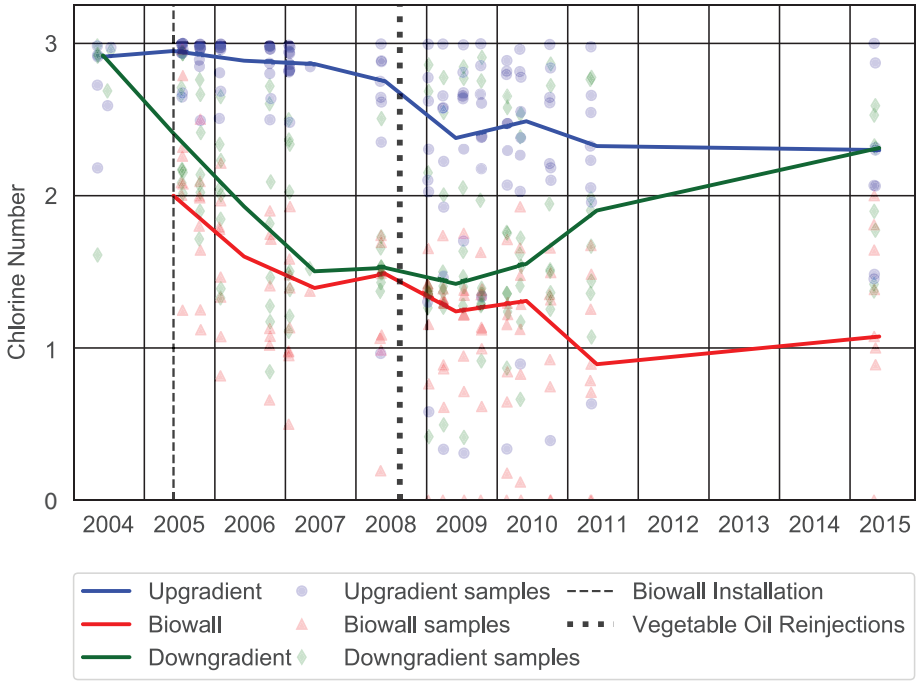

Figure 3. Historical trends in the chlorine number in upgradient, biowall, and downgradient monitoring wells at seven sampled transects. Solid lines represent the median annual chlorine number. A chlorine number of 3 represents a groundwater composition composed of 100% TCE.

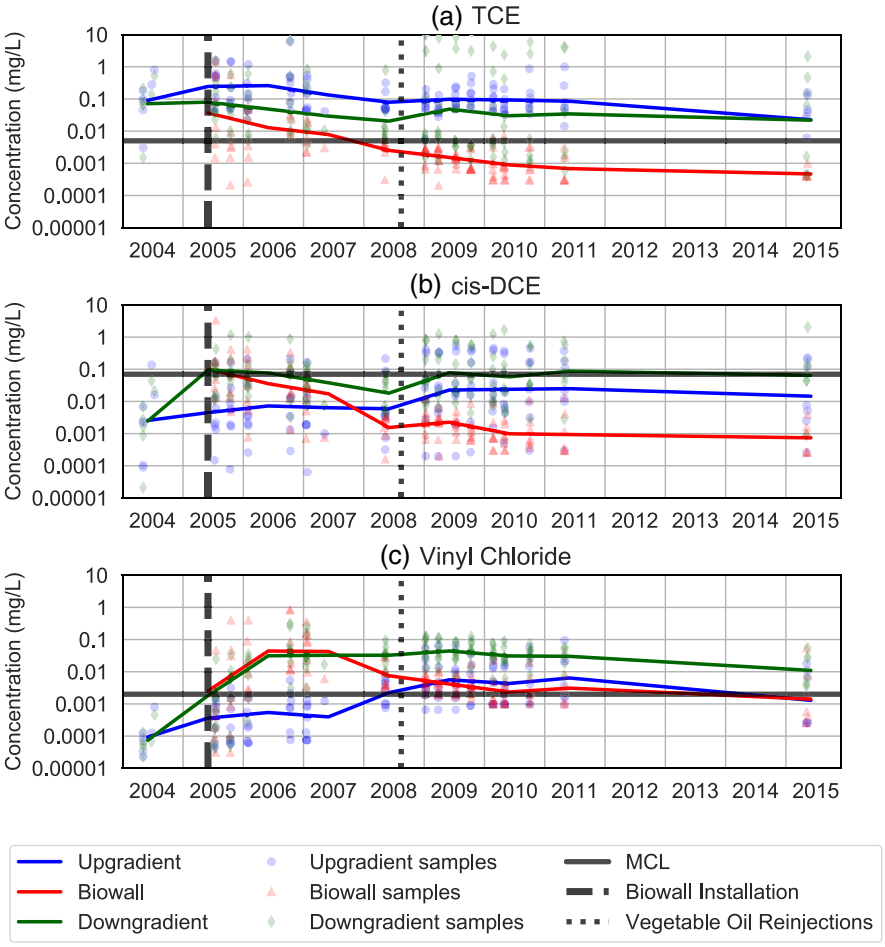

Figure 4. Historical trends in TCE (top), cis-1,2-DCE (middle), and vinyl chloride (bottom) in upgradient, biowall, and downgradient monitoring wells at seven sampled transects. Solid lines represent the median annual concentration.

the biowall has remained stable (Mann-Kendall S = −2, confidence factor = 0.625) and does not demonstrate rebound, thus demonstrating the long-term sustainability of the mulch as a carbon source over the performance period evaluated.

In contrast, the chlorine number at the downgradient locations indicated an initial drop in chlorine number to between 1 and 2, consistent with the biowall locations, but since approximately 2009, the chlorine number has increased to approximately 2.3 (Mann-Kendall increasing trend since 2008; S = 6, confidence factor = 0.958) and was consistent with the upgradient groundwater CVOC composition by 2015. These results suggest an initial flushing of the higher permeability zones with cleaner water emanating from the biowalls after treatment. We believe that this initial decreasing trend, followed by a slow but gradual increase in the chlorine number, suggests matrix diffusion of CVOCs from lower permeability zones back into the higher permeability zones.

It is important to note that the trends of Figure 3 (as well as individual trends of TCE, cis-DCE, and VC shown on Figure 4) do not exhibit any appreciable impact from the 2008 vegetable oil injections into the biowall. While a slight decrease in chlorine number was noted within and downgradient of the biowall in 2008, this decrease was also noted in the upgradient transects as well, which would not be expected to be impacted by the vegetable oil injections within the biowall, and the time series plots of individual CVOCs do not demonstrate a noticeable impact from the vegetable oil injections into the biowall (Figure 4). As such, it is concluded that the injections had no discernible influence on the analyses presented herein.

First-order point decay rates of TCE provide evidence of baseline CVOC degradation in the aquifer matrix, increased removal within the biowalls, and the influence of matrix diffusion downgradient of the biowalls (Figure 5). Upgradient and biowall locations generally demonstrate positive decay rates, indicating the ongoing degradation of the parent compound and further evidence of sustained treatment within the biowalls. Downgradient locations show wider variability, with rates at three locations indicating increasing TCE concentrations, potentially due to matrix diffusion. In general, the decay rates for the biowall locations are higher than the upgradient and downgradient locations, although not at statistically significant levels. The median half-life of TCE within the biowall is 1.5 years, lower than the median half-lives of TCE at the upgradient (2.7 years) and downgradient (4.0 years) locations, thus demonstrating that TCE degradation is enhanced within the biowalls. Similar patterns exist for cis-DCE and vinyl chloride (data not shown). The tendency for degradation to follow a first-order relationship, as well as the lack of concentration rebound, particularly within the biowall, provides evidence that treatment was sustained over an extended period and not due solely to activity within the initial post-installation period.

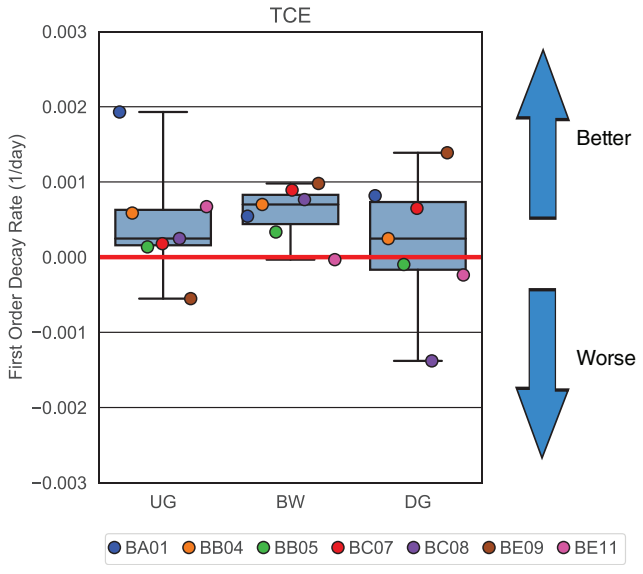

Figure 5. Boxplot of first-order decay rates of TCE (1/d) in upgradient (UG), biowall (BW), and downgradient (DG) groundwater monitoring wells. The dots show the individual sampling results for each transect.

Biowall Geochemical Environment

Additional evidence of ongoing treatment within the biowalls approximately 10 years after installation is provided by geochemical parameters (Figure 6). For example, the redox conditions within the biowalls are much more reducing than the upgradient and downgradient locations, demonstrating an enhanced environment geochemically favorable for reductive dechlorination. Consistent with the altered geochemistry, methane concentrations are elevated and sulfate concentrations are lowered within the biowalls, further evidence of sustained highly reducing conditions (i.e., sulfate-reducing and methanogenesis reactions) within the biowalls.

TOC concentrations within the biowalls were substantially higher than concentrations outside the biowalls at six of the seven transects (Figure 6), which indicates that the biowalls continue to produce elevated levels of organic carbon. Furthermore, TOC concentrations in these six transects were more than 2 to 17 times greater than the 20 mg/L threshold that has been reported as indicative of sustained treatment (Suthersan et al. 2013). Additionally, the TOC in the biowall (median concentration of 44 mg/L) remains elevated relative to upgradient and downgradient locations, indicating that the biowall continues to serve as a carbon source for microbiological activity. Furthermore, a comparison of TOC results within the biowall to the average TOC collected from monitoring wells between July 2005 and July 2006 indicates that TOC concentrations measured in 2015 are similar or greater than the average concentrations measured within approximately 1 year of biowall installation, with two of the three transects showing an increase in TOC from after biowall installation to 2015, and one transect (BB04) showing a small decrease (58 to 50 mg/L) (Table SI-2). This comparison of TOC results over a 10-year window indicates that TOC has not been appreciably depleted since installation and that the biowall remains an ongoing source of organic carbon to groundwater.

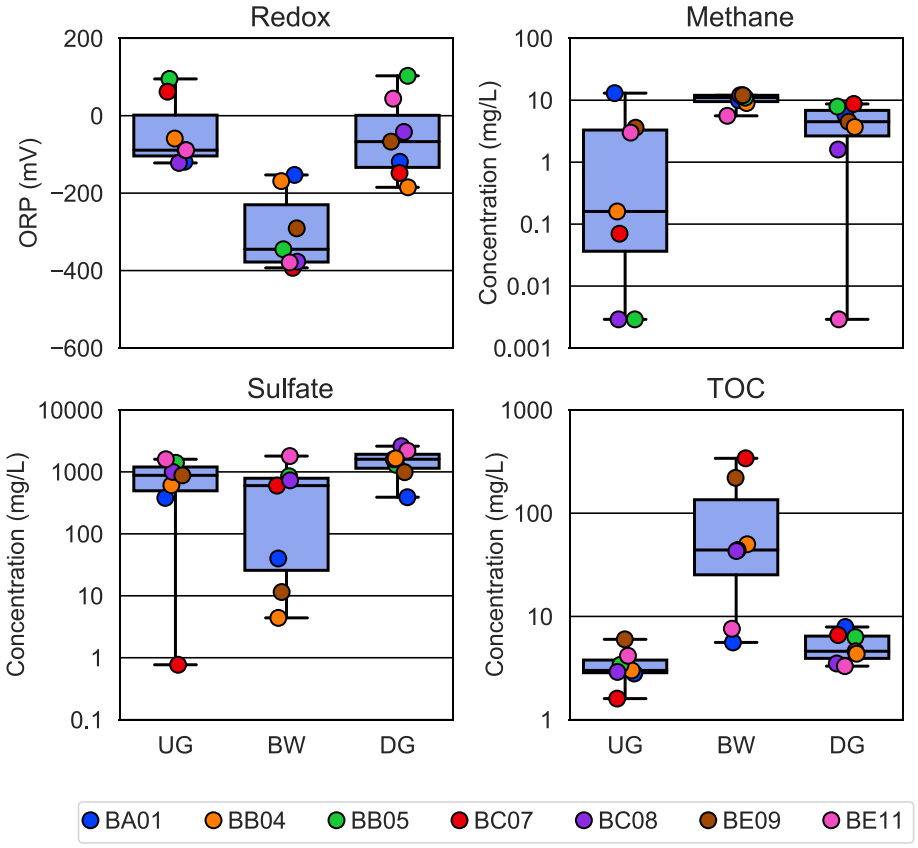

Figure 6. Boxplot of redox conditions (upper left), methane (upper right), sulfate (lower left), and total organic carbon (TOC) (lower right) from 2015 groundwater sampling results in upgradient (UG), biowall (BW), and downgradient (DG) groundwater monitoring wells. The dots show the individual sampling results for each transect.

Biowall Mulch Composition

The TOC results are supported by forage analysis results (Table SI-3) of mulch samples collected from within the biowall, which also indicate an ongoing source of organic carbon 10 years after biowall installation. Cellulose fractions within the biowalls remain high, ranging between 79.5 and 92.8% of the dry matter. Lignin fractions are between 2.02 and 5.83% of the dry matter. High cellulose content and low lignin content have been associated with favorable mulch characteristics for sustainable release of bioavailable organic carbon from the mulch (Ahmad et al. 2007). While the introduction of a vegetable oil substrate in 2008 was intended to supplement the carbon source within the biowall, no cellulose was associated with the vegetable oil injections. Instead, the finding that cellulose fractions remain elevated 10 years later suggests the inherent long-term viability of the mulch matrix material itself as a long-lived carbon source capable of ongoing chemical treatment. In addition, PBOC measured within the biowall ranged from 310 to 5213 mg/kg, which is generally an order of magnitude higher than what was observed at upgradient and downgradient locations, reflecting the bioavailability of carbon within the mulch biowalls.

Microbial Environment

Molecular biological tools were utilized to evaluate the microbial community present and capable of dechlorination. Figure 7 shows concentrations of microbial analyses in upgradient, biowall, and downgradient groundwater monitoring wells for each transect (see also Table SI-4). This figure illustrates that both the abundance and diversity of microbes are typically greater within the biowall relative to both the upgradient and downgradient locations, and these analyses confirm that microbial communities and the genes encoding functional enzymes capable of complete dechlorination are present. Furthermore, within the biowalls, concentrations of *Dehalococcoides sp.* (DHC) exceed the threshold level of 10^4 cells/mL for "useful" biodegradation rates (Lu et al. 2006) in four of seven transects. Despite redox conditions indicative of an anaerobic environment, the biowalls also contain elevated levels of genes encoding oxygenase enzymes capable of cometabolic degradation, indicating the potential for microhabitats within the biowalls.

The higher abundance of sulfate reducing bacteria and methanogens within the biowall wells corroborates the elevated methane and lowered sulfate results within the biowalls relative to the upgradient and downgradient locations (Figure 6).

DHC concentrations in groundwater in 2015 were compared to a limited dataset of DHC concentrations collected in August 2005 and January 2006 after biowall installation at three transects (BB-04, BE-09, and BC-07) (Table SI-5). In each case, the abundance of DHC was consistent with or greater in 2015 than maximum reported concentrations

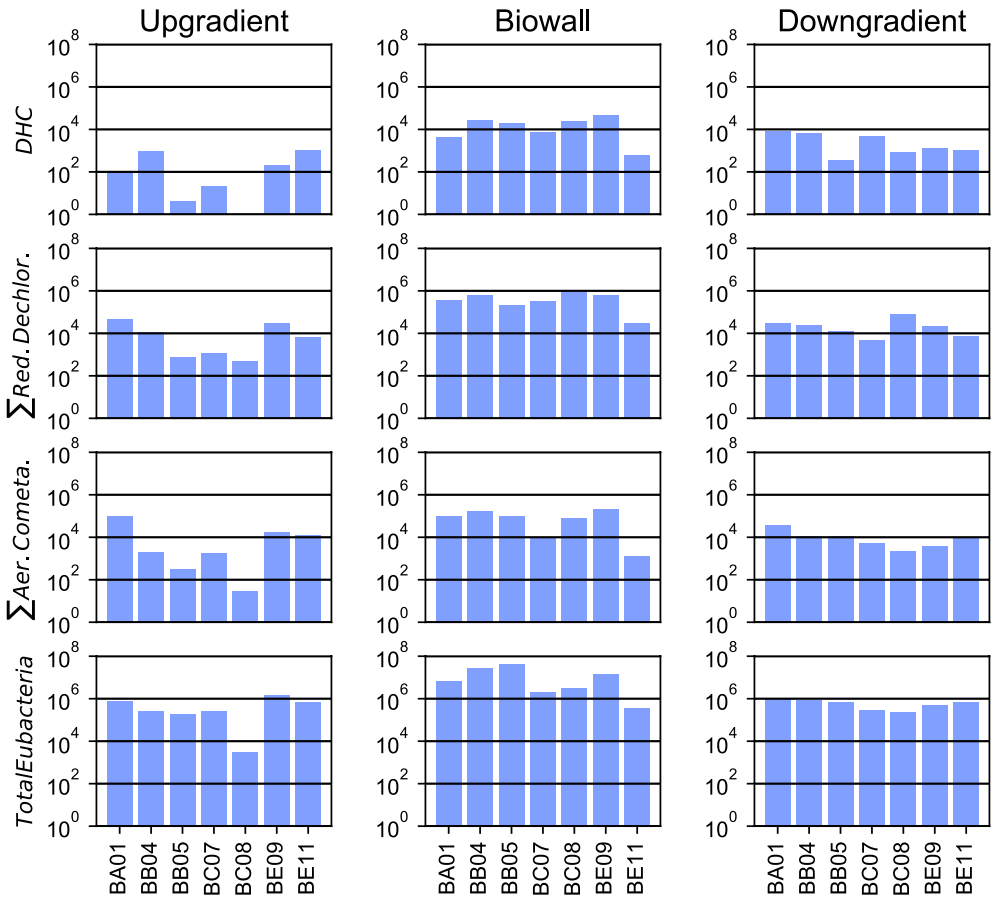

Figure 7. Concentrations of microbial analyses in upgradient, biowall, and downgradient groundwater monitoring wells for each transect. Concentrations are in cell/mL. Red. Dechlor. shows the sum in concentration of the microorganisms responsible for reductive dechlorination except DHC. Aer. Cometa. shows the sum in concentration of the microorganisms responsible for aerobic cometabolism. Nondetect organisms were not added to the sum.

in 2005 and 2006, demonstrating that DHC continues to remain active within the biowalls.

Downgradient Effects

These lines of evidence also suggest that the mulch biowalls are affecting the downgradient groundwater conditions compared to upgradient concentrations. For example, methane concentrations at the downgradient locations are greater than upgradient locations at five of seven transects (Figure 6). Likewise, TOC is greater at downgradient locations compared to upgradient locations at five of seven transects (Figure 6).

The typically greater abundance and diversity of downgradient microbial communities compared to the upgradient locations provides further evidence that the biowall is influencing the downgradient microbial community. For example, methanogens are greater in downgradient wells at six transects, and sulfate reducing bacteria populations are greater in five transects. The abundance of DHC, tceA reductase, and vinyl chloride reductase are each higher in downgradient wells in at least six of the seven sampled transects. These elevated microbial populations suggest that the stimulation and/or migration of microbial communities capable of biological destruction of chlorinated solvents is taking place downgradient as a result of the biowalls.

Correlation Analyses

Figure 8 shows relationships between selected groundwater parameters collected within the biowalls, PBOC from adjacent soil borings, and first-order point decay rates of TCE within the mulch biowalls at the seven sampled transects. Based on a nonparametric correlation test, first-order point decay rates of TCE show a generally positive relationship with methane (Spearman rho = 0.82), TOC (Spearman rho = 0.71), and DHC (Spearman rho = 0.68), indicating that the presence of organic carbon (TOC) and bacteria (DHC) correlate well with increasing degradation rate of TCE. Furthermore, the amount of TOC and DHC show a positive relationship (Spearman rho = 0.57), with higher DHC concentrations generally found in the presence of greater TOC. Not surprisingly, higher degradation rates of TCE are found in more anaerobic environments, as demonstrated by lower DO concentrations (Spearman rho = −0.75). These correlations each support reductive dechlorination as a prominent process within the biowalls.

PBOC, which is operationally defined as the fraction of natural organic carbon most loosely associated with sediment, and thus readily available for reductive dechlorination, has been proposed as a useful measure for assessing natural attenuation (Thomas et al. 2012, 2013). However, quantifying PBOC can be labor-intensive because it requires collecting a soil core followed by subsampling of relevant

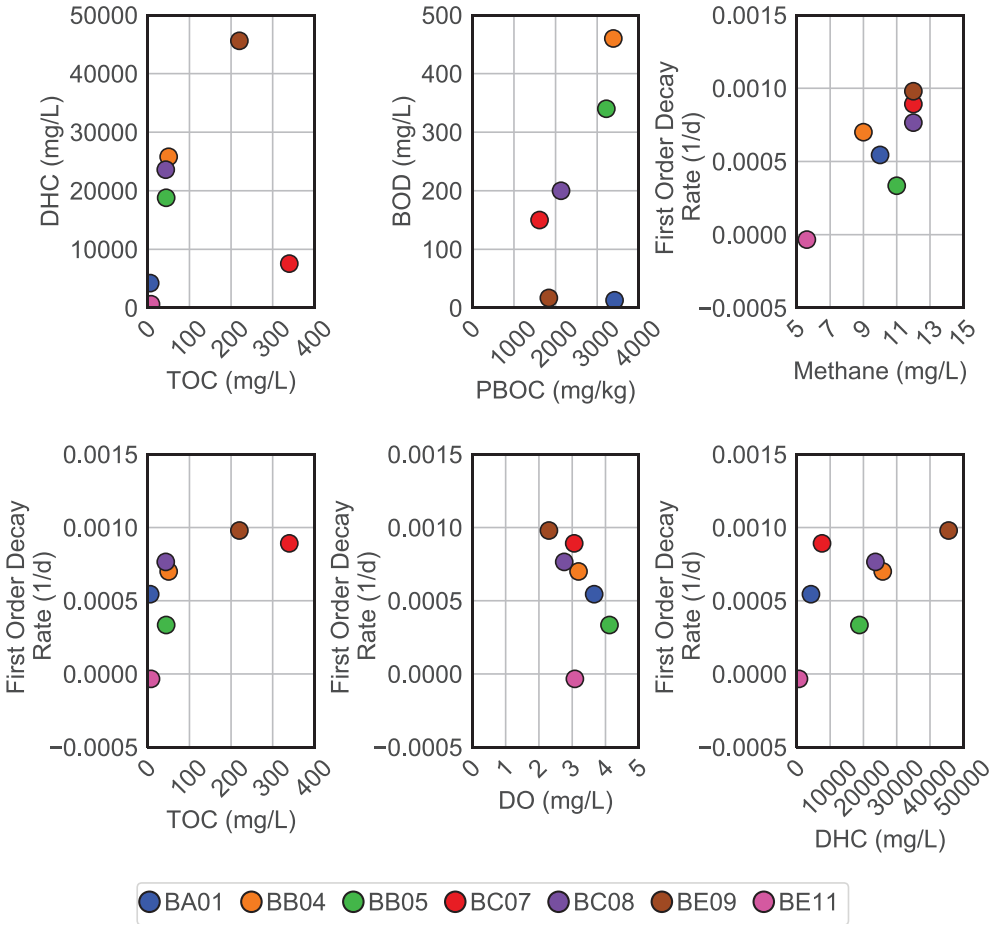

Figure 8. Scatterplots of selected groundwater parameters and first-order point decay rates of TCE within biowall samples at the seven sampled transects.

depth intervals from the core. The amount of PBOC, a soil measurement, shows a promising relationship with BOD, a water measurement commonly employed in the wastewater treatment industry (a similar relationship was also observed with COD; data not shown). While meriting further investigation, this relationship suggests that sampling for BOD (or COD) in groundwater monitoring wells may provide a cost-effective surrogate for PBOC. Because BOD is typically used to quantify organic carbon being degraded aerobically, it is not expected to be a perfect surrogate for organic carbon being degraded via anaerobic processes in the subsurface. However, using BOD (or COD) may be particularly cost-effective for time-series analyses of bioavailable organic carbon, which otherwise would require mobilization of a drill rig for each sampling event.

Summary and Conclusions

Sampling results from the 2015 field sampling program demonstrate that the mulch biowalls continue to function and degrade parent TCE to daughter products. TCE concentrations within each of the biowall samples remained below USEPA MCLs. The geochemical environment remains strongly reducing, and bioavailable organic carbon and microbial populations are present and available in sufficient quantities to continue to treat the groundwater plume as it passes through the biowall. These sampling results, as well as the historical trends of the chlorinated solvents, demonstrate the long-term sustainability of the mulch biowalls at Altus AFB 10 years after installation.

The concentration patterns, reducing geochemical environment, and microbial community suggest that reductive dechlorination is an active mechanism within the biowall and downgradient aquifer matrix. Whereas Whiting et al. 2014 calculated that 98–100% of the VOC removal patterns at BB-04 and BB-05 were due to abiotic, rather than biotic, degradation mechanisms, it appears, based on our findings of microbial abundance and the patterns in daughter product formation, biodegradation is a relevant removal mechanism for TCE within the biowalls. This discrepancy may be due to changing patterns of the fraction of biotic vs. abiotic degradation over time (Whiting et al. [2014] collected samples in 2007-2008) or due to differences in methodology.

Immediately downgradient of the biowalls, sampling results indicate that the biowalls have cast a "shadow" of favorable conditions for CVOC biodegradation. However, only modest CVOC reductions have been observed to date, potentially due to the strength of back-diffusion from low-permeability strata. Since the biowalls potentially may not extend to the full depth of the impacted groundwater-bearing unit, some impacted groundwater may be bypassing the biowall underneath the bottom of the biowalls via the fracture

network. However, we believe that matrix diffusion of TCE and daughter products out of the low-permeability matrix into the higher-permeability zones at least partially explains the elevated downgradient CVOC concentrations relative to the biowall. Historically, the dissolved groundwater plume extended downgradient of the biowall transects prior to biowall installation, thus providing a source of CVOCs into the lower-permeability matrix. Back diffusion from low-permeability materials within shale formations was reported downgradient of an electrolytic barrier installed at Pueblo Chemical Depot to treat energetic compounds (Sale et al. 2010), such that the short-term performance in downgradient wells was clearly influenced by this process. At Altus AFB, the ongoing efficacy of treatment within the biowalls, however, has helped to cutoff downgradient loading to the low-permeability zone for an extended period, and downgradient CVOC concentrations should eventually decrease due to biotic and abiotic degradation, as well as flushing from treated water emanating from the biowalls. Consequently, a monitored natural attenuation approach may be appropriate for managing the downgradient groundwater based on a site-specific risk-based evaluation on potential receptors, if any. While the evidence presented in this paper supports the conclusion that the biowalls continue to treat CVOCs flowing through the biowalls, future research could focus on quantifying the contribution of matrix diffusion versus flow bypass to CVOCs measured in the downgradient monitoring wells.

Given the ongoing performance metrics described here, further augmentation of the biowalls with carbon injections do not appear warranted at this time, and we anticipate that the biowalls will continue to treat CVOCs effectively as they pass through the biowall, thus reducing the chemical loading of downgradient low-permeability zones. Furthermore, available evidence suggests that the biowalls contribute carbon and biogeochemical conditions downgradient that assist in degradation of remaining CVOCs in those low-permeability zones.

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Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally not peer reviewed.

Table S1-1. Groundwater Constituents
Table S1-2. Total Organic Carbon Concentrations
Table S1-3. Biowall Mulch Analyses
Table S1-4. Microbiological Parameters in Groundwater
Table S1-5. Dehalococcoides Concentrations

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