Flux Reduction of TCE with use of an EHC® Liquid PRB at a Former Manufacturing Facility in New Jersey

Summary

The objective of this pilot test was to demonstrate flux reduction of TCE downgradient of an EHC® Liquid permeable reactive barrier (PRB). The flux calculations demonstrated a 73% reduction in 8 months. Advanced techniques such as real-time monitoring, microbial characterization and diagnostics and hi-res imaging were used to characterize and track remedial progress.

Site Background

The site is a former manufacturing facility within an industrial complex in central New Jersey. Previous environmental studies at the site indicated that discharge of process water resulted in chlorinated volatile organic compounds (CVOCs) impacts to soil and groundwater. Primarily, TCE as well as other CVOCs (PCE, 1,1-DCA, and 1,1-DCE) are present in groundwater above the New Jersey Department of Environmental Protection (NJDEP) Class II-A Groundwater Quality Criteria (GWQC). The highest concentrations are found behind the former manufacturing building where TCE concentrations range from 10 to 100 mg/L (ppm). Groundwater is encountered at a depth of between 5 to 10 ft bgs. The site geology consists of 160 ft of unconsolidated sediments of the Kirkwood Formation (clayey to silty mud rock, massive sand and thin pebbly lenses), followed by the Manasquan Formation (clay) which acts as an aquitard. The Lower Member of the Kirkwood Formation is where most of the contaminants reside and is comprised of 10 to 30 ft of coarse sand with components of silt and gravel. Groundwater velocity is estimated at 35 ft/yr in the central portion of the main plume. Figure 1 shows the site map and the TCE plume.

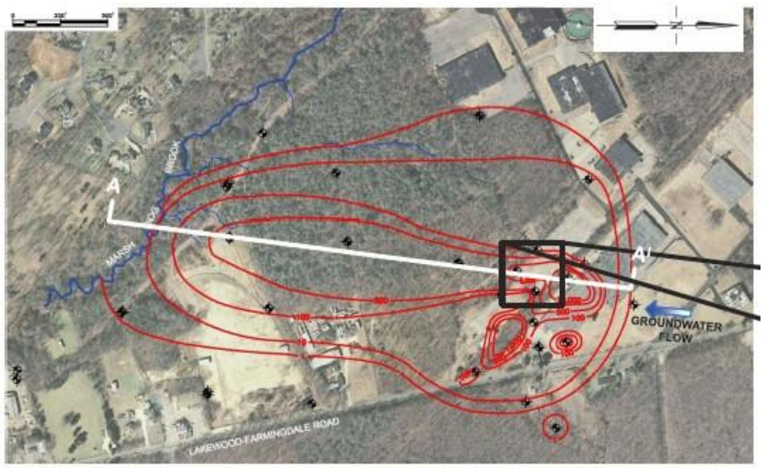


Figure 1: Site Plan Showing TCE Isoconcentrations

EHC® Liquid Overview

EHC Liquid is a water-soluble product, designed for emplacement through wells or hydraulic networks in addition to direct push injections. EHC Liquid supports both biotic and abiotic reductive processes with a balanced composition of carbon and iron to treat chlorinated solvents and related contaminants. In addition, EHC Liquid contains the amino acid cysteine which functions as a redox buffer and facilitates the longevity of the reductive process.

With respect to the iron moiety, it is documented that iron is not only able to reductively dechlorinate by direct action, but that it can also serve as a basis for a “ferrous-ferric redox cycle”. In this important process, secondary iron mineral formation (formation of sulfides, oxides, oxyhydroxides, etc.) can serve as a very long-term ongoing mechanism for abiotic dechlorination.

EHC Liquid is delivered as two components which are mixed together in the field. The first component is 25% ELS™ Microemulsion of carbon substrate (lecithin). The second component is the EHC Liquid ferrous iron powder mix. The 25% emulsion is further diluted (typically ten times) before injection in the field.

Pilot Test Objectives

1. Show reduction in concentration of CVOCs within and downgradient of the EHC Liquid PRB.
2. Show reduction in mass flux/mass discharge of CVOCs through and downgradient of the PRB.
3. Utilize molecular biotechnology tools to study the response of microbial communities.
4. Use isotopic proof that the compounds of concern are actually being destroyed using compound specific isotopic analysis (CSIA) tools.
5. Show in-situ chemical reduction (ISCR) conditions induced by EHC Liquid are established using real-time sensor monitoring followed by groundwater sampling
6. Collect key data to develop a full-scale remediation strategy for CVOCs in groundwater at the site.

Pilot Test Design

An EHC Liquid pilot test was conducted to demonstrate the efficacy of ISCR technology for treating site-specific CVOCs. As shown in Figure 2, the PRB was approximately 50 ft long, 25 ft deep (from 5 ft bgs to 30 ft bgs) and 10 ft wide. EHC Liquid injections were performed via direct push technology. A total of five injection points were advanced. Injections were first conducted at 10 ft bgs followed by deeper intervals to the final depth of 35 ft bgs using a top-down approach. As shown in Figure 2, nine new monitoring well nests (shallow and deep) were installed for monitoring of groundwater parameters during the pilot test. Each well was four inches in inside diameter (ID) and constructed from PVC. The screened intervals were from 5 to 15 ft bgs (shallow) and from 15 to 30 ft bgs (deep). Injection points are shown as black circles and monitoring wells are shown as red circles. One well pair was installed upgradient of the PRB, two well pairs were installed within the PRB, and six well pairs were installed downgradient of the PRB as shown in Figure 2.

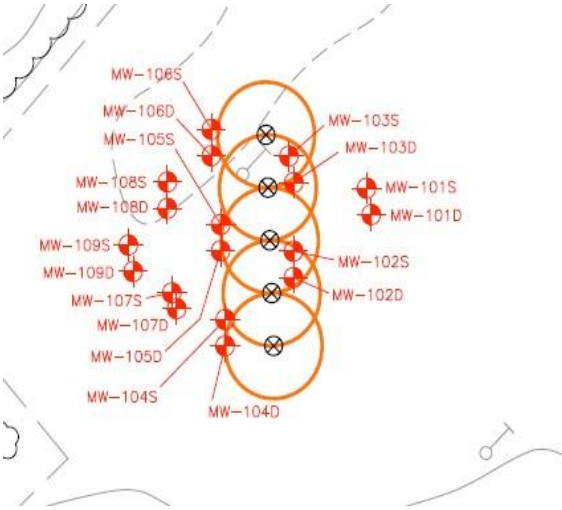


Figure 2: EHC Liquid PRB Injection Points and Monitoring Wells Locations

Figure 3: EHC Liquid Injection Preparation

High Resolution Imaging

In addition to sampling for CVOCs in groundwater through monitoring wells, soil and groundwater impacts from CVOCs in the pilot test area (approximately 50 ft x 100 ft) were delineated in three dimensions using high resolution remediation focused technologies (Figure 4). Membrane Interface Probe (MIP), Hydraulic Profiling Tool (HPT), Electrical Conductivity (EC) and Laser Induced Fluorescence (LIF) tools were deployed to gain a better understanding of the contaminant mass distribution in addition to the soil characteristics of the subsurface and distribution of EHC Liquid. EHC Liquid was dyed with fluorescein dye and its distribution was mapped using ultraviolet optical scanning technology. This work was conducted by Columbia Technologies.

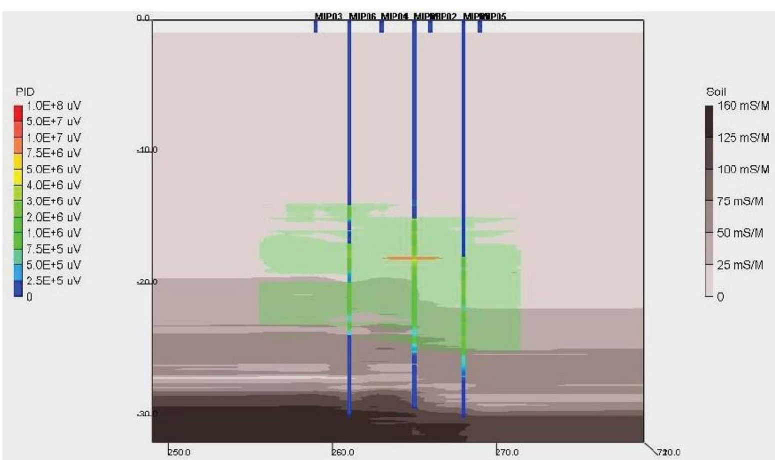


Figure 4: MIP Map Showing Extent of CVOCs Impacts

Environmental Molecular Diagnostics

Samples for advanced molecular diagnostics were are taken via the deployment of a Bio-trap® sampler. A Bio-trap is comprised of inert Nomex-coated carbon beads that serve as seed locations for microbes in the water column in the well can colonize. The beads are put into a small PVC tube with slots and lowered into the well and then withdrawn after an incubation period of about 60 days. The beads and the organisms that are growing on them are analyzed with 1) the molecular biological methods and 2) the CSIA protocols. While CSIA involves isotopes we are simply measuring the naturally occurring isotopes and how they change in response to the impact of the treatment. The shifts in the native isotopic ratios in the contaminants can be interpreted as to how effective the EHC Liquid performed.

Two molecular biotechnology tools (MBTs) were employed to understand the nature of the microbial ecology and the potential for the degradation of CVOCs – DNA Microarrays and Conventional qPCR analysis. No RDase or hydrogenase enzyme genes were detected in baseline samples. Only 16S rRNA “taxonomic” genes were detected for potential dechlorinators but no *Dhc* was detected. *Dhc* 16S rRNA, *Dhc* RDase and *Dhc* hydrogenase genes were detected in post injection samples. 16S rRNA genes of other potential dechlorinators were detected or signal intensity was increased over baseline (Figure 5).

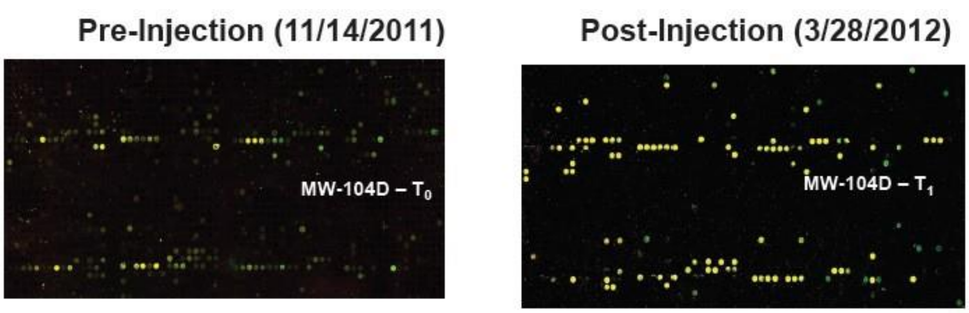


Figure 5

CSIA conducted on MW-104S, MW-104D, and M-1W02D showed that degradation was clearly occurring in M1W0-2D in contrast to other processes such as dilution or volatilization. Isotopic composition of the produced cis-DCE was slightly more positive than the original composition of its parent TCE, which suggests cis-DCE was also degrading. A small amount of vinyl chloride was also observed. The results for MW-104S/D were similar to MW-102D except that degradation was more of a trend at these well locations at this time. Field data collection indicated that a large amount of EHC Liquid was preferentially deposited in the vicinity of MW-102D which explains why the results of MW-102D are more definitive than the trend values of MW-104S and MW-104D. The CSIA and MBT analysis were conducted by Microseeps, Microbial Insights and at University of Tennessee.

Monitoring for Demonstration of Flux Reduction

Researchers at Groundswell Technologies (GT), Inc., have developed and patented a method for automatically processing sensor data to generate contour maps of the distribution of these parameters using geostatistical applications integrated with digital mapping applications (U.S. Patent Number 6,915,211), effectively eliminating the need for manual entry of sensor data into a GIS or alternative contouring packages. Recent upgrades enable users to track remediation system performance through an automated flux model updating routine, where 2D and 3D distributions of relative mobile mass are automatically displayed and cumulative mass discharge estimates through user-selected control planes are reported for each measurement event and range of events (Kram et al., 2011).

Figure 6: Sensors and Telemetry System

For this project, a network of sensors tracking water level, dissolved oxygen, conductivity, and oxidation reduction potential were deployed and monitored to evaluate amendment injection activities, geochemical impacts, and to optimize amendment injection locations during field operations. Sensor data were delivered to the GT platform via telemetry, and then automatically processed for immediate assessment (Figure 6).

Real Time Continuous Monitoring of Standard Physical and Chemical Parameters

In-Situ provided sensors to allow for generation of pre-amendment solute mass flux distributions. This data consisted of surveyed locations and measurements of hydraulic head (or water table elevation) for specific time-stamped monitoring events, solute concentration values for specific time-stamped monitoring events and locations, and site-specific measurements of hydraulic conductivity. Figure 7 shows a plot of real-time measurements of ORP from the sensors deployed in monitoring wells.

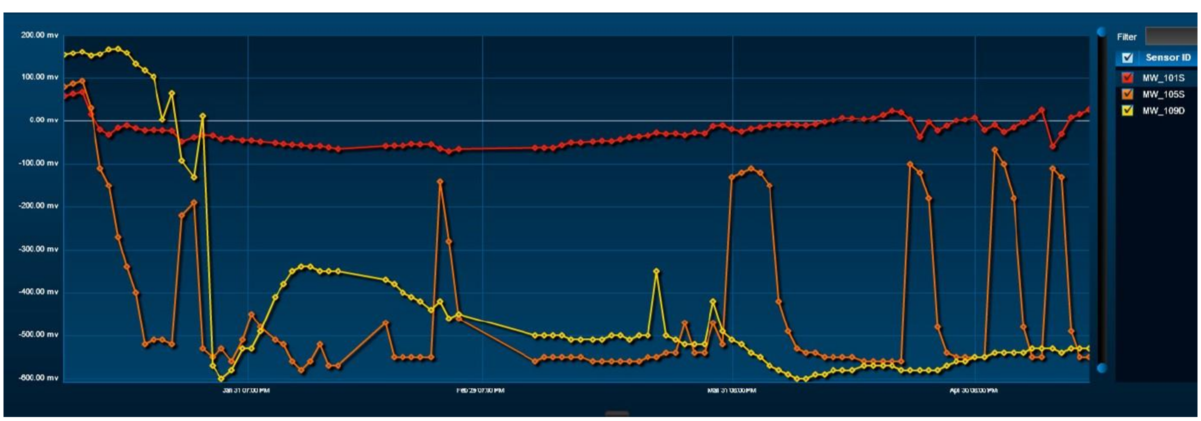
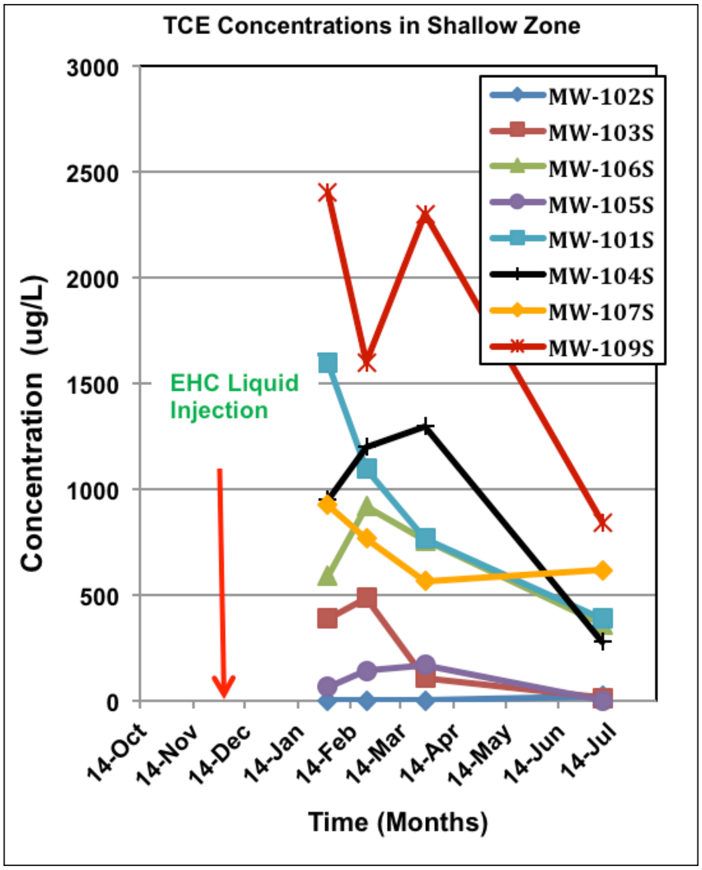
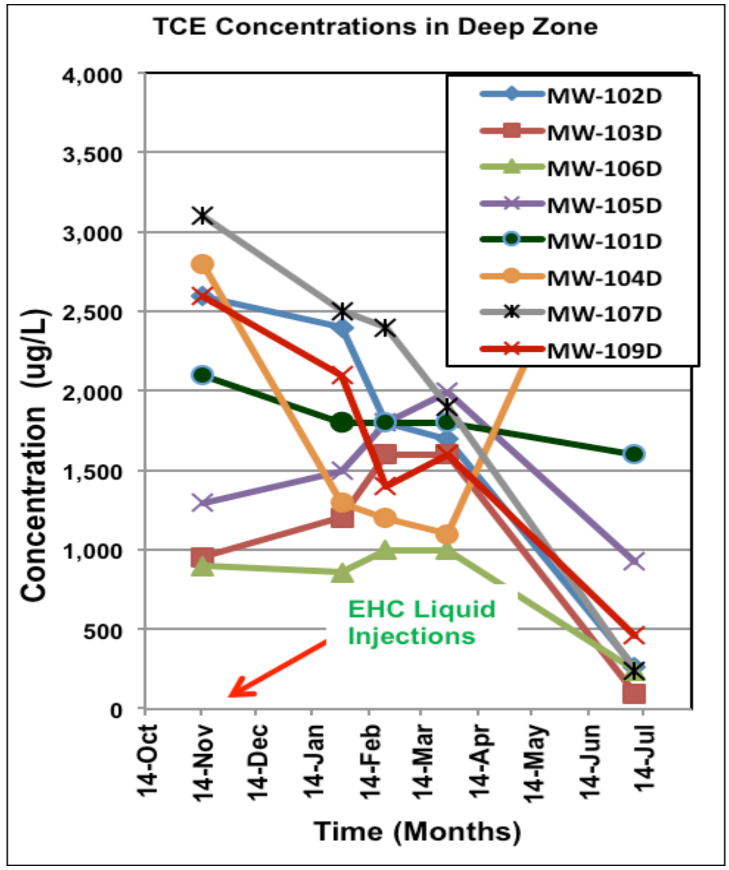


Figure 7: Real-Time measurements of ORP show reduction after injection of EHC Liquid. ORP remains low at downgradient well locations. The upgradient well MW-101S shows a slight recovery, Pre and Post EHC Liquid Injection.

One baseline (pre-injection) and three post-injection rounds of groundwater sampling and analysis was conducted by EXCEL. Representative groundwater samples were collected in accordance with NJDEP-recommended procedures. Groundwater samples were collected using Snap Samplers technology. Figures 8 and 9 below show trends in concentrations of TCE in shallow and deep monitoring wells.

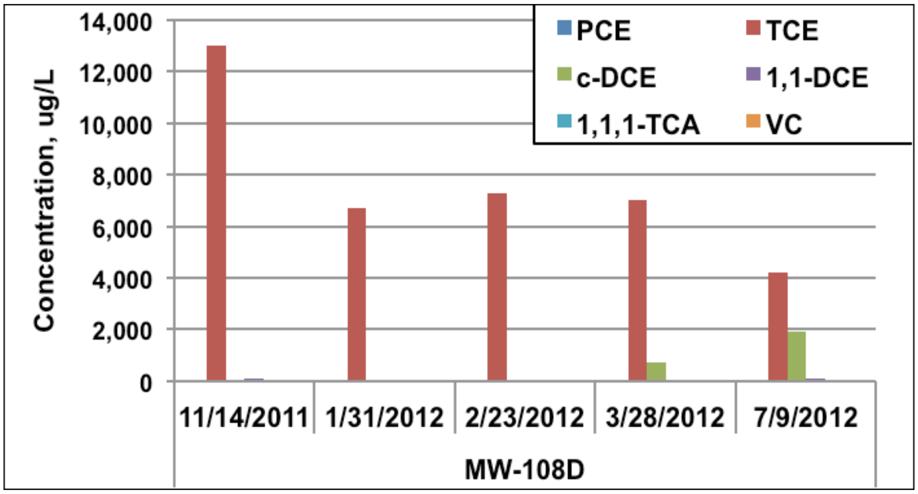


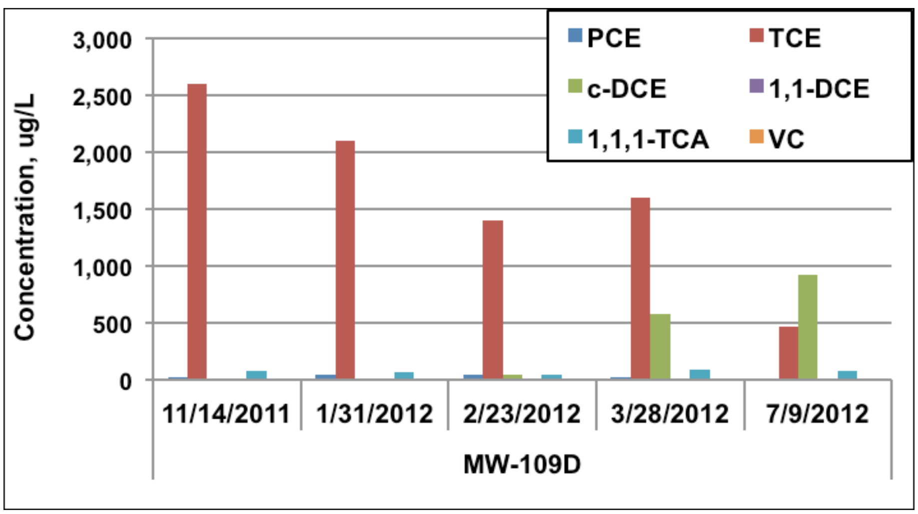


Figures 8 and 9: Trends in TCE concentration in shallow and deep monitoring wells post EHC Liquid Injection.

TCE concentrations decreased in all monitoring wells within the PRB and downgradient of the PRB except well MW-104D which was located at the downgradient edge of the PRB. Figure 10 shows the trends in CVOCs concentration in monitoring well MW-108D (20 ft downgradient from the PRB). Figure 11 shows trends in CVOCs concentrations in monitoring well MW-109D (25 ft downgradient of the PRB). Both wells show significant reduction in concentrations of TCE with some generation of cis-1,2 DCE after six months. Vinyl chloride (VC) generation was none to minimal in these wells. Some wells showed close to 100% conversion of TCE to cis-1,2 DCE.

Concentrations of cis-1,2 DCE ranged from ND to 3,800 ppb. Nine out of sixteen wells had cis-1,2 DCE concentrations above the regulatory limit of 70 ppb after six months. Concentrations of VC ranged from ND to 39 ppb. Seven out of sixteen wells had VC concentrations above the regulatory limit of 1 ppb after six months.

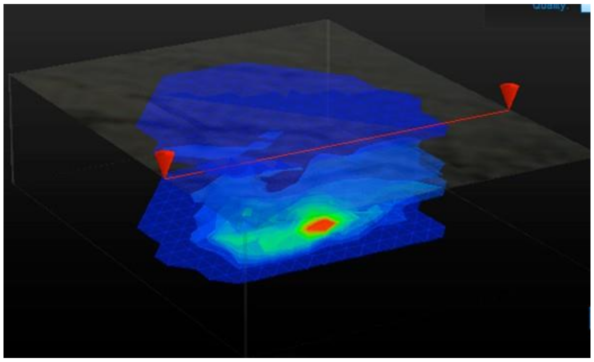


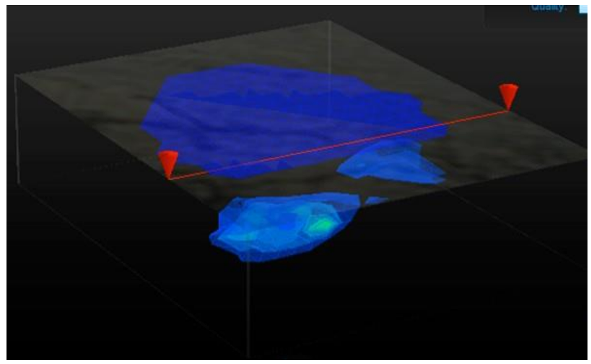


Figures 10 and 11

Post-injection analysis showed the presence of *Dhc* hydogenase genes. Due to the short evaluation time for the pilot test (6-months) and the high concentrations of CVOCs, the increase in concentration of cis-1,2 DCE could be transitory. Microbial analysis and geochemical conditions monitored suggest that with time, cis-1,2 DCE concentrations would decrease.

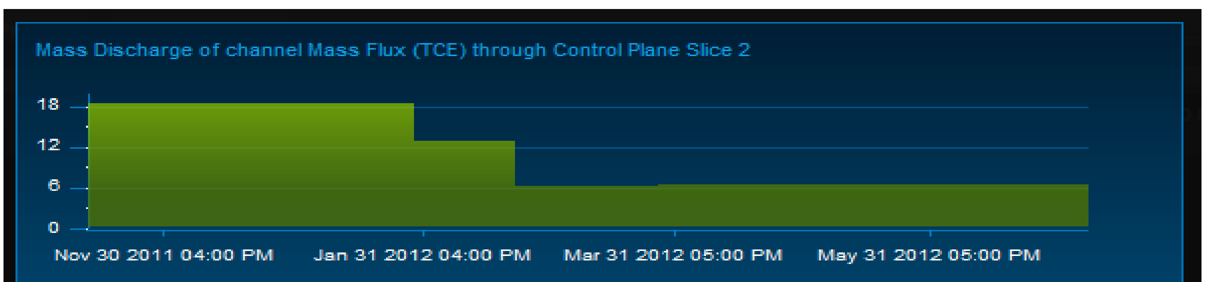
The primary objective of the pilot test was to show flux reduction of TCE downgradient of the EHC Liquid PRB. Figures 12 and 13 show pre and post-injection distribution of TCE in the pilot test area. The figures show a slice taken downgradient where the flux of TCE is calculated.





Figures 12 and 13: Pre and Post EHC Liquid injection distribution of TCE in the pilot test area.

The flux calculations showed that there was a 73% reduction (from 18.56 g/day to 5.08 g/day) in discharge of TCE between Nov 2011 and July 2012 as shown in Figure 14.



Date	g/day
Nov 12 2011 09:00 PM	1.8559e+1
Jan 29 2012 09:00 PM	1.3052e+1
Feb 22 2012 09:00 PM	6.4193
Mar 27 2012 09:00 PM	6.6073
Jul 08 2012 09:00 PM	5.0751

Figure 14: Reduction in TCE flux downgradient of the EHC Liquid PRB

Conclusions

This integrated approach utilizing high resolution technologies resulted in a better understanding of both the contaminant and reagent distribution which can optimize remedial action solutions.

- Real-time geochemical data over time indicate a significant and sustained decrease of ORP following reagent injection.
- The use of advanced diagnostic tools such as CSIA confirmed that degradation mechanisms were implicated in contaminant reduction.
- MBTs confirmed the involvement of contaminant degrading microorganisms in the process on an individual and metagenomic basis.
- The assessment of TCE concentrations over time, using traditional analytical evaluation methods, coupled with the calculation of mass flux and mass discharge confirmed that contaminant concentrations were attenuating.
- The mass flux and mass discharge metrics in particular are very expressive at a "whole systems" level and enhances the value of evaluating discrete changes in individual wells.
- The data will also be useful in evaluating vertical injection intervals and spacing that will result in cost-savings for the client.
- In essence, the use of multiple diagnostic tools to understand the performance of a reagent was fruitful.
- This data will be used to estimate the full-scale treatment scope and time frames, predict plume response to source treatment, and evaluate natural attenuation rates to gain the client's confidence in the efficacy of the remedial approach.
- It should be noted that all the participants in this study donated their time and resources at no or very little cost to collectively demonstrate a new standard in verification of reagent performance.
- Bioaugmentation with *Dhc* culture would have helped with continued degradation of cis-1,2 DCE and VC.
- The pilot test was officially concluded in July 2012. However, monitoring of select wells in the pilot test area will continue to evaluate the efficacy of EHC Liquid.