PROJECT

Application: EHC PRB for Treatment of CT, installed April 2005

Site: Grain Silo Facility, Kansas (Confidential Client)

COCs: CT, CF

Consultant: Malcolm Pirnie, Inc.

SUMMARY

Groundwater emanating from a former grain storage area is impacted with carbon tetrachloride (CT). The CT plume extends approximately 2,500 ft (760 m) from a grain elevator where it discharges into a small creek. The CT source area is elusive and access restrictions due to residential housing further complicates source clean-up. Therefore, as an interim measure to prevent further plume migration, a permeable reactive barrier (PRB) was installed across the plume in April 2005. The PRB was created by injecting EHC® *in situ* chemical reduction (ISCR) reagent in a line of direct push injection points installed along the first available roadway located downgradient from the source area. This project represents the first full-scale application of EHC into a flow-through reactive zone and the purpose of this paper is to assess longterm performance of the PRB over time.

SITE BACKGROUND

Site groundwater is impacted with CT at concentrations of up to 2,700 ppb. The CT plume extends approximately 2,500 ft (760 m) from a grain elevator where it discharges into a small creek (Figure 1). The CT source area is elusive, but impacts are likely the result of using CT as a fumigant in the grain silos on the site. There is a complex geologic history in the study area which resulted in a mix of interbedded sand, gravel, clay and silt. Two primary saturated sand units have been identified, named as the upper and lower saturated sand units. The upper sand unit is approximately 3 to 4 ft (0.9 to 1.2 m) thick. The thickness of the lower sand unit varies considerably across the site and ranges from 0 to 13 ft (0 to 4 m) thick. The groundwater table is encountered at approximately 23 ft (7 m) bgs at the PRB area; CT impacts extend down to a maximum of approximately 45 ft (14 m) bgs. The bedrock rises to an elevation of approximately 10 feet (3 meters) above the present day water table at the presumed source area. The

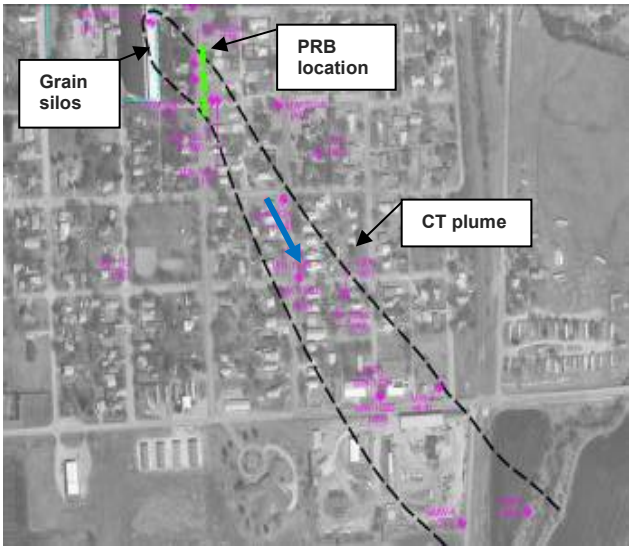

Figure 1. Direction of groundwater plume

CT is believed to have transported along the topography of the bedrock surface to the downgradient aquifer. Access restrictions due to residential properties further complicates source area clean-up.

REMEDIAL GOAL

The remedial goal is to treat CT to <5 ppb, chloroform (CF) to <100 ppb, Chloromethane (CM) to < 20 ppb and methylene chloride (MC) to <5 ppb. The target goal for the PRB set forth in the Voluntary Clean-up Plan developed for the site is to maintain a removal efficiency of at least 95% reduction in CT compared to baseline concentrations at compliance points located 70 and 140 ft (21 and 43 m) downgradient from the PRB.

IMPLEMENTATION

In April 2005, a total of 48,000 lbs (21,818 kg) of EHC was injected into an area measuring approximately 270 ft (83 m) long x 15 ft (5 m) wide x 10 ft (3 m) thick on average. The reactive zone was installed along the side of a road and extended across the plume. The EHC powder was mixed with water on site into slurry and injected using direct push technology. The injections specifically targeted the two saturated sand and gravel units identified during the pre-injection field investigation. Injections were not attempted into the surrounding clay layers as these were not deemed to be water bearing. The EHC was emplaced at an average application rate of 1% to soil mass within the sand units.

Figure 2. Injection set-up

At the initiation of the field implementation, after one injection point had been completed, verification borings were collected around the injection point to confirm EHC placement. Fractures were detected in soil cores collected up to 5 ft (1.5 m) away from the injection location suggestion a radius of influence of at least 5 ft (1.5 m). Horizontal as well as vertically rising fractures were observed with an increased dip observed with distance from the injection location. Based on observations from the soil coring an injection spacing of 10 ft (3 m) was employed. Furthermore, it was decided to install individual borings for each injection depth at each location to ensure proper vertical distribution and to avoid injecting the majority of the EHC slurry into the bottom intervals.

Mixing and pump unit and direct push probe

Horizontal EHC fracture

Vertical dipping fracture

Figure 3. Injection set-up and soil verification borings

RESULTS

Following the installation of the PRB, performance monitoring was conducted on a quarterly bases for the first three years and then bi-annually since April 2008. Figure 4 and 5 show the concentrations of CT and daughter products measured in the two wells located immediately downgradient from the PRB, specified as compliance points for PRB replenishment. CT removal rates peaked 16 months after installation with >99 percent removal observed 70 ft (21 m) downgradient of the PRB (from a baseline of 1,000 ppb to <5 ppb). Two years after installation these rates decreased slightly to approximately 95-98 percent removal and stabilized there for 7 more years. In October 2014, 9.5 years after the PRB installation, breakthrough started to be observed with the 95 percent guideline set forth in the Voluntary Clean-up Plan not being met for the first time. However, in the most recent sampling event available, conducted in October 2017, removal rates were back at 95%. Concentrations at the second compliance well, located 140 ft (43 m) downgradient from PRB and at the edge of the plume, has remained non-detect (100% removal) for all analytes since August 2005.

Chloroform (CF) concentrations initially increased as a result of the CT degradation. However, by February 2007 CF had decreased below baseline and inflowing concentrations at the compliance well located 70 ft (21 m) downgradient of the PRB. DCM and CM have remained below the detection limits in both the upgradient and downgradient wells since the May 2006 monitoring event.

In February 2007, 22 months after the PRB installation, effects of the PRB started being observed as far as 600 ft (183 m) downgradient from the PRB (Figure 6). In the most recent sampling event conducted in October 2017, CT was measured at 5.6 ppb; all degradation products were below the detection limit.

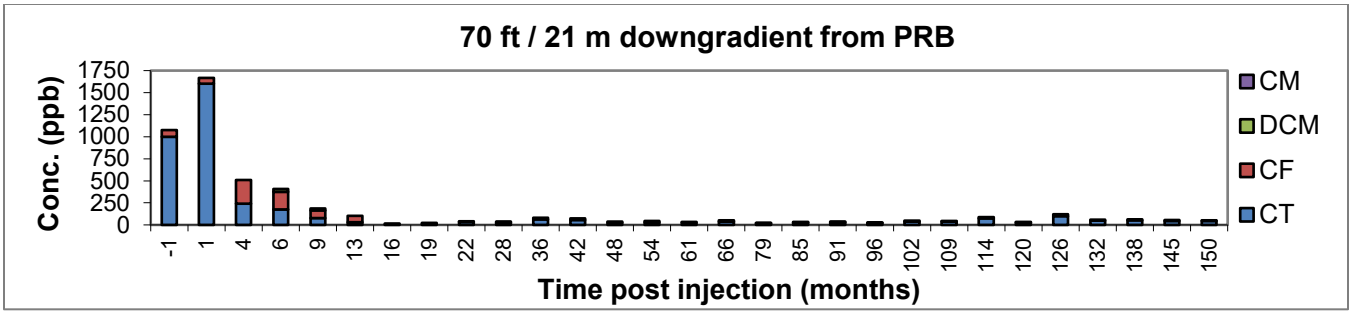

Figure 4. CT and degradation products measured in compliance well located 70 ft (21 m) downgradient from PRB at the center of the plume

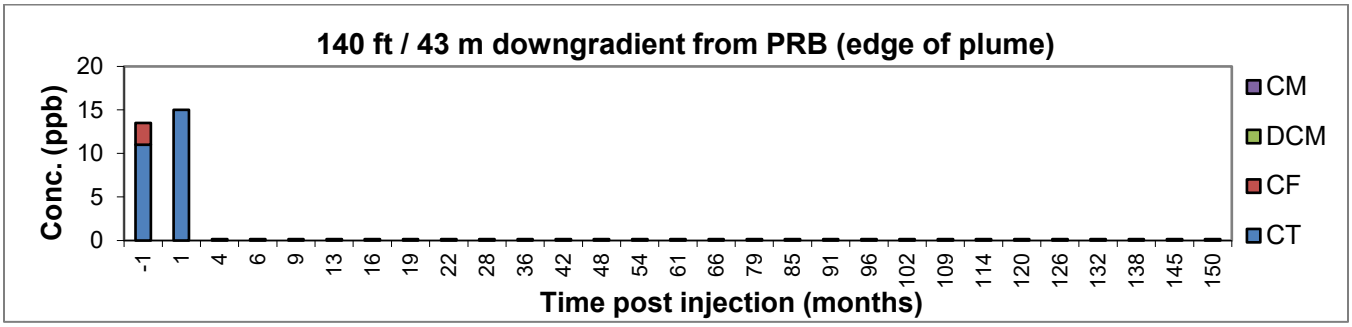

Figure 5. CT and degradation products measured in compliance well located 140 ft (42 m) downgradient from PRB at the edge of the plume

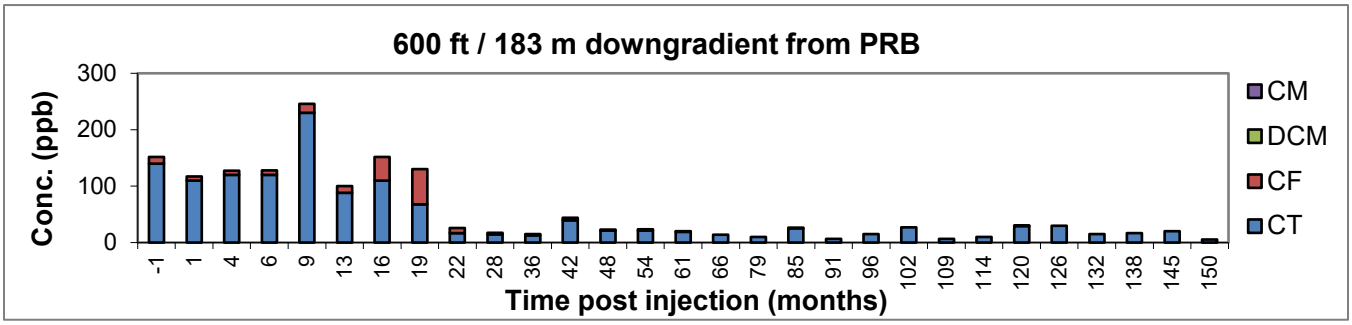

Figure 6. CT and degradation products measured 600 ft (183 m) downgradient from PRB

Meanwhile, inflowing concentrations have fluctuated with a high of 2,700 ppb measured in February 2007 (Figure 7). The more recent years decline in inflowing concentrations may be explained by remedial efforts conducted at the source area which were initiated in August 2011 (76 months after PRB installation) and expanded on in 2012 and 2013, where a shorter-lived liquid organic carbon substrate (molasses plus water) was injected via fixed wells at the highest concentration area applied over a total of eight injection events. Two injection events with emulsified vegetable oil was also conducted at the source area in 2014 and 2015.

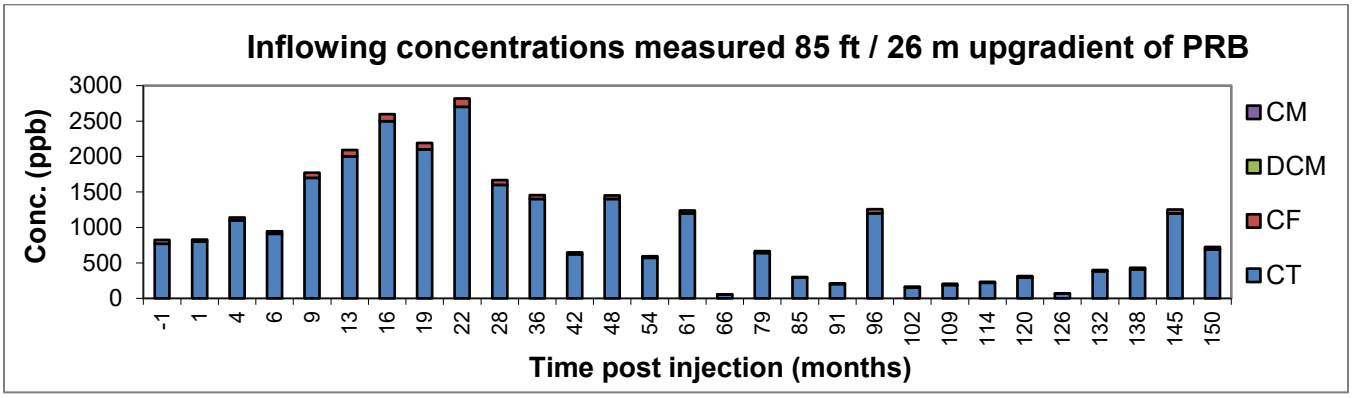

Figure 7. Inflowing concentrations measured in well located 85 ft (26 m) upgradient from PRB

Figure 8, below, shows the progression of the CT plume prior to and after installation of the EHC PRB. Groundwater levels measured over time did not indicate a change in groundwater direction following the installation of the PRB.

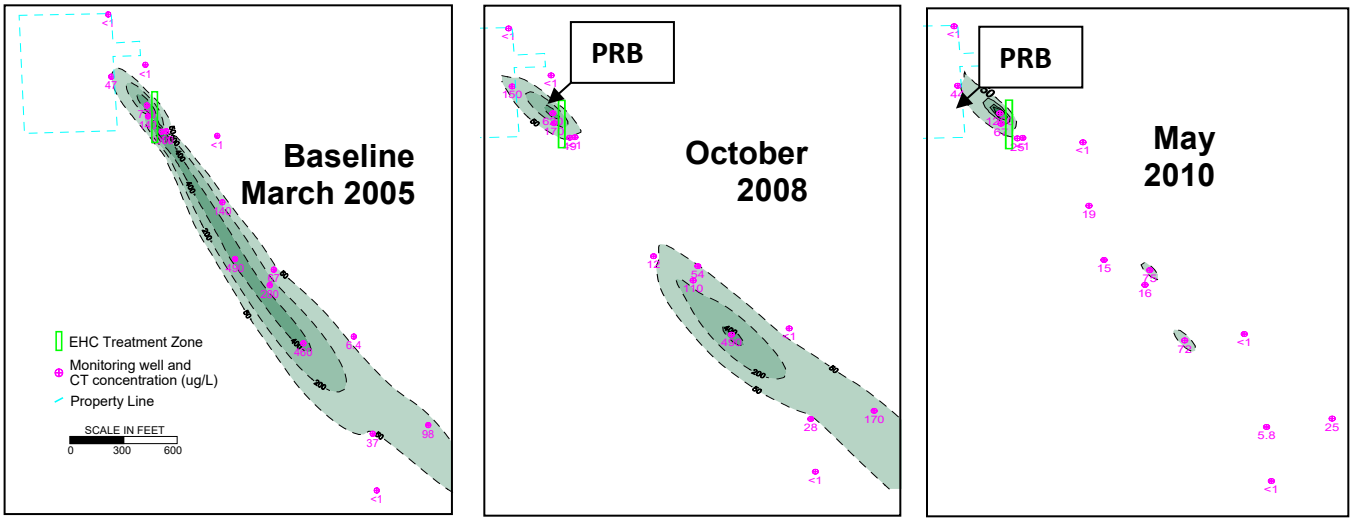

Figure 8. Impact of EHC PRB on extent of CT plume

A significant increase in TOC was measured 70 ft (21 m) downgradient from the PRB during the first two years. Since then, TOC levels have returned closer to background levels, suggesting that the more readily degradable carbon component (cellulose) had been consumed. During this initial phase redox conditions also reached their lowest point concurrently with significant reductions in inflowing nitrate and sulfate. After TOC levels returned closer to background, sulfate levels also moved closer to inflowing concentrations while ORP remained significantly below background (Figure 9). Theoretical ZVI consumption calculations suggest that the ZVI may be consumed after 2.7 years if reacting Stoichiometrically with inflowing sulfate. However, geochemical data suggest that ZVI by itself is not supporting significant sulfate reduction. The probable explanation for the long PRB reactive life is the formation of an iron sulfide mineral based reactive zone created downgradient of the PRB during the initial sulfate reduction phase and since acting as an electron reservoir. This zone may also be continuously rejuvenated by low levels of TOC present in inflowing groundwater (~2 mg/L) and from the hydrogen produced from ongoing ZVI corrosion.

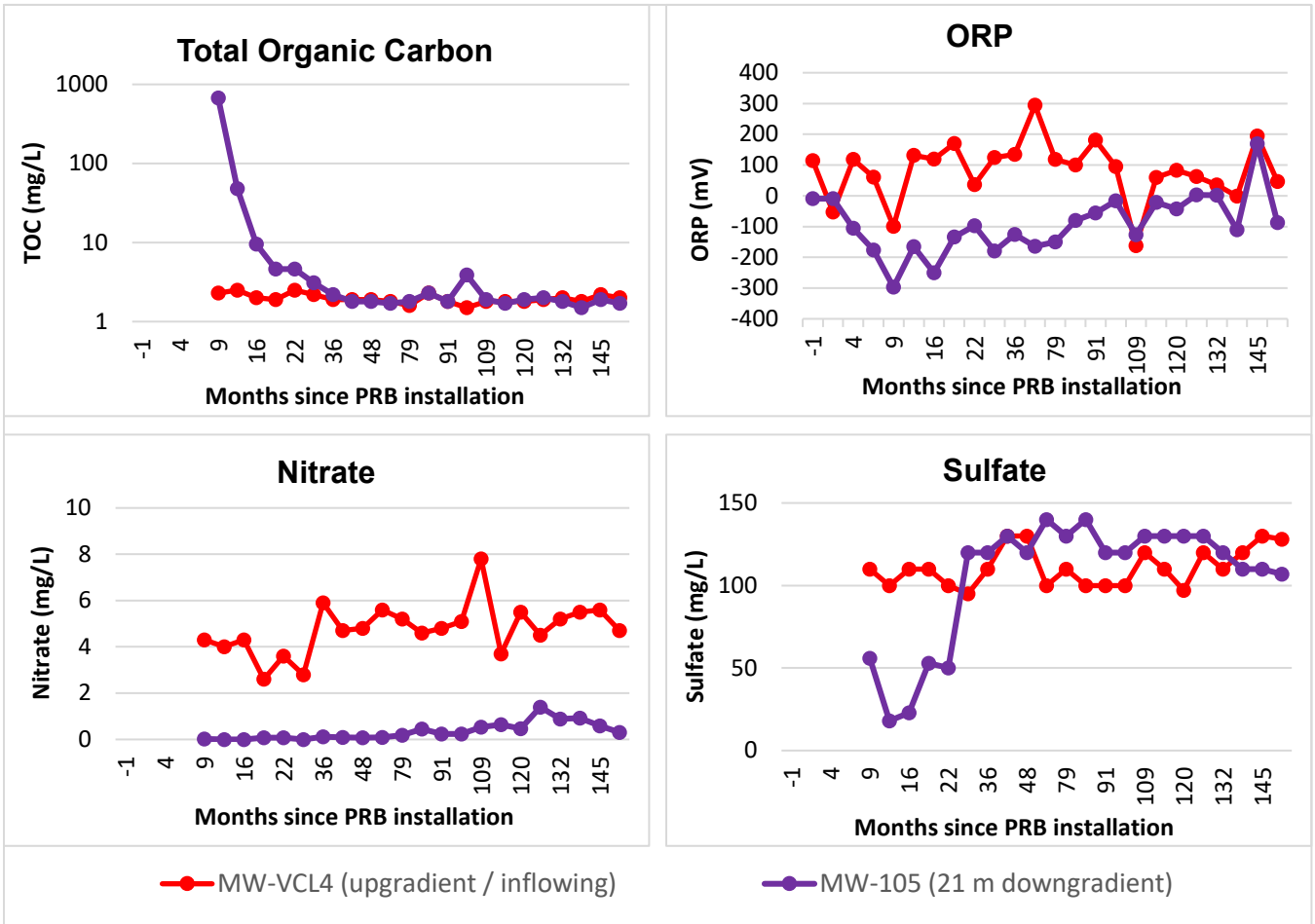

Figure 9. Effect on geochemistry downgradient from EHC PRB shown relative to inflowing conentrations over time.

COST AND TIMELINE

In 2005 the EHC material cost for the PRB measuring 270 ft (83 m) long x 10 ft (3 m) thick on average was around $100,000, resulting in a cost of $37/ft^2 ($395/m^2) of PRB cross-section. The installation was completed in 12 days (between March 30 and April 10, 2005). Using an estimated linear groundwater flow velocity of 1.8 ft/day (1.6 to 2.2 ft/day estimated) and a porosity of 30%, the PRB is treating an estimated total of 516,000 ft^3 (14,600 m^3) of groundwater per year (270 ft long x 9.7 ft average depth x 365 days x 1.8 ft/day x 30%). With a confirmed life of at least 12 years, the PRB has treated an estimated total of 6,000,000 ft^3 (175,000 m^3) of groundwater during its life-time at a product cost of <$0.02/ft^3 ($0.57/m^3).

It can therefore be concluded that ERD/ISCR using the EHC technology offers a safe, effective and cost-efficient remedial solution for similarly impacted environments. The reactive zone constitutes a green solution (no energy requirements) and maintenance costs are limited to groundwater monitoring over the life of the PRB.

CONCLUSIONS

Removal Efficiency: Groundwater sampling results have shown up to 99.5% decline in CT concentration at the core of the plume 70 ft (21 m) downgradient of the PRB (from an initial concentration of 1,000 ppb to 5 ppb measured in August 2006), without accumulation of catabolites.

Longevity: A single application of EHC has remained active for a period of 12+ years, continuously supporting >90% removal of CT, without the accumulation of catabolites.

Plume Impacts: Since the installation of the PRB it has served to significantly reduce the size and concentration of the downgradient plume.