MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

FIELD ASSESSMENT AND SUPPORT TEAM (FAST)

Evaluation of a Permeable Reactive Barrier For TCE Treatment: 20 Years On

MassDEP RTN 3-386

Prepared by Natalie Johnson, PhD

Reviewed by John Fitzgerald, PE

August 2024

Report Summary and Findings

The objective of this report is to evaluate the long-term performance of a permeable reactive barrier (PRB) installed by MassDEP and their contractor at the Microwave Development Laboratories (MDL) site in 2001. In order to achieve this goal, we spent a considerable effort to review and evaluate numerous technical reports, including documentation of the basis of design, the Phase II Comprehensive Site Assessment report for the MDL site, recent status reports, and numerous quarterly/annual groundwater data reports. The sheer number of relevant submissions, particularly groundwater data reports, may have led to unintentional omissions or misinterpretations.

Our findings are summarized below:

- PRB performance began to decline 5–7 years after installation, and trichloroethylene (TCE) reduction had ceased in many portions of the PRB by 2011. Although some TCE reduction is continuing to occur in the northern and southern ends, the effective lifespan of the installation was about 10 years, in that the concentration of TCE upgradient and downgradient of the PRB was largely the same across most of the wall by 10 years post-construction.
- While the longevity of the PRB was somewhat less than expected, TCE concentrations upgradient of the PRB also unexpectedly declined significantly 1–4 years after the PRB was installed. This decline is attributed to remedial actions conducted at the MDL property, specifically, groundwater recovery wells that were installed in 1993. When the PRB was installed, travel time estimates based on hydraulic conductivity measurements indicated that any reduction from the recovery wells would not be apparent until at least 2018.
- The decline in PRB performance is likely the result of (1) a loss of reactivity via a combination of surface passivation of the reactive iron species and consumption of the reactive iron species in flow zones within the PRB media, and (2) the clogging of pore spaces within some portions of PRB media by precipitates and/or microbial mass that reduced access/contact times with unreacted iron species. Based upon a mass balance assessment of electron demand and electron capacity, it appears that up to 50% or more of the ZVI in the wall was not effectively utilized because of the presumed uneven flow of groundwater through the wall.
- Data from the downgradient sentinel wells indicate that long term performance of the PRB has been acceptable, with most sentinel wells containing TCE < 5 ug/L since 2005. Importantly, the PRB was effective at reducing TCE concentrations when upgradient concentrations were most elevated.
- Data from post-PRB construction indicates that blended/treated water from the downgradient Wellesley wellfield did not contain detectable levels of TCE, though data is not available to determine whether untreated water from individual wells in the wellfield were impacted by the TCE or its degradation products.

The remedial objective of the PRB was to eliminate or mitigate impacts to the Wellesley well field until plume propagation from the MDL property was eliminated. As it turned out, source control measures on the MDL property attenuated contaminant levels in downgradient impact areas much quicker than predicted, substantially reducing the expected loading of the ZVI media. Nevertheless, the PRB removed a significant mass of TCE from the environment, especially in its first several years of operation, and reduced and perhaps largely eliminated impacts to a public drinking water supply.

Table of Contents

List of Figures

List of Acronyms and Abbreviations

cis-1,2-DCE: cis-1,2-Dichloroethylene
DO: dissolved oxygen
Fe: Iron
MassDEP: Massachusetts Department of Environmental Protection
MCL: maximum contaminant level
MDL: Microwave Development Laboratories
O_2: Oxygen gas
ORP: oxidation-reduction potential
PRB: permeable reactive barrier
TCE: trichloroethylene
ZVI: zero valent iron

mg/L: milligrams per liter
µg/L: micrograms per Liter

Background

In the summer of 2001, the Massachusetts Department of Environmental Protection (MassDEP) installed a permeable reactive barrier (PRB) to intercept and treat a chlorinated solvent groundwater plume emanating from a former electronics manufacturer in Needham, MA (the Microwave Development Laboratories [MDL] site at 101–145 Crescent Road). Trichloroethylene (TCE) was the primary contaminant of concern; lower concentrations of cis-1,2-dichloroethylene (cis-1,2-DCE) and other degradation products were also present.

At MDL, TCE was historically released from subsurface waste disposal structures (e.g., cesspools) and later through corroded and leaky sewer lines. TCE was used for degreasing operations until about 1984. The MDL property is located near the top of a hill, and overburden groundwater follows surface topography flowing down and to the west towards Rosemary Meadow, under Central Avenue, and then turns north towards a public drinking water supply wellfield operated by the Town of Wellesley (Figure 1).

By 2001, the TCE plume was approximately 4,500 ft long. Overburden geology consists of 80+ ft of dense glacial till overlying bedrock at the MDL property; in the Rosemary Meadow area, approximately 40 ft of unconsolidated glacial outwash overlies bedrock. A significant (up to 40 ft) layer of peat is present west of Central Avenue, above the glacial outwash (Woodard & Curran 1997; as appended to Cygnus 2000).

At the time of installation, PRBs using zero valent iron (ZVI) were an innovative technology with a limited track record, with the first full-scale installation occurring in Sunnyvale California only 7 years prior, in 1994 (ITRC 2011). The company that designed the Needham PRB, EnviroMetal Technologies, Inc., had only installed 3 full-scale systems by June 1997 (EPA 1997), just before the design process for the Needham installation was initiated.

The objective of this report is to evaluate the performance of this then innovative technology approximately 20 years after construction using available monitoring data. A more complete discussion of the MDL site was presented in a recent MassDEP (2022) report evaluating the efficacy of recovery well and *in situ* oxidation treatment conducted at and near the MDL property. That report can be found here: https://eeaonline.eea.state.ma.us/EEA/fileviewer/Rtn.aspx?rtn=3-0000386

PRB Construction

The PRB was installed beneath Central Avenue in Needham, MA, in June and July 2001. This installation is about 2000 ft downgradient of the source area, and 3000 feet upgradient of the Wellesley well field., and was designed to reduce the downgradient TCE concentration below the maximum contaminant level (MCL) of 5 µg/L. The PRB is 535 ft long, 2 ft wide, and extends from the water table to bedrock (19–55 ft deep) (Geo-Con 2002) The PRB consists of a mixture of zero-valent iron (ZVI) and sand in two zones: Zone A contains 10% sand and thus is considered to have 1.7 “effective feet” of iron, and Zone B contains 67% sand and is considered to have 0.5 “effective feet” of iron.

The PRB was constructed using a biopolymer slurry trench method. The trench was excavated as a series of panels, each 30–60 ft long, and extended to the bedrock surface. A biopolymer (G-150 guar gum) was placed inside the trench to support the walls during backfill placement. The iron-sand mixture was placed using a tremie pipe and gravity flow; the trench was filled until the iron-sand mixture reached the highest measured groundwater elevation. Above the water table, backfill consisted of the

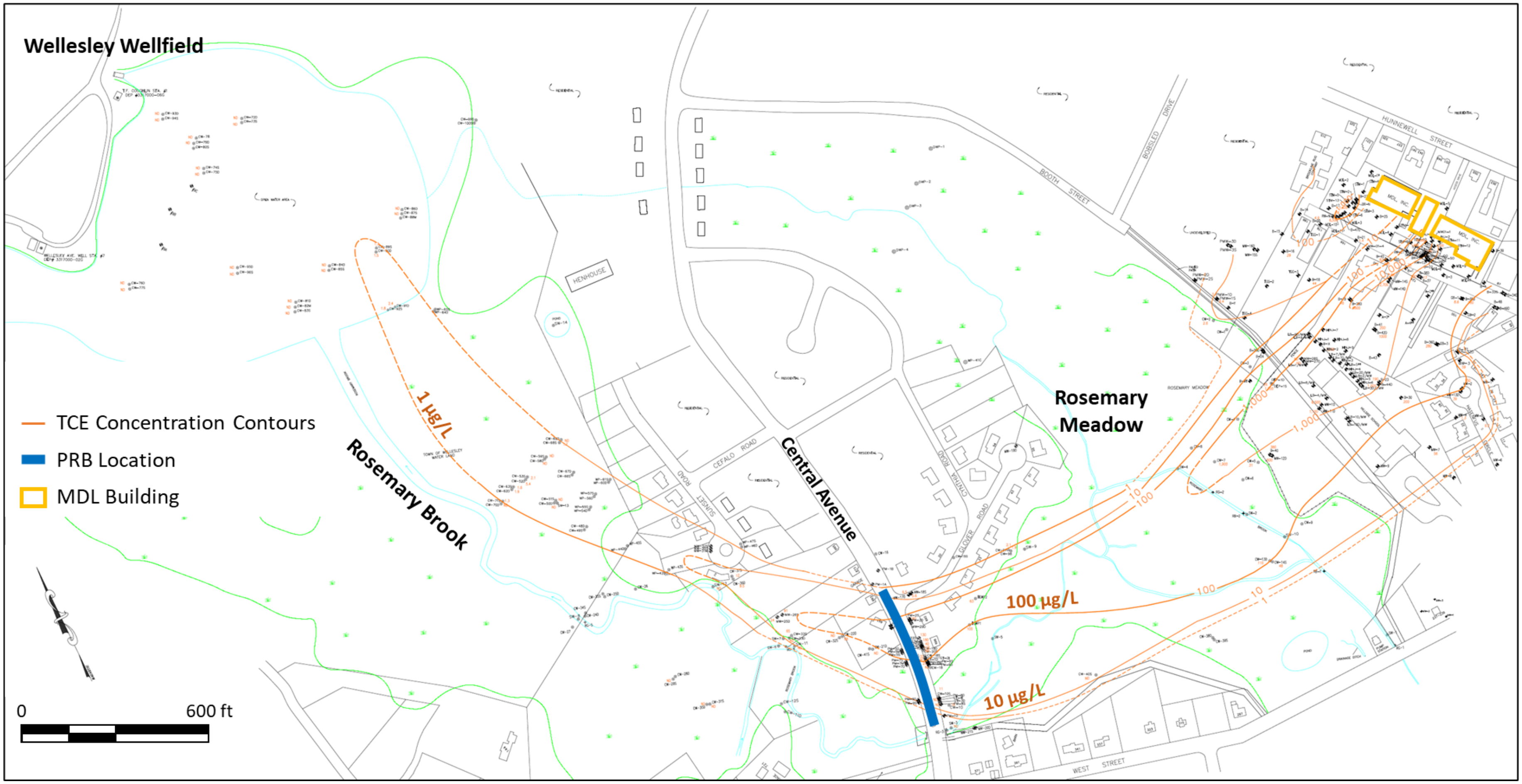


Figure 1. The TCE plume originated at the MDL property (yellow) and migrated downhill and west, across Rosemary Meadow, and beneath Central Avenue before turning north towards the Wellesley Wellfield. TCE data are from 1999/2000 (Figure adapted from Lord Environmental [R. Tella, personal communication, 3/30/2022]).

sand/iron mixture, soil, or backfill from off-site. The trench was then flushed with enzyme breakers to degrade the biopolymer slurry.

During construction, several challenges arose that could potentially impact the PRB performance. For example, a boulder located at the overburden-bedrock surface was left in place in Panel 6. Also, warm weather resulted in rapid degradation of the slurry, and preservatives (which enhance biopolymer stability) were not used due to concerns of impacting the Wellesley wellfield. Degrading slurry resulted in two official “breaks,” defined as a drop in slurry viscosity below a pre-determined threshold. The first occurred in Panel 2 on June 11. The pH of the slurry was raised using soda ash and lime to stabilize the trench long enough for backfilling operations to finish. The second break occurred in Panel 8 on June 29. A portion of the sidewalls caved in—the panel was re-excavated to 20’ and backfilling operations were completed on July 7. The locations of these incidents are shown on Figure 2.

A total of eight nested monitoring wells were installed on the upgradient and downgradient sides of the PRB to monitor performance over time (PM-2 through PM-9).[1] The nested wells contain at least one shallow and one deep well at each location; one upgradient and one downgradient location also contain an intermediate depth well. Several monitoring wells were also installed within the PRB—four pairs of shallow and deep wells were sampled in August 2001 but no subsequent data were identified. Monitoring well locations are shown on Figure 2.

---

[1] PM-1B and PM-1A were installed adjacent to and downgradient of, respectively, the PRB at its northern terminus.

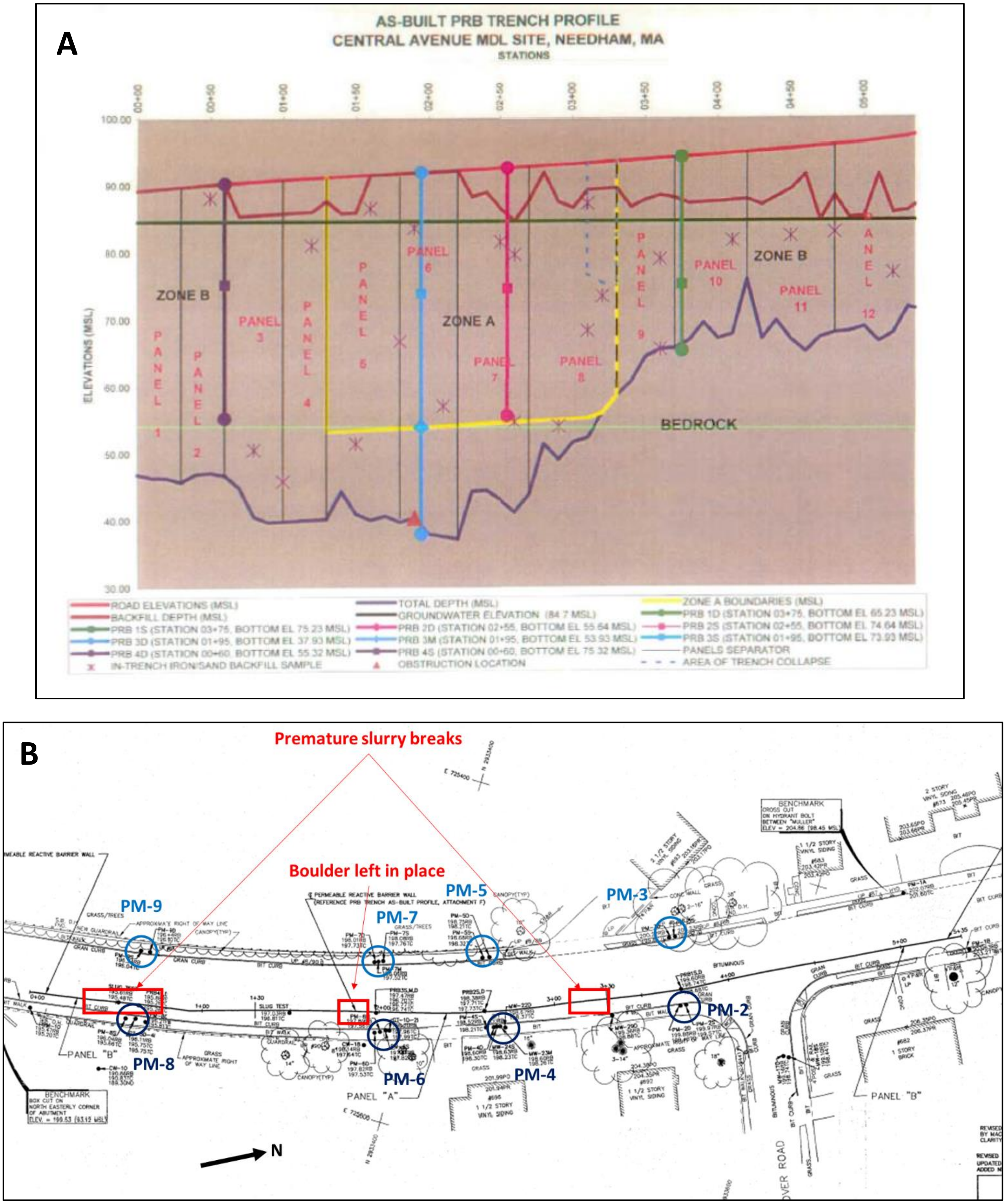
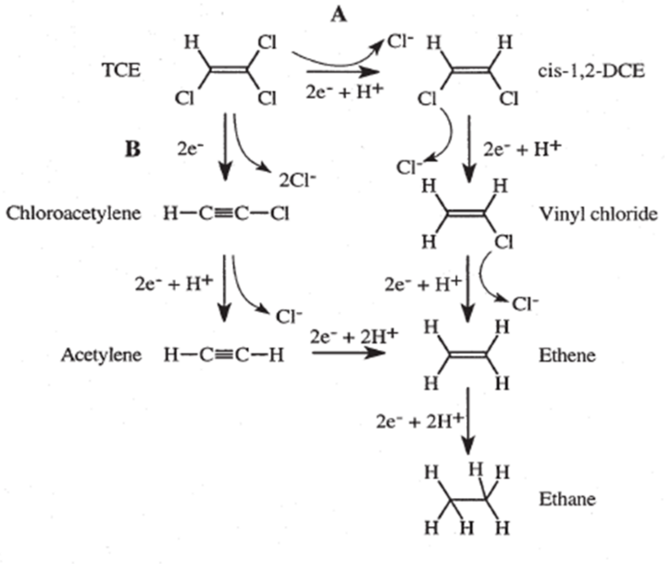


Figure 2. PRB cross section showing construction panels and four wells installed within the PRB (A). Top view of PRB showing performance monitoring wells and construction incidents (B).

PRB Chemistry

The permeable reactive barrier contains zero valent iron as a reactant. The iron is easily oxidized by donating an electron; however, in order for oxidation to occur, there must be an electron acceptor present. Chlorinated solvents, such as TCE, can serve as electron acceptors and undergo degradation via reductive dichlorination or reductive beta-elimination (Figure 3). In reductive dechlorination, TCE accepts two electrons (from the iron) and a proton (hydrogen ion in groundwater) and sheds a chloride ion to become cis-1,2-DCE. Similarly, cis,1-2-DCE accepts two electrons and a proton (and sheds a chloride ion) to become vinyl chloride, and vinyl chloride transforms to ethene. The reaction rate for TCE dichlorination is faster than cis-1,2-DCE and vinyl chloride dichlorination. In reductive beta-elimination, TCE is degraded to an intermediate, chloroacetylene, which rapidly degrades to acetylene. Acetylene is also an electron acceptor and will be reduced to ethene. In both cases, the zero valent iron is consumed as it oxidizes to iron oxide or iron hydroxide, and three iron molecules, each donating two electrons, are needed to convert TCE to ethene.



Reaction A: Sequential hydrogenolysis

Reaction B: Reductive beta-elimination

Net chemical reaction for both pathways:

$$3Fe^{0} + C_2HCl_3 + 3H^{+} \rightarrow C_2H_4 + 3Cl^{-} + 3Fe^{2+}$$

Figure 3. Reaction pathways for the reduction of TCE to ethene (adapted from EPA 1998).

It is important to note that contaminants like TCE are not the only compounds in groundwater that are potential electron acceptors for the iron. Most notably, dissolved oxygen is a competing oxidant and will be preferentially reduced over TCE. That means dissolved oxygen will be consumed by the iron before TCE can be treated, which is of critical importance since DO concentrations can be an order of magnitude higher than the concentrations of contaminants like TCE. For optimal/cost-effective operations, DO should be less than 4 mg/L (ITRC 2011). Fluctuating DO levels in upgradient groundwater can lead to decreased and/or variable PRB performance and incomplete TCE degradation.

The consumption of DO by iron makes it a useful indicator of PRB performance; concentrations in downgradient wells less than 0.5 mg/L are consistent with proper operations (ITRC, 2011). A related parameter, oxidation-reduction potential (ORP) is also a useful indicator and under effective operating conditions, should be below -100 mV in downgradient monitoring wells.

Previous Analysis of PRB Performance

Richards (2008) evaluated the PRB performance over the initial seven years of operation. He assessed the chemical data and water quality parameters and determined that “the PRB is significantly reducing TCE concentrations along its length.” However, he identified two discrete areas where the PRB was not effective, with little change in the TCE concentrations in upgradient and downgradient wells. Specifically, Richards (2008) determined that the PRB performance was inadequate at PM-7D and PM-9D, both of which are deep wells located on the southern portion of the PRB (Figure 2).

Richards (2008) considered several explanations for the poor performance in these two wells. The combination of slight upward vertical hydraulic gradients, coupled with low bedrock permeability and lower concentrations of TCE in bedrock wells, suggested that upwelling from the bedrock was an unlikely cause of elevated TCE downgradient from the PRB. Desorption of TCE from soils was also unlikely given the overburden composition (sands with trace silt) and low levels of organic carbon. Ultimately, Richards (2008) concluded that construction issues resulted in the inadequate performance observed in wells PM-7D and PM-9D.

Analysis

The passage of 20 years provides an opportunity to conduct a current and retrospective review and analysis of PRB performance and environmental outcomes. Chemical data from downgradient wells[2] were evaluated to determine efficacy and identify temporal trends. The major conclusions are:

- TCE concentrations in the upgradient wells generally peaked in 2001–2004 and declined until about 2008, likely due to the operation of recovery wells at the MDL property (which became operational in 1993). The lag between 1993 and 2001–2004 suggests a contaminant travel time of approximately 8–11 years from the MDL property to Central Avenue.
- *In situ* chemical oxidation operations at the MDL property were conducted in 2004, 2007, 2010, 2011, and 2013. Based on the travel time estimated above, we expect to see contaminant reduction from these operations by approximately 2015, 2018, and 2021 upgradient of the PRB. Several wells (e.g., PM-4D, PM-6M, PM-8S, PM-8D) do show a decline in TCE concentrations between 2016 and 2018, but it’s difficult to discern if this decline is significant given the year-to-year variation in the data. Also, there are persistently high levels of TCE on the Hillside School property, located between the MDL property and Central Avenue; the impact of this contamination on downgradient groundwater is not clear.
- Two well pairs in the deep overburden have shown poor performance for nearly the duration of operations. These wells were previously identified by Richards (2008) and have continued to demonstrate little to no reactivity, most likely because of preferential flow paths created during the installation process which result in higher flow velocity and shorter residence time.
- Across the central portion of the PRB, performance declined significantly between 2006 and 2012. The data suggest a 5–10-year lifetime of the PRB in the center of the plume, where upgradient TCE concentrations were highest. The area with more iron (i.e., area “A”), performed better for a longer period than the portion of the wall with a less iron.

---

[2] Data were obtained from recent (Lord 2021a) and historical (Cygnus 2000) reports, as well as a range of quarterly and annual groundwater data reports. Given that there was no single document consolidating all relevant data, it’s possible that some data points were not included in the analysis.

- Ongoing evidence of chemical reduction is present in periphery wells located at the northern and southern ends of the plume, particularly in the shallow overburden.

Upgradient Concentrations declined soon after the PRB was installed

Shallow and deep TCE concentrations upgradient of the PRB were highest in the years immediately following PRB installation, and generally peaked between 2001 and 2004. Following the peaks was a decline in TCE concentrations across nearly all upgradient wells, with two main exceptions (Figure 4):

- Well PM-6D remained elevated after TCE concentrations declined in other upgradient wells and demonstrated a slower decline than other deep and shallow wells; and
- Variability in well PM-8D makes it difficult to discern a trend of declining TCE concentrations in the early–mid 2000s.

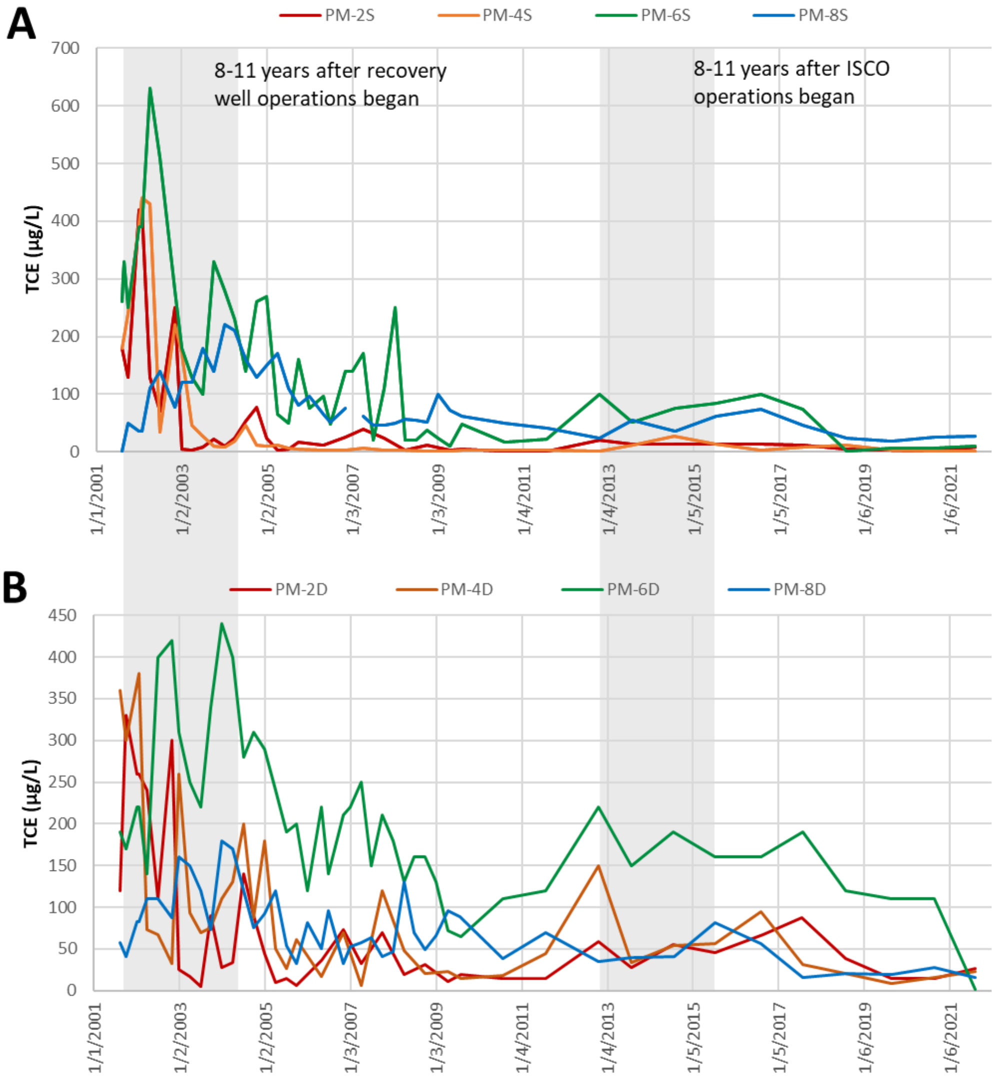


Figure 4. TCE in upgradient shallow (A) and deep (B) wells declined approximately 8-11 years after recovery well operations began near source areas on the MDL property. The initial ISCO application (2004) may have caused the short-term increase in TCE approximately 8 years later, particularly in the deep wells (B).

Across the remaining wells, the decline in TCE concentrations was most likely due to source treatment at the MDL property. In 1993, three recovery wells began extracting contaminated groundwater from two source areas on the MDL property. TCE concentrations near Central Avenue (i.e., upgradient of the PRB), began to decline approximately 8–11 years after commencement of recovery well operations. In 2004, an *in situ* chemical oxidation (ISCO) pilot project was completed at the MDL property. In the following two years, several wells located near the MDL property showed a temporally limited increase in TCE concentrations. Several wells near Central Avenue show a similar spike in TCE concentrations in 2012, about 8 years after the initial ISCO injections. Thus, the data suggest an approximate contaminant travel time as short as eight years from the MDL property to the PRB beneath Central Avenue, which is less than expected based on hydraulic conductivity measurements.

Until recently, TCE concentrations remained most elevated in PM-6D (>100 µg/L). In 2021, TCE was not detected in this well. At least one additional monitoring event is needed to determine if the data from 2021 are anomalous or represent a real decline in TCE concentrations at this location.

20 years post-installation, wells located directly upgradient and downgradient show mixed results

The nearfield analysis consists of the well pairs located directly upgradient and downgradient of the PRB. The goal of this analysis is to determine which sections of the PRB are still functioning well, and which show signs of degradation/reduced efficacy over time. We reviewed all available data from quarterly and annual reports, and broadly categorized the well pairs into three groups: poor PRB performance, decline in PRB performance over time, and good PRB performance.

- *Poor PRB performance* is primarily characterized by an initial and continuing lack of TCE reduction between the upgradient and downgradient wells. Other indicators of poor performance are elevated dissolved oxygen in the downgradient well, elevated degradation products in the downgradient well, and oxidation/reduction potential (ORP) greater than zero. All of these indicators are signs that reductive dichlorination is not occurring within the PRB, likely due to a "short circuiting" of groundwater flow through the sand/ZVI media. We note that the upgradient TCE concentrations are much lower in 2021 than they were when the PRB was constructed, so it's possible to observe poor performance and still meet the remedial goal of 5 µg/L downgradient of the PRB.
- A *decline in PRB performance over time* is characterized by initial data showing good performance (i.e., TCE reduction to the remedial goal), with a change to poor performance over time. This trend is likely attributable to passivation and the gradual clogging of pore spaces with precipitates and/or microbial mass. It's important to note that the efficacy of TCE removal was expected to decline over time, and the goal of the PRB installation was to protect the Wellesley Water Supply Wells temporarily while source area treatments were applied.
- *Good PRB performance* is characterized by evidence of ongoing reductive dechlorination throughout the operational period of the PRB. This is suggestive of proper installation techniques and establishment of more uniform flow paths through the wall which was able to maximize the use and capacity of available ZVI.

Each well pair is discussed in the following sections, starting at the southern end of the PRB (wells PM-8 and PM-9) and progressing to the northern end of the PRB (wells PM-2 and PM-3). In some cases, differences in performance were noted within various vertical increments, as measured by deep (D), shallow (S), and intermediate (M) performance monitoring (PM) wells.

PM 8S/9S: Good Performance

Data from the upgradient/downgradient shallow wells PM-8S/9S show good PRB performance over the initial seven years of operation, with some performance degradation occurring since January 2009. In general, data from the past 12 years indicates that TCE reduction is ongoing, with lower downgradient concentrations than upgradient, and generally lower dissolved oxygen concentrations and ORP in the downgradient well. However, the efficacy is lower in the post-2009 data. In the past 12 years, downgradient TCE concentrations have reached as high as 100 µg/L, 20 times higher than the design criteria concentration of 5 µg/L. The median concentration over that period of time is lower than the design criteria (2.3 µg/L), with multiple instances of TCE below the detection limit in the past five years. Thus, the performance, though less robust than during the initial years of operation, is sufficient.

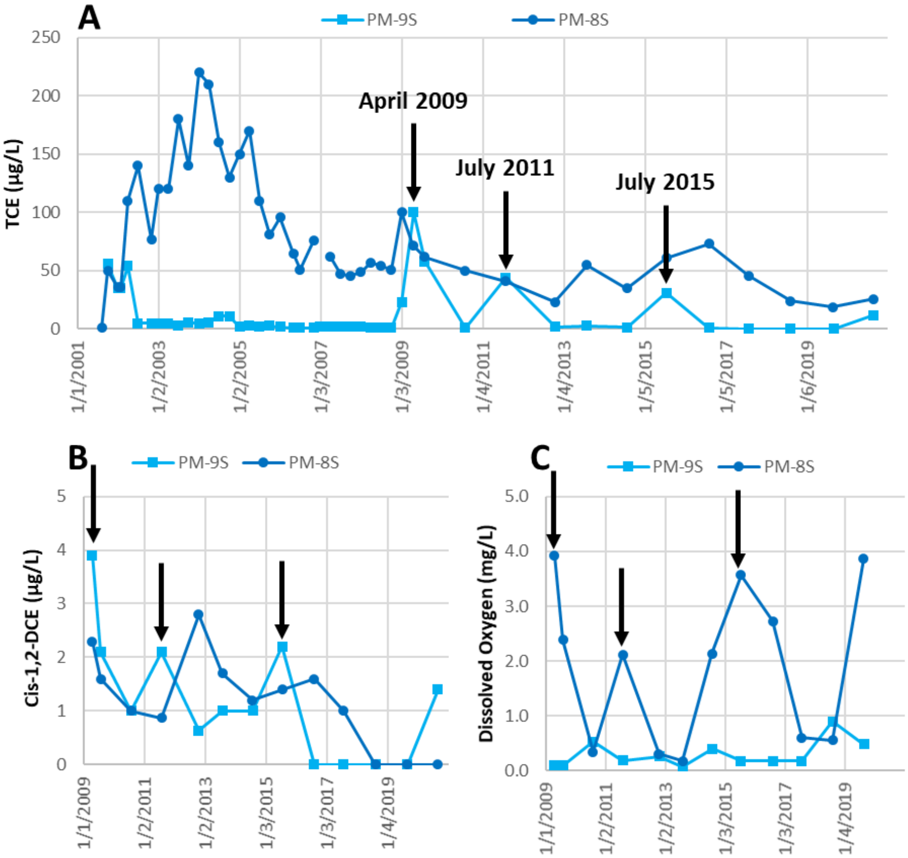


Figure 5. Data from upgradient/downgradient well pair PM-8S/9S shows reduced efficacy beginning in 2009 (A). Elevated TCE in the downgradient well is correlated with higher concentrations of cis-1,2-DCE in the downgradient well than the upgradient well (B) and elevated dissolved oxygen in the upgradient well (C).

The apparent reduced efficacy of treatment at PM-8S/9S may have several causes. First, there may be transport from other, more contaminated areas into well PM-9S (such as PM-9D). Also possible is a reduction in reactivity of the PRB due to coatings on the iron particles or consumption of the reactive species. We evaluated the other available data to identify the possible cause for reduction in treatment efficacy at this location, and observed some evidence for partial reduction (e.g., cis-1,2-DCE elevated downgradient relative to upgradient of the PRB), particularly when the downgradient TCE concentrations were highest (April 2009, July 2011, and July 2015). These dates are also associated with elevated dissolved oxygen in the upgradient well. Thus, it appears that when upgradient dissolved oxygen is high, the residence time within the PRB is insufficient to reduce the TCE to concentrations below the design criteria; only partial reduction occurs.

PM-8D/9D: Poor PRB Performance

As observed in Richards (2008), downgradient well PM-9D has demonstrated poor performance for nearly the entire existence of the PRB (Figure 6A). The first two samples collected after installation of the PRB showed lower TCE relative to the upgradient well (PM-8D), but samples collected since 2002 have contained nearly the same (or higher) TCE concentration as the upgradient well. Though TCE concentrations in PM-9D have decreased over time, the decline is attributed to decreasing TCE in upgradient groundwater, likely due to ongoing treatment at and near the source area.

Water quality parameters, such as ORP, also indicate incomplete reaction. Over the past 10 years, the downgradient ORP ranged from -63 to 236 mV (Figure 6C), which is higher than the expected value of -100 mV or less. Dissolved oxygen concentrations in the downgradient well are lower than the upgradient well, which indicates that some reduction has occurred (Figure 6B). However, based on the available data, it’s clear that the reduction is incomplete, and the residence time and/or availability of unpassivated ZVI within the flow paths through this section of the PRB is insufficient to reduce all the oxygen, much less the chlorinated compounds.

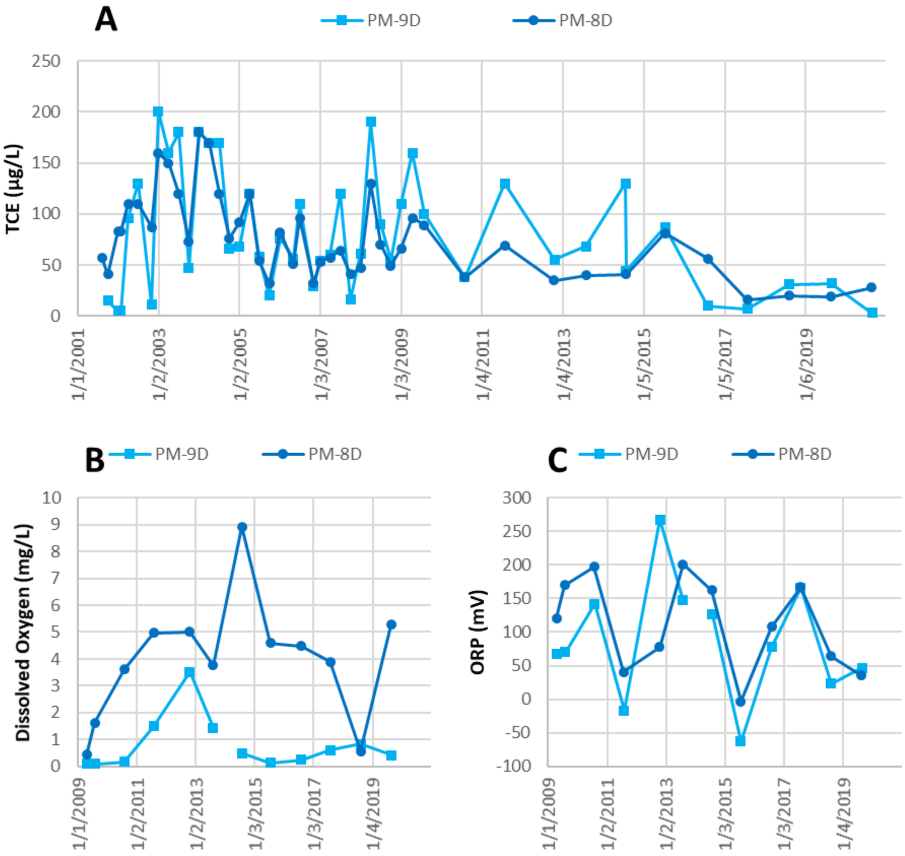


Figure 6. Data from upgradient/downgradient well pair PM-8D/9D indicates insufficient performance based on TCE concentrations (A), dissolved oxygen (B), and ORP (C).

The vertical hydraulic gradient in well PM-9D has changed over time. The mean gradient (2001–2022) is slightly downwards, but data from the past 12 years indicate upward flow from the deep to shallow well. However, the poor TCE degradation performance has been ongoing for nearly 20 years, so the change in vertical flow is not the only factor.

The available evidence is supportive of Richards (2008) conclusion that construction-related issues likely resulted in the poor performance observed in well PM-9D.[3] This well is directly downgradient of the premature slurry break in Panel 2 (Figure 2), which may have impacted the PRB construction in this area. Specifically, the pH was increased to increase the slurry viscosity and allow for completion of backfilling operations. It's not clear if the addition of alkaline components may have impacted long-term performance of the PRB (e.g., through induced precipitation of iron hydroxide), or if the issue was with placement of backfill materials. The water quality parameters indicate that partial reduction is occurring, but there is insufficient residence time for complete oxygen, much less TCE, reduction to occur. The poor performance has been apparent since January 2002, six months after construction completion.

PM-6S/7S: Loss of efficacy over time

Upgradient/downgradient wells PM-6S/7S, located about 125 ft north of well PM-8S/9S and in the zone with a higher percentage of iron in the PRB ("Zone A"), initially demonstrated effective TCE reduction across the PRB. TCE was reduced to or below the design criteria of 5 µg/L with few exceptions until April 2007 (mean concentration = 5.99, median = 5 µg/L), with an average reduction of 96% across the PRB. From 2007 to 2020, the performance was notably worse, with a mean TCE concentration of 29.6 µg/L in the downgradient well (median = 26.5 µg/L). The increase in downgradient TCE is particularly striking after 2009. Based on the TCE data, it appears that this section of the PRB has had little, if any effect on TCE concentrations since 2007.

The apparent reduction in PRB efficacy in the shallow zone cannot be attributed to vertical groundwater flow. Before 2012, there was little vertical hydraulic gradient. Between 2013 and 2019, several gauging events measured a vertical upwards flow (2018, 2019) or diverging flow from the intermediate groundwater to both shallow and deep (2013). Since 2012, vertical flow could be responsible for some TCE in the shallow well. However, the trend of reduced efficacy began in 2007, years before there was any change in the vertical flow.

Other chemical data and water quality indicators suggests that PRB reactivity has been declining in this section of the installation and may be negligible as of this report. From 2008–2019, dissolved oxygen was lower in the downgradient well, and less than 1 mg/L at all sampling events except one (Figure 7). However, in 2020 and 2021, the dissolved oxygen concentration in the downgradient well has tracked upwards, roughly matching the trend in the upgradient well. Given that oxygen is the preferred electron receptor, it appears that the PRB in this area is no longer reducing oxygen as of about 2020.

A decrease in the upgradient TCE concentrations is apparent between 2001 and about 2008. This decline is most likely due to treatment at the MDL property, specifically the recovery wells installed in the early 1990s. Even though reactivity of the PRB in this area declined after 2007, it effectively reduced downgradient TCE concentrations during the period of high upgradient TCE concentrations, allowing additional time for the source area remedial actions to impact the area proximate to the PRB.

---

[3] We also evaluated lateral flow from well PM-7D, which contains higher concentrations of TCE, but determined that to be unlikely because the hydraulic gradient favors flow from 9D towards 7D.

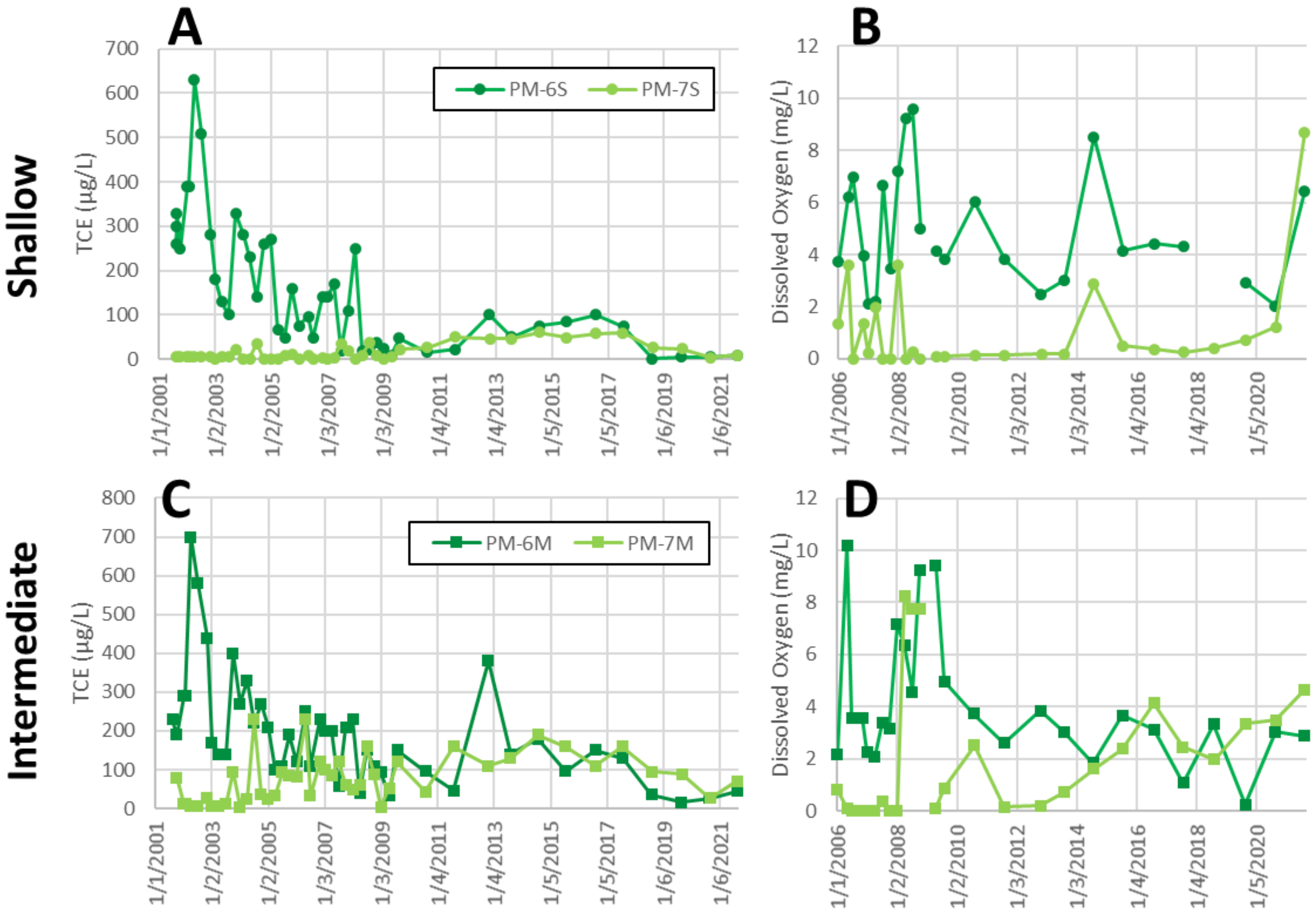


Figure 7. TCE (A,C) and dissolved oxygen (B,D) concentrations upgradient and downgradient of this section of the PRB show declining reactivity over time in both the shallow (A,B) and intermediate (C,D) wells.

PM-6M/7M: Loss of efficacy over time

PRB performance in the intermediate groundwater at upgradient/downgradient wells PM-6M/7M is slightly worse than the shallow; TCE concentrations were initially reduced downgradient, but the impact of the PRB on TCE appears to have dissipated by 2006 (Figure 7). Oxygen, the preferred electron acceptor, was reliably reduced until 2008 and sporadically reduced from 2009–2013. The ORP shows evidence of ongoing reduction until 2012. Since 2013, chemical indicators suggest that there has been no reactivity across the PRB in this location/depth, either because the iron in active flow paths was consumed or passivated.

Similar to what was observed in other upgradient wells, the upgradient TCE concentration declined markedly from 2001, when the PRB was constructed, to 2005. Between 2001 and 2002, the average TCE concentration was 389 µg/L. Between 2008 and 2009, the average concentration was 115 µg/L. More recently (2019–2021), the average TCE concentration was 29 µg/L in upgradient well PM-6M. The decline in TCE concentrations upgradient of the PRB is likely due to treatment at the MDL property.

In recent years, TCE in downgradient well PM-7M has been higher than the upgradient well. Upwelling from deeper in the aquifer may be contributing TCE to the intermediate well, as TCE concentrations in the deep well (PM-7D) are elevated and the hydraulic gradient is slightly upwards in this area. However, the data strongly suggest that the PRB is no longer active in this area.

PM-6D/7D: Poor PRB Performance

Data from upgradient/downgradient wells PM-6D/7D show little indications of effective TCE reduction as far back as 2002. This well pair was discussed by Richards (2008) as it was clearly underperforming within a year of PRB installation. Data since 2008 has continued to show no evidence of reactivity within the PRB. Reactivity in this area of the PRB is even worse than at PM-8D/9D, as there has been no reduction in dissolved oxygen concentrations across the PRB since at least 2006 (whereas PM-9D contained lower dissolved oxygen than the upgradient well until 2019).

The two most likely scenarios explaining the lack of reactivity in this area are short circuiting/a preferential flow path through the PRB, such as around the boulder left in place on the bedrock surface, or underflow through the bedrock and upwelling. As noted by Richards (2008), vertical hydraulic gradients were consistently upwards from the bedrock to the overburden with a magnitude of about 0.1 ft/ft. However, permeability testing in 2007 found 3–4x higher permeability in the overburden compared to the bedrock, and TCE concentrations in bedrock were 1–2 orders of magnitude lower than in the overburden. Thus, it does not appear that upwelling from the bedrock contributes a significant amount of TCE to the downgradient deep overburden. Instead, it appears that preferential flow paths developed soon after the PRB was installed and resulted in the rapid passivation/consumption of the ZVI in the preferred flow pathways and/or insufficient residence time within the PRB.

PM-4/5: Loss of efficacy over time

The upgradient/downgradient well series PM-4 and PM-5 are located about 60 ft north of the PM-6/7 series; the shallow wells were screened up- and downgradient of Zone A of the PRB (greater iron content) and the deep wells were screened up- and downgradient of Zone B. The data for both the shallow and deep wells indicates good initial performance, followed by a decline in performance and complete loss of reactivity in recent years (Figure 8).

The reduction of TCE concentrations across the PRB indicate initial high levels of reactivity, with an average reduction of 91% (shallow) and 86% (deep) from 2001 to 2003. However, the reduction of TCE concentrations began to decline, and was negligible by 2012–2013 in both the shallow and deep overburden. Further evidence of a reduction in reactivity towards TCE includes the presence of elevated levels of intermediate compounds, such as cis-1,2-DCE, in the downgradient wells beginning in 2012 (shallow and deep). Water quality indicators such as dissolved oxygen and ORP showed continuing reactivity, with oxygen as the preferred electron acceptor, until about 2020. By 2021, data suggests that no chemical reduction was occurring in groundwater passing through the PRB.

Since 2014, the shallow aquifer downgradient of the PRB has consistently contained higher levels of TCE than the upgradient shallow aquifer. Two possibilities include vertical migration upwards from the deeper aquifer, where TCE concentrations are higher, and desorption of TCE from soil or PRB construction materials. The possibility of vertical migration is supported by the timing of increased TCE concentrations, as it corresponds to the loss of TCE reduction reactivity in the deep PRB and subsequent rise in deep overburden TCE concentrations. However, there is no significant vertical gradient in this area, based on water level measurements in PM-5S and PM-5D. Conversely, desorption is possible given the historically high values of TCE flowing into the PRB, but one would expect rebound due to desorption to have occurred earlier, especially given the loss of reactivity in approximately 2008.

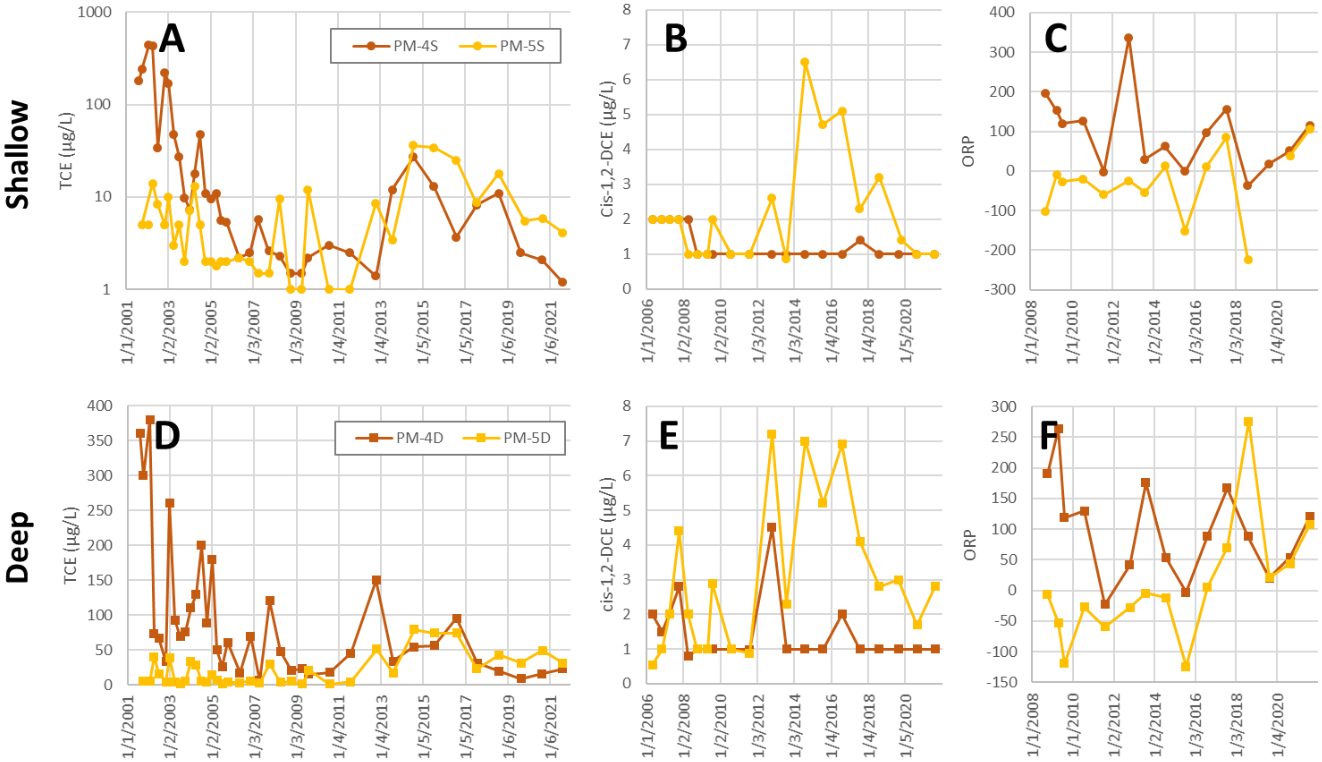


Figure 8. A decline in TCE concentrations across this section of the PRB was apparent until about 2012 (A,D), when cis-1,2-DCE concentrations began to increase in the downgradient wells (B,E). ORP data indicate that PRB reactivity was negligible as early as 2019–2020 (C,F).

PM-2/3: Good Performance

The upgradient/downgradient wells PM-2 and PM-3 are the northernmost set of monitoring wells installed to evaluate PRB performance, and are located near the intersection of Glover Road and Central Avenue. The shallow and deep wells at PM-2 (upgradient) and PM-3 (downgradient) have both demonstrated good PRB performance over the 20 years of PRB operations. In the years immediately following PRB installation, upgradient TCE concentrations were up to 420 (shallow) and 330 (deep) µg/L (both in January 2002). Downgradient of the PRB, concentrations were generally less than 15 µg/L, with a few exceptions. During the first 5 years of operations, TCE concentrations were reduced by an average of 67% (shallow) and 76% (deep) across the PRB.

Over the past 5 years (2016–2021), evidence of effective TCE reduction includes a decrease in TCE concentrations (average reduction of 68% in deep groundwater and 73% in shallow groundwater), very low concentrations of dissolved oxygen in downgradient groundwater, and nondetectable concentrations of reductive dechlorination intermediates (e.g., cis-1,2-DCE and vinyl chloride).

The upgradient concentrations in both the shallow and deep wells declined significantly between 2001 and 2003, likely due to treatment at the source area (specifically, implementation of a recovery well in 1993). Because of this decline, the “inlet” concentrations at this section of the wall have been lower than other portions of the wall, meaning the actual residence time required to achieve the remedial goal has been lower than the designed residence time for most of the PRB lifetime (e.g., the wall thickness is larger than needed).

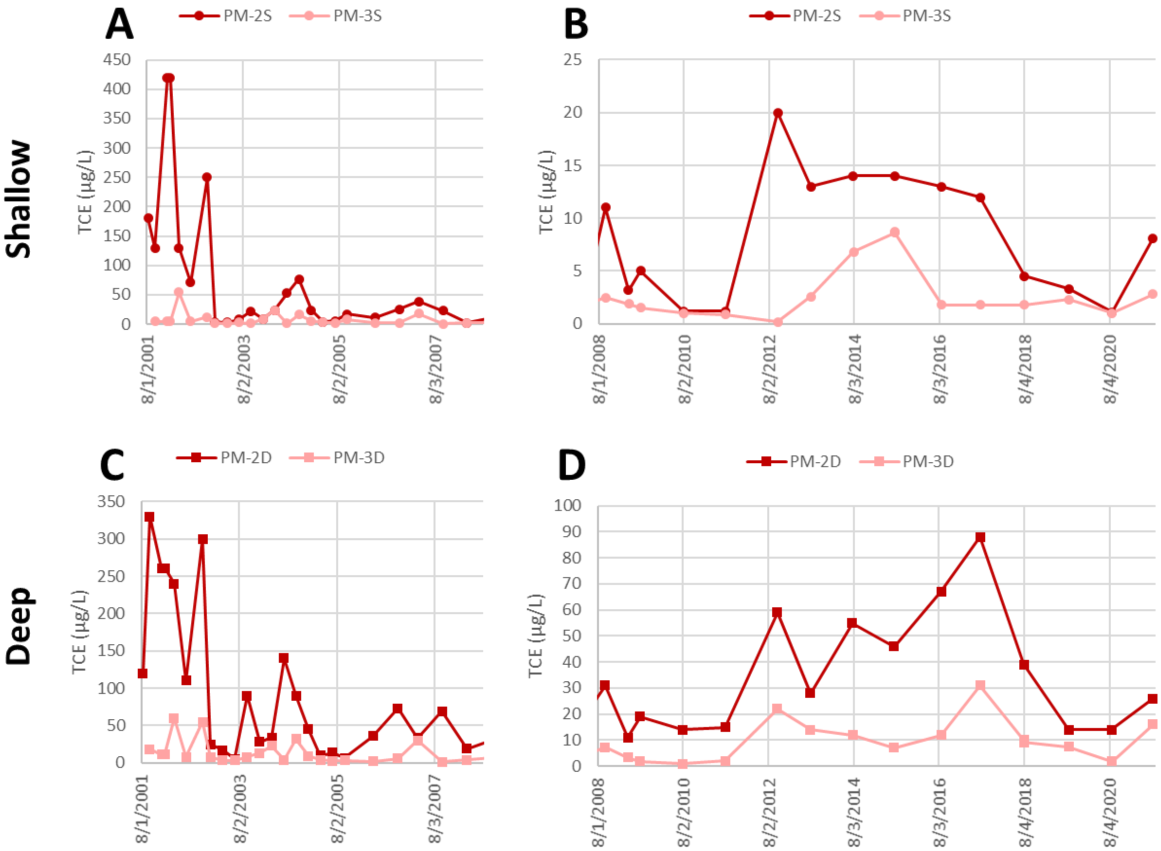


Figure 9. The PRB effectively reduced TCE concentrations in the shallow (A-B) and deep (C-D) groundwater at PM-2 and PM-3.

Evaluation of Reactivity Loss

The PRB thickness (and volume of ZVI) was designed to ensure sufficient residence time to reduce TCE to concentrations below the remedial goal based on the kinetics of the TCE reduction reaction. Specifically, the upgradient concentrations, average groundwater velocity, contaminant half-life, and remedial goals were used to calculate the required thickness of the reactive layer for Zone A and Zone B (EnvironMetal Technologies 1999). After supplemental hydraulic conductivity measurements, the minimum required thicknesses of Zone A and Zone B were calculated to be 1.7 ft (27-hour residence time) and 0.5 ft (10-hour residence time), respectively (HLA 2000). It does not appear that any calculations were performed to estimate the lifetime of the PRB or the total mass of chlorinated volatile organic compounds that could be reduced by the mass of ZVI emplaced within the PRB.

Iron Consumption

Given that iron is consumed during the reaction that reduces TCE to ethene, we calculated the theoretical maximum mass of TCE that could have been destroyed, assuming all iron was consumed. This calculation required knowledge of the initial volume of iron placed in the PRB, the iron density, reaction stoichiometry, and molar masses. The concentration of dissolved oxygen was also used, as it is an order of magnitude higher than even the most conservative TCE concentrations, and thus the primary electron acceptor within the PRB.

The total backfill areas associated with areas A and B were presented in the PRB Construction Completion Report (Geo-Con 2002). Multiplying those areas by the effective ZVI thickness associated with each area yields the volume of ZVI placed within the PRB, and further multiplication by the density results in the mass of ZVI in the PRB. Division by the molar mass and multiplication by a factor of 2 (because each iron atom can contribute 2 electrons) yields the total "electron supply" contained within the PRB.

Then, average dissolved oxygen and TCE concentrations were converted to "electron demand" in mol/L using their respective molar masses and the stoichiometry of the TCE reduction reaction (Figure 3). An average flow rate, taken from the design calculations (HLA 2000), and the cross-sectional area of the PRB were used to calculate the 20-year "electron demand" for both TCE and dissolved oxygen (assuming constant concentrations of both constituents over time). Values used in the calculation are presented in Table 1.

The calculations are not sensitive to the TCE concentration because the predominant electron acceptor is oxygen; each dissolved oxygen molecule accepts four electrons and the oxygen concentration is an order of magnitude higher than the concentration of TCE (which accepts 6 electrons to produce ethene). Products of oxygen reduction include hydrogen peroxide, water, and potentially the hydroxyl radical, and are shown in Figure 10. Iron cations react with dissolved oxygen species to generate a range of solid iron oxides and hydroxides, some of which precipitate on the ZVI surfaces.

Table 1. Values used to calculate the maximum theoretical TCE mass reduced.

Electron Demand Calculations		**Electron Supply Calculations**	
TCE concentration (ug/L)	300	Zone A: area backfilled (sq ft)	5500
O_2 concentration (mg/L)	4	Zone A: Effective Fe thickness (ft)	1.7
TCE molar mass (g/mol)	131.4	Zone B: Area backfilled (sq ft)	11,478
O_2 molar mass (g/mol)	32	Zone B: Effective Fe thickness (ft)	0.5
electron demand (mol/L)	0.00051	Total Fe volume (cu ft)	15,089
Groundwater velocity (ft/day)[a]	1.5	Fe density (lb/cu ft)	185
PRB cross-sectional area (sq ft)	16,978	Fe molar mass (g/mol)	55.85
Groundwater flow rate (L/day)	721,142	Electrons donated per Fe[b]	2
20-year electron demand (mol)	**2,704,282**	**Total electron supply (mol)**	**45,300,000**

a. The average groundwater velocity was calculated from Table 2 in HLA (2000).

b. Each iron atom may donate 2 or 3 electrons. Assuming an average of 3 electrons donated per Fe results in a 33% larger total electron supply.

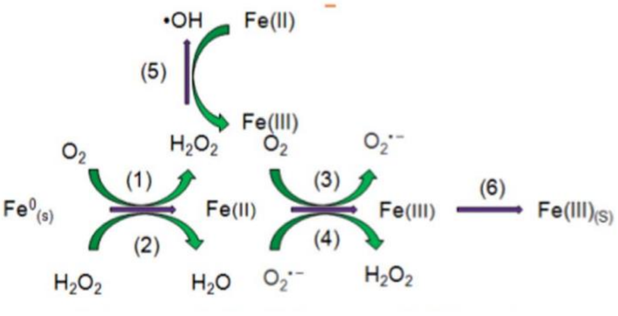


Figure 10. Oxygen reduction reactions in the presence of ZVI (from Guan et al. 2015).

The dominance of oxygen as an electron acceptor in this system means that we would *not* expect areas of the PRB that saw higher TCE concentrations to lose reactivity faster, as the oxygen concentration drives iron consumption rather than TCE. Also, it's not critical to accurately capture the influent TCE concentration at any given time. Conversely, it is important to correctly characterize the influent dissolved oxygen concentration; the calculations are very sensitive to oxygen concentration. We took an average of the dissolved oxygen values that we had tabulated for each upgradient well and found a range of 3–4 mg/L; to be conservative, we used a value of 4 mg/L in the calculations.

A comparison of "electron supply" (based on the mass of ZVI emplaced within the PRB) and "electron demand" over 20 years (based on conservative assumptions about the reduced species passing through the PRB) shows that the supply exceeds the demand by a factor of approximately 17, which is likely indicative of a degree of "waste" inherent in PRB technologies (though there is a large range of uncertainty in the calculations). Though much of the TCE reactivity loss was observed 5–10 years after installation, oxygen reduction continued in these wells for additional years (e.g., until about 2019 between PM-6S/7S), which is consistent with oxygen being the preferred electron acceptor compared to TCE.

Passivation and Short Circuiting

The theoretical supply and demand of electrons discussed above is predicated on uniform flow of contaminated groundwater through homogeneous and isotropic ZVI and sand media, where all installed iron is within active flow channels and where reactions continue to occur until all iron is oxidized to Fe^{2+} or Fe^{3+}. This idealization is simplified and unrealistic because a number of actions occur to impede or prevent the full consumption of the ZVI incorporated into the PRB.

Problems began with the initial installation of the wall, which involved the mixing and placement of ZVI and sand into the subsurface. The presence of boulders and premature "slurry breaks," as previously discussed, can lead to the creation of preferred flow paths through the wall. Even with perfect installations, bedrock and formation conditions can lead to flow under or around the PRB, or the creation of preferred flow paths horizontally and vertically within the installation. These preferred flow paths are short circuits that overload and increase velocity in the active flow channels, with a concomitant underutilization of ZVI in low-flow and "dead end" pathways.

Within the active flow pathways, precipitation of carbonate minerals or iron (oxy)hydroxides may over time coat unreacted iron surfaces, reducing the surface area available for reaction with TCE. This "passivation" phenomenon impedes the transfer of electrons from the ZVI but does not clog pore spaces or change flow patterns. Initial signs of this process can be the appearance of intermediate breakdown products in downgradient wells, such as cis-1,2-DCE.

Finally, and perhaps most importantly, the accumulation of precipitates over time can physically clog pore spaces in the sand/ZVI mixture, which can further change groundwater flow paths and velocities through and within the PRB (Figure 11). Precipitate accumulation can reduce residence times and deplete reactivity in the flow paths, and prevent contaminated groundwater from contacting "fresher" ZVI. Based upon the analysis of core samples from a 3-year-old PRB of similar length, depth, thickness and construction, researchers in Italy estimated a "pore reduction rate of 4.9% per year" from mineral precipitation, which was expected to decrease over time due to the passivation of the ZVI (Zolla, 2009). Predictions of this nature are however highly site-specific, based upon groundwater chemistry and biochemistry, and in particular the concentrations of bicarbonate, sulfate, chloride, and nitrate.[4] Of equal or greater concern is the clogging of pore spaces by the overgrowth of bacteria within the iron/sand media; at the PRB in Italy, slug testing within the barrier suggested a reduction in hydraulic conductivity of two orders of magnitude in its third year of operation (Zolla, 2009). Notably, this PRB was constructed using a biopolymer slurry technique utilizing guar gum, like the Needham installation, and researchers indicated that the residual byproducts of guar gum degradation, such as glucose, "may have greatly enhanced" microbial activity (Zolla, 2009). Other researchers have also noted potential issues with reduced permeability in PRBs due to biomass, especially at the upgradient formation/PRB interface, but have noted that biofouling had not been an issue of concern at most ZVI PRB sites (ITRC, 2011).

The clogging of PRB pore spaces can lead to an increase in hydrostatic pressure and groundwater mounding on the upgradient side of the PRB. Though the data suggest that byproduct precipitation has reduced the iron surface area, there is no indication of significant groundwater mounding on the upgradient side of the PRB.[5]

Short circuiting, resulting in shorter residence times and incomplete reaction, can also result from construction-related issues. As previously identified by Richards (2008), there has been evidence of contaminated groundwater moving through the PRB with minimal change in chemistry since at least 2002. In particular, the areas where short circuiting appears to occur are near PM-8D/9D and PM-6D/7D. At both locations, the data have indicated poor performance for nearly the entire lifetime of the PRB, suggestive of construction-related short-circuiting.

In other areas of the PRB, including the shallow and intermediate mid sections PM-6/PM-7 and PM-4/PM-5, performance

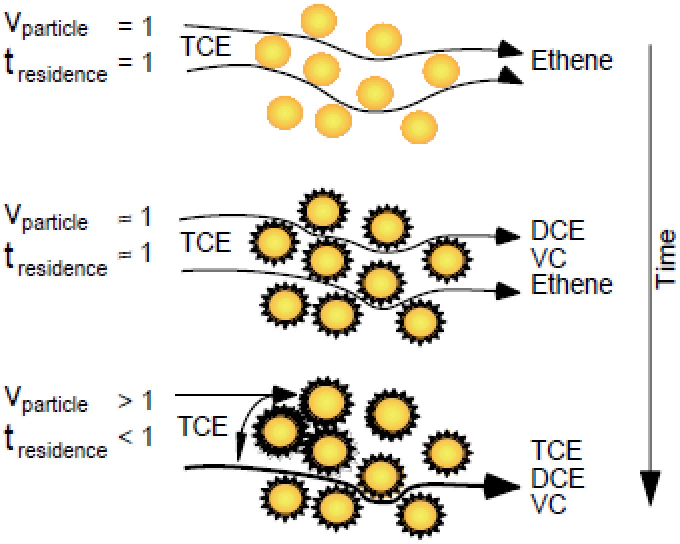


Figure 11. Diagram of surface passivation/pore clogging and its impact on PRB reactivity (from EPA 1998).

---

[4] Unlike the Needham PRB, groundwater at the site of the PRB in Italy had low D.O. (mean = 0.35 mg/L) and high sulfates (mean = 150 mg/L).

[5] Water level gauging has not been consistently performed/reported since 2013, but available data indicate that any potential increase in groundwater elevation on the upgradient side of the PRB is well within the range of variability observed during the initial 5 years of operations.

gradually declined over time, suggestive of passivation potentially followed by progressive pore clogging. The northern portion of the PRB, in the vicinity of PM-2/PM-3, performed well over an extended period of time, but eventually showed signs of passivation, clogging, and iron consumption.

The significance of DO concentrations in groundwater upgradient of the PRB is also evident in the review of performance data, most notably in Figure 5, where increased influent DO is correlated with increased levels of TCE and degradation products in downgradient wells. Presumably, there was insufficient ZVI and/or residence time to degrade both oxygen and chlorinated contaminants, with oxygen “outcompeting” TCE.

Downgradient Sentinel Wells

As discussed earlier, the PRB was installed with the goal of protecting the Wellesley water supply wells from the migrating TCE plume that originated at the MDL property in Needham. Before the PRB was installed, TCE concentrations near Central Avenue were as high as 1,100 µg/L (CW-19D in November 1996) and >200 µg/L on the west/downgradient side of Central Avenue (e.g., CW-22D in August 1996). The TCE plume extended beneath the surface water body slightly south of the wellfield (Figure 1) with concentrations up to 13 µg/L (CW-91D in May 1997).

There is evidence that TCE concentrations downgradient of the PRB began to drop even before the PRB was installed, particularly in the centerline of the plume where concentrations were highest. For example, at well CW-22D, the average TCE concentration was 159 µg/L between 1996 and 1998. From 1999–2001, the average TCE concentration was 49 µg/L. The comparison is not perfect because sampling was initially quarterly, so there are more data points representing a range of seasons in the 1996–1998 range; however, the available data do not indicate that seasonal trends could account for the observed difference in 3-year average concentrations.[6] Other wells showed significant variation in TCE concentrations, such as CW-33S (ranging from 2–200 µg/L in 1996–1998 with a mean concentration of 80 µg/L). The cause of TCE variability in this particular well may be related to relative surface water levels: the well is located close to Rosemary Brook, which appears to recharge groundwater in this area (the vertical gradient is downwards).

Though it’s not possible to know if TCE concentrations downgradient of the PRB would have continued to decline in the absence of the PRB, it’s clear that a rapid decline occurred one–two years after the PRB was constructed. Such a decline was most apparent in deep wells, such as CW-22D (94% decline from July 2001 to July 2002), CW-23D (98%). In shallow wells MW-26S and CW-33S, the decline in TCE concentrations occurred over two years (94% and 92% reduction in TCE, respectively). During the initial years post-installation, upgradient TCE concentrations were still very elevated, so it is likely that the downgradient reductions observed during this time result from successful treatment within the PRB. TCE concentrations versus time for are shown in Figure 12.

Over the long term, concentrations downgradient have remained generally below the remedial goal of 5 µg/L. All deep wells examined during this review contained <10 µg/L since July 2003 and <5 µg/L since

---

[6] When sampling was quarterly, two of the three highest concentrations were detected in August, the third was in February. Annual sampling was (and still is) conducted during the summer months, when concentrations were historically elevated relative to other seasons.

July 2005 (with 3 exceptions).[7] Exceedances of the remedial goal were more common in the shallow groundwater, occurring in 2008, 2009, 2012, and 2019. Higher performance in the deep overburden is somewhat surprising, as the PRB was less effective at treating this interval due in large part to apparent short-circuiting near PM-9D and PM-7D. Importantly, it's clear that downgradient mixing/dilution effects were sufficient to mitigate the possible preferential flow paths that allowed contaminated groundwater to pass through the PRB with minimal TCE reduction.

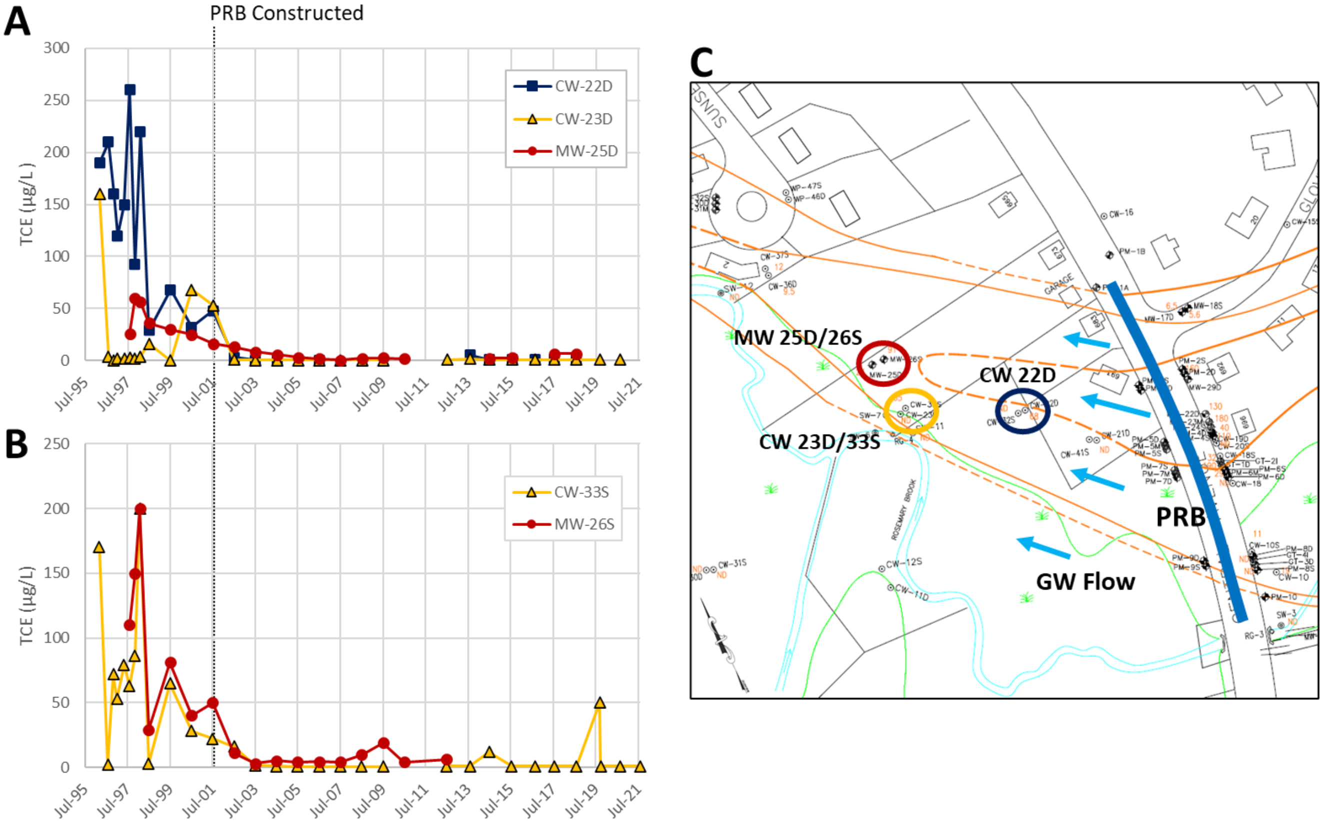


Figure 12. Downgradient of the PRB, deep (A) and shallow (B) wells contained less TCE after the PRB was installed. The wells reviewed are located within the historical TCE plume (C) (data from 1999/2000).

Conclusions

In the 1990s, a TCE plume over 4,000 ft long stretched from the MDL property in Needham nearly to a water supply wellfield used by the Town of Wellesley. Response actions were taken at the MDL property beginning in 1993 with the installation of three recovery wells. However, there was significant uncertainty regarding the travel time between the MDL property and the wellfield, with estimates exceeding 25 years, and concern that the TCE plume could continue to grow in area and magnitude. Thus, MassDEP evaluated options for plume treatment, and decided to install a PRB to intercept the plume upgradient of the wellfield. The PRB was installed in the summer of 2001.

---

[7] Well CW-22D contained 5.2 µg/L TCE in August 2013; TCE was not detected in 2014–2018, and the well has not been sampled since 2018. Well MW-25D contained 6.4 µg/L in 2018–2019, but has not been sampled since and was not located during the most recently sampling event (Lord 2021).

To evaluate the performance of the PRB 20 years post-installation, we reviewed groundwater data (chemistry and water level elevations) from up and downgradient of the PRB, as well as historical design and construction documents. The primary conclusions are:

- TCE concentrations declined at many upgradient wells soon after the PRB was installed (2001–2004), likely due to recovery well operations that began at the MDL property in 1993. This decline occurred earlier than expected because the contaminant travel time from the MDL property was faster than predicted. For example, the travel time from the MDL property to Central Avenue was expected to be >25 years, but data from the early 2000s suggested a much shorter travel time of 8–11 years.
- TCE concentrations in downgradient "sentinel wells" located between the PRB and the wellfield declined before the PRB was installed, though levels were still an order of magnitude above the drinking water standard of 5 µg/L. The cause of this decline is not clear. Some wells showed significant variation, possibly resulting from interactions between groundwater and surface water. TCE concentrations declined significantly (>90%) in the 1–2 years after the PRB was installed. This decline is attributable to the installation of the PRB.
- With two exceptions, the PRB was initially very effective at reducing TCE concentrations in groundwater passing through it. However, the reactivity in the center of the plume, where TCE concentrations were highest, began to decline and the PRB was no longer effective at reducing TCE concentrations 5–10 years after installation. The northern and southern portions of the wall are still reactive and appear to be reducing TCE (though there is evidence that reactivity is declining).
- Construction issues, including problems with a loss of slurry viscosity—and the steps needed to address these problems—appear to have adversely impacted the short and long term effectiveness of the PRB.
- Data from the downgradient sentinel wells indicate that long term performance has been acceptable, with most sentinel wells containing TCE < 5 ug/L since 2005. Importantly, the PRB was effective at reducing TCE concentrations when upgradient concentrations were most elevated, especially from 2001–2003.
- Despite nearly two decades of poor performance at two locations on the PRB, downgradient mixing and/or dilution mitigated the portion of contaminated groundwater that passed through the PRB, such that concentrations in sentinel wells declined below their pre-PRB concentrations.

Most importantly, the Wellesley wellfield has been protected from the TCE plume. The data indicate that the PRB effectively reduced TCE concentrations and cut off the plume, at least during the initial 5–10 years of operation. The subsequent reduction of upgradient TCE concentrations, presumably due to source-area treatments at the MDL property, has reduced the need for the PRB. However, TCE concentrations on the upgradient side of the PRB remain above 5 µg/L, and elevated concentrations of TCE are still present in upgradient groundwater (specifically at the Hillside School). Thus, it may be premature to state that the PRB can be abandoned, and monitoring in this area should continue to ensure the wellfield remains protected.

References

Cygnus 2000. Final Phase II Comprehensive Site Assessment Report: Microwave Development Laboratories, Inc. Site. 101–145 Crescent Road, Needham, Massachusetts. Volume 1. RTN # 3-0386. June 30. 430 pp.

EnviroMetal Technologies Inc., 1999. Potential Application of Permeable Reactive Barrier Technology to VOC Plume Remediation at Needham, MA. August. 9 pp.

EPA, 1997. EnviroMetal Technologies, Inc. Metal-Enhanced Dechlorination of Volatile Organic Compounds Using an Above-Ground Reactor Innovative Technology Evaluation Report, EPA/540/R-96/503, 94 pp.

EPA. 1998. Permeable Reactive Barrier Technologies for Contaminant Remediation. Office of Research and Development. EPA/600/R-98/125. 102 pp.

Geo-Con. 2002. Construction Completion Report, Permeable Reactive Barrier Installation. Microwave Development Laboratories, Inc., Site. Needham, MA. MADEP Project #BWSC-2000-001. July 15. 567 pp.

Guan, X., Y. Sun, H. Quin, J. Li, I.M. Lo, D. He, and H. Dong. 2015. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding counter measures: the development in zero-valent iron technology in the last two decades (1994–2014). *Water Research* 15:224–248.

HLA. 2000. Letter re: Permeable Reactive Wall (PRB) Flow Through Thickness, Microwave Development Laboratories, Inc., Site, 101-145 Crescent Road, Needham, Massachusetts. Release Tracking No.: 3-0386. From Harding Lawson Associates. To Mr. Stephen Johnson, MassDEP. January 7.

ITRC (Interstate Technology & Regulatory Council). 2011. Permeable Reactive Barrier: Technology Update. PRB-5. Washington, D.C.: Interstate Technology & Regulatory Council, PRB: Technology Update Team. 234 pp.

MassDEP. 2022. Evaluation of In Situ Chemical Oxidation at the MDL Site in Needham. MassDEP RTN 3-386. June.

Richards. 2008. Seven-year Performance Evaluation of a Permeable Reactive Barrier. *Remediation Journal: The Journal of Environmental Cleanup Costs, Technologies, & Techniques* 18(3):63–78.

Woodard & Curran. 1997. TCE in Groundwater, May 1997, Geologic Cross Section H-H’. Rosemary Meadow, Wellesley, Massachusetts. 1 pp.

Zolla et. al., 2009. Hydrogeochemical and Biological Processes Affecting the Long-term Performance of an Iron-Based Permeable Reactive Barrier, *J. Environ. Qual*. 38:897–908