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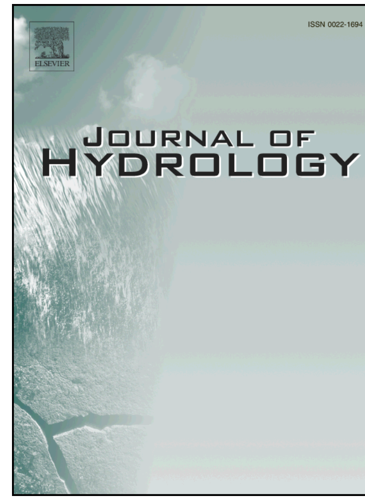

Research papers

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Actively Facilitated Permeable Reactive Barrier for Remediation of TCE from a Low Permeability Aquifer: Field Application

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Declarations of interest

None

Abstract

Proven in situ treatment and remediation approaches are limited for low-permeability aquifers materials, particularly because of limitations to the delivery of reactive chemicals or access to contaminated plumes. In this paper, we describe the development of a cutting-edge solution for the remediation of contaminated groundwater in a low-permeability and low water-bearing aquifer contaminated with the chlorinated hydrocarbon trichloroethylene (TCE). The remediation technique introduced coupling of large-diameter permeable reactive barrier wells (PRB wells) with: (1) extraction wells through in a highly impacted plume; and (2) re-injection wells at the fringe of the plume. A pump-and-treat system (PTS) was employed at the site in a separate plume to reduce the mass of TCE near the second source zone. This research focuses only on the large diameter PRB well system. Conceptual site model development, design considerations, implementation and performance evaluation demonstrated how each of these elements were applied in the field. Approaches for coupling technologies to increase technical and economic feasibility are presented. Extraction and reinjection wells of treated groundwater at the fringe of the plume promoted a positive hydraulic gradient, facilitated groundwater transport through the reactive media, and contained the plume. Detailed geospatial and statistical analysis with over 10 years' monitoring data showed that dissolved TCE plume delineation shrank, and still concentration continues to decline, and were projected to meet the demands of remediation compliance regulations in the next few years. The results of this study indicate that significant remediation was achieved despite the challenging hydraulic conditions of the aquifer. The developed the remediation technology and conclusions indicate the system's usefulness at other sites.

Keywords: permeable reactive barriers; groundwater; remediation; trichloroethylene; low hydraulic conductivity

1 Introduction

Volatile organic compounds (VOCs) are currently regarded as some of the most widely occurring environmental contaminants due to their widespread production and use as organic solvents and hydrocarbon fuels (Geller et al., 2000; Grandel and Dahmke, 2004). Remediation of trichloroethylene (TCE) contamination of groundwater is a priority as it occurs frequently at industrial sites and has been identified as a likely human carcinogen (Chiu et al., 2013; U.S. EPA, 2012a). There is much interest in sustainable, low-cost and environmentally benign groundwater remediation techniques for complex aquifer systems. Selecting the appropriate remediation technology to decontaminate groundwater depends on the chemistry of the contaminants and site-specific conditions, as well as technology performance, cost, sustainability of the process, operation & management of the remediation etc., (He et al., 2006; Hyman and Dupont, 2001; Naidu, 2013).

Environmental remediation denotes the process and result of removing or lessening the negative impact of pollution or contaminants from environmental media in the subsurface (soil, rock, or groundwater)(Warner and Hadley, 2015). Remediation of contaminated sites with complex aquifer systems such as those with low to moderate permeability materials, fractured rock aquifers and slow groundwater flow velocities require significant improvements on existing conventional *in situ* remediation approaches. The potential for aquifer remediation decreases with increasing complexity of aquifer systems migration behavior, economics and presence of sensitive receptor. In 1993, the U.S. EPA issued technical impracticability (TI) waiver guidance (U.S. EPA, 1993) and in Australia state regulators have shown a growing interest in an informal concept of 'clean-up to the extent practical' (CUTEP) (Fowler R and Cole D, 2010). The U.S. guidance specified that waivers were appropriate for sites where the Agency deemed that remediation to drinking water standards is impractical. By August 2012 the U.S. EPA issued 91 TI waivers, 85 of which applied to groundwater (U.S. EPA, 2012b). The majority (67%) of the TI waivers granted related to volatile organic compound contamination.

Over the last four decades technical advances in the remediation of groundwater have resulted in impressive innovations and the application of technical and economic solutions at more complex contaminated sites (Hyman and Dupont, 2001; Leeson et al., 2013; Naidu, 2013). The past 30 years of research have focused heavily on the development of *in situ* treatment technologies (ITRC, 2011) such as permeable reactive barriers (PRB). The first passive *in situ* treatment method introduced consisted of permeable reactive barriers (PRBs) using granular zero-valent iron (ZVI), which are still considered as state-of-the art (Naidu et al., 2014).

A variety of PRB configurations have been employed. Zero valent iron (ZVI) has been the most common reactive medium for PRBs, a continued effort to develop new reactive materials resulted in a range of other PRB materials for the remediation of organic (zeolite, activated carbon, clays, and Ferrous minerals etc.) and inorganic contaminants (activated carbon, bauxite, peat, and exchange resin etc.) has been employed (ITRC, 2011; Thangavadivel et al., 2013; Thiruvenkatachari et al., 2008; Warner et al., 1994). The major drawback, however, is that PRBs efficiency depends on the rate and volume of groundwater passing through the reactive media (Dermont et al., 2008). This has two direct impacts: firstly, the extended duration of the remediation; and secondly, availability of land for resale or reuse. The applicability of conventional PRB and pump-and-treat (PTS) techniques is critically limited by the hydraulic gradient and conductivity of aquifers, and are not suitable for sites with limited water-bearing and low-permeability units or strata.

In order to design an effective groundwater remediation technology for complex contaminated aquifers there has been recent recognition that a combination of two or more approaches, i.e. incorporating both active and passive systems, and *in situ* and *ex situ* methods (Hudak, 2018; Roehl et al., 2005). Multiple technologies applied concurrently or sequentially are often referred to as treatment trains, and are usually developed to address overall site remediation. It is recognized that no single specific remediation technology can be considered as a solution for all contaminated site problems (FRTR, 2007; Khan et al., 2004). Remediation technology implemented at most contaminated sites is not a stand-alone or one-size-fits-all remedy; it is in fact generally part of a treatment train.

Cases studies on the commonly used pump-and-treat system (PTS) technologies shows that it rarely restored sites that had contaminated groundwater to background conditions (USEPA, 1989;

USEPA, 1992). One of the most promising remediation technologies is the use of PRBs with deep trench filled with reactive material(s) to intercept and decontaminate plumes in the subsurface. In the last decade, there has been an extensive activities directed at the development and implementation of PRBs (Thiruvenkatachari et al., 2008). In this paper, we present an innovative technique that achieves remediation of contaminated groundwater in a low permeability and low water-bearing aquifer. The technology has been fully demonstrated to field-scale application from laboratory-scale tests. The innovative technology is based on an efficacious, green-remediation technique coupling passive and active methodologies powered entirely by solar power as an energy source. Grundfos stainless steel solar operated submersible pump with the level controller and Programmable Logic Controller (PLC) connection, with dry run protection, and a 750 watts panel GF100 fixed solar array with IO-101 AC interface backup which allows a generator or 240-volt interface. This replicated system is used for the group of nearby recirculation wells. The field testing of facilitated permeable reactive barrier wells (PRB wells) remediation was monitored for over 10 years, fostering an understanding of how the coupled remediation technique will lead to more effective protocols. This specifically refers to the clean-up of contaminated sites with complex hydrogeological settings.

This paper focuses on demonstrating the progress of remediation with long-term groundwater monitoring geospatial and statistical data analyses. Understanding the progress of remediation is very important so that the potential design and implementation of the technology can be applied to other sites. A comprehensive overview of the remediation technology development, field scale-up and remediation progress to date are reported.

2 Site Description

The remediation technology was tested at a Australian Department of Defence, Royal Australian Airforce (RAAF) Base in South Australia. The site was contaminated with chlorinated solvents, and in particular trichloroethylene (TCE), which originated from a long history of degreasing activities. The site was used previously an explosives factory when built in 1940 and included the manufacture of explosives, the assembly of components, and the filling of various forms of ammunition. Although the explosives factory was operational for only a short time (between 1941 and 1945) the site was subsequently used for other defence operations. The TCE had spread over an area of around 20 hectares and has an average water table depth 20 m below the ground surface with a saturated thickness up to 7 m.

The high-concentration TCE source areas throughout the site are documented as two separate source locations. During detailed site investigations TCE concentrations at these source locations ranged from 400 to 8,890 μg/L (Figure 1). TCE is the primary contaminant of concern, and some of its biodegradation products (- 1,1-, cis-1,2- and trans-1,2- dichloroethylene [DCE]) were also detected. The site characterization for soil contamination using spilt core driller samples were taken at vertical discrete interval of 50 cm in the unsaturated zone near at the source area. The soils samples were below laboratory reporting limits which demonstrated that TCE is present only in the dissolved phase. Subsequently, there are no ongoing contributions to sources at the site. Similarly, in the plume area dissolved TCE concentrations in groundwater were significantly lower than the solubility limits indicating that TCE was not present as a dense non-aqueous-phase liquid.

3 Geology and Hydrogeological setting

The site comprises three aquifers located on the lower Adelaide Alluvial Plain (South Australian Dept of Mines and Energy, 1989). The system can be considered as a continuous multilayered aquifer with the "upper aquifer" or "middle aquifer" which is bounded both laterally and at the base by dense thick clayey deposits. The upper phreatic aquifer developed in Quaternary sediments of mixtures of silt and clay and has a saturated thickness varying up to a maximum of 6 m with low hydraulic conductivity (K), Porosity (which is a measure of the water-bearing capacity of formation) and hydraulic gradient. The measured K values are between $4.8*10^{-7}$ m/s and $5.2*10^{-9}$ m/s. The average of the slug tests in four other wells amounts to $3.7*10^{-7}$ m/s with a fluctuation range of ½ decimal power. The conductivity tests are consistent and lead to rather uniform hydraulic conductivity values that are typical for clays and clayey silts indicating a low to very low hydraulic conductivity of the aquifer. The average hydraulic gradient prior to remediation activity was approximately 0.001 in the vicinity of the plume. The groundwater seepage velocities range from less than 0.1 m/day to more than 1 m /day. The middle aquifer is developed in sandy clay eluvium of massive granite. It is separated from the upper aquifer by a 1.0– 4.0 m thick high plasticity dense clay layer. The thickness of the saturated confined middle aquifer is 5 to 7 m. Recharge is due in part to subsurface contributions from the surrounding catchment and in part to direct local infiltration of precipitation from the surface.

Most of the land is currently covered with grass paddocks and large eucalyptus trees and only a few large buildings are present (Figure 1). The land use at the site has a significant influence on the hydraulic conditions and on dispersal of contaminants. The eucalyptus trees in the area amount to approximately 20% of the surface. The remaining vegetation consists of sparse grassland and paved surfaces including buildings and roads. The climate at the site is slightly arid - the region has evapotranspiration rates of 400 to 500 mm and the average annual rainfall is 429 mm (Bureau of Meteorology, 2018). Evapotranspiration at the site is strongly influenced by the eucalyptus trees due to their deep roots extending more than 8 m below the ground surface. They are able to access the whole unsaturated zone down to the capillary fringe. The contribution of rainfall infiltration to the groundwater hydraulic gradient is lost through evapotranspiration and consequently, natural recharge has limited contribution to the overall groundwater table fluctuation.

Splint examinations with the trees at site 9 have shown that the Eucalyptus spec. ingests the TCE contaminants. Since no contaminants have been detected in the unsaturated zone, this indicates that the suction of the roots reaches the groundwater table. Therefore, we conclude that the trees also influence the position of the groundwater table due to their suction of groundwater. Bearing in mind that there is hardly any inflow of water from the boundaries at site 9, this all-season withdrawal of groundwater (about 0.8 mm/d (Roberts et al., 2001)) may influence the local hydraulic situation significantly.

A comprehensive aquifer testing using slug-tests has been done in a number of monitoring wells as part of the PRB well design. A constant pumping and recovery slug test was conducted from 10 monitoring wells representative of spatial dimensions of the plume and a repeated test to increase the accuracy. Slug tests were conducted using entirely filtered wells (filter screen over the whole aquifer). The groundwater piezometric head for the upper aquifer system (Q1- Aquifer) on March 2007 shows that around the TCE plume and further west there was no, or hardly any, hydraulic decline with minimal flow velocities (Figure 1) thereby limiting the pumping rate of from extraction PRB wells for the contaminant passing through the reactive material resulting in stagnant plume and affect the overall remediation rate. The water table at the site ranges from 12 to 15 m below ground surface.

Figure 1 Baseline groundwater piezometric head of Q1-Aquifer system, March 2007

The groundwater chemistry data analysis using Piper and Schoeller-Berkaloff diagrams for the upper and middle aquifer system indicates that it has Ca-Cl^- facies with high mineral content. The groundwater has brackish to saline with values ranging from 1048 µS/cm to 7754 µS/cm, mean values of 4933 µS/cm and standard deviation of 1487. The groundwater field parameter indicated that the conditions were slightly to highly aerobic with high dissolved oxygen (DO) concentrations (i.e., 4.2±1.4, average± standard deviation), variable oxidation-reduction potential (ORP) values (ranging from -154.3 mV to 140 mV with a mean value of 88±51). The groundwater chemistry revealed high sulfate concentrations (202 ± 57 mg/L), high chloride concentrations (1127 ± 413 mg/L), and low nitrate concentrations (2.5 ± 1.9 mg/L).

4 Environmental contamination site characterization

Detailed hydrogeological data of the Q1-unconfined aquifer (Figure 2) were investigated. The project involved three phases. The initial phase involved detailed site characterization (DSI) necessary for the hydrogeological and hydrogeochemical analyses. Groundwater samples were collected every six months using low flow sampling techniques. Samples were analyzed for field parameters YSI® handheld multiparameter instrument (dissolved oxygen, oxidation-reduction potential, temperature, pH, and specific conductance), geochemical parameters were analysed at the laboratory using Thermo fisher DIONEX Integrion IC, C/N analyzer (dissolved iron, sulfate, nitrate, chloride, phosphate, alkalinity, and total organic carbon [TOC]), and Agilent GC-MS 7693 for volatile organic compounds (VOCs). The DSI results showed that the groundwater at the site was contaminated with TCE, and degradation compounds such as DCE were reported in some samples slightly above the laboratory limit of reporting (LOR) of 25µg/l) and vinyl chloride (VC) were below detection at all time. The groundwater TCE plume distributed with its two source zone indicated in the Figure 2, to the South and North zone of the site. The vertical contaminant concentrations plume showed that Q2- confined aquifer was slightly impacted near source zone. The designed remediation system doesn't target the Q2 aquifer and few monitoring wells were installed and sampled to evaluate on-going impact before and post-remediation activity. The geological characteristics of the aquifer were defined, with particular reference to lithologies and hydrogeological aquifer parameters. In total, 51 groundwater monitoring wells were monitored for over 10 with bi-annual measurements. The major ions and water quality parameters were measured using YSI® tools and the concentrations of TCE and daughter products determined at each monitoring time as recommended by the U.S. EPA (2003). The second phase involved determination of groundwater chemistry and conducting a long-term column study for selecting reactive material and PRB wells design. The third step was the actual construction of two remediation systems on two separate plumes i.e., large PRB wells and source removal using the pump-and-treat system. A traditional PTS groundwater remediation system was installed and operated near the source zone in the south portion of the site, and the PRB wells system were distributed in the northern plume area of the site (Figure 2).

Figure 2 Baseline TCE concentrations plume in Q1 aquifer and source zone location Q1- unconfined Aquifer

5 Column study and pilot test

A reactive material was evaluated in a large column study using contaminated groundwater sampled and transported to the laboratory using airtight canisters to avoid volatilization. During the column tests the water from well MW-902 from TCE-contaminated source area -1 was used. The column test was conducted for 12 months during which performance data were monitored by measuring TCE concentration and daughter products in outflow and in the vertical intervals. The PRB reactive material was selected for long-term *in situ remediation*; its testing and selection have been described (forthcoming Bekele et al., 2018). The reactive material (matCARE-GW^{TM}) used in this research project is developed with enhanced organic matter mixed with rubber chips to enrich the permeability and compressive/compaction strength to the overburden soil. The material was selected based on batch experiment and column tests and the aims here were to:

- Evaluate the effectiveness of the material for sorption and desorption kinetics;
- Check its compatibility with the site's geochemistry, i.e. highly saline and aerobic conditions;
- Estimate the longevity of PRB reactive material were tested in terms of removing TCE; and
- Determine TCE mass reduction in the column test for the source area.

6 PRB well design and full-scale field implementation

In groundwater remediation design, numerical simulation plays a central role (Zheng and Wang, 2002). Detailed site investigation and calibrated groundwater fate and transport model simulations (FEFLOW® 5.1) were set up so that the locations for extraction and re-injection of large diameter PRB wells could be selected. The modeling work for this research study is published by Sreenivasulu (2014). The objective was to achieve effective and rapid remediation of the entire TCE plume with a minimum number of wells, considering the pumping rates of the wells were governed by the low hydraulic conductivity of the aquifer. Using the groundwater flow model, the positions of the extraction wells were selected so as to increase the groundwater flow velocity through connected cones of depression zones for each extraction well, and therefore increase the hydraulic gradient. A totals of 14 extraction wells and 14 re-injection wells were systematically placed down gradient of the dissolved plume (Figure 3). Using the flow model, the re-injection wells was located at the fringe of the plume head and acted as the plume containment within the site boundary. Groundwater model simulation for contaminant plume were implemented to determine the capture zone from particle tracking calculations. The treated water passing through the extraction PRB wells was then re-injected up-gradient of the extraction well network. The extraction well was pump is equipped with dynamic water level data logger which is connected to an automated PLC system. In addition, the extraction pump is programmed with 2 hours pumping per day duration and if the well goes dry the pumping system switched off. The rate of extraction pump is also governed by average aquifer recharge rate which is 1.5 liters per minute. The hydraulic mound resulting from the re-injection wells provided an increased groundwater head gradient towards the extraction wells and also provided a hydraulic containment of dissolved plume migration. Conventional on-site PTS was installed at the south plume in a shipping container and operated through a network of six large diameter extraction and five re-injection wells (Figure 3).

Model simulations, however, revealed that an increase in the hydraulic gradient was only achieved with a large number of extraction and injection wells, because even with maximum pumping and injection rates the cones of depression of groundwater elevation of each well covered only a very small zone. Consequently, a method was devised, based on the simulation results so that the extraction wells were positioned only a short distance with an average of 20 m apart from each other. The cones of depression formed a connected drawdown from the extraction well and mound from the nearby reinjection well enhanced the hydraulic gradient across the plume zone significantly. Whether the whole contaminant plume was captured by the pumping had to be derived from a particle tracking groundwater simulation model. The particle tracking method therefore represents an important control for the correct positioning of PRB wells and re-injection well system.

The hydraulic changes through extraction/injection of groundwater required a long time to exhibit the intended effect due to the low hydraulic conductivity of the aquifer. In order to check this, the groundwater simulations were considered using transient hydraulic conditions. The results show that stable hydraulic conditions are only reached after a duration of about 1 year. The extraction and re-injection of water in large-diameter PRB wells were constructed in order to: firstly, clean up the inner zones of the plume; and secondly, select the best positioning of the PRB wells to ensure they were distributed evenly in the center. This has to be considered in the remediation design (Sreenivasulu et al., 2014).

The system was fully automated, controlled and monitored by a programmed logic control system. The primary focus of the research was applying large-diameter PRB wells coupled with active remediation systems. It was implemented at and around source zone 1 (Figure 3).

Figure 3 Optimised locations of extraction and re-injection wells, PTS remediation near the south-eastern corner of the site and PRB wells at the northern section of the site

An active-and-passive PRB wells system comprised of twelve large diameter extraction wells (1.5 m) and twelve injection wells (1.2 m diameter) were installed to depths of 15 m to 16 m below ground surface (bgs). The extraction and re-injection wells were installed as close as practically possible to locations identified in the groundwater model simulation, so as to maximize TCE contaminant recovery. The method of well construction included drilling using a civil construction piling rig fitted with 1.5 m and 1.2 m augers, as illustrated in Figure 4. A machine- slotted 150 mm diameter UPVC riser was placed in the centre of each drilled hole and backfilled with PRB reactive material to approximately 2 m above the extraction wells' water table, and, for injection wells, backfilling 50 mm aggregate to approximately 2 m above the water table. Geotextile was placed on the top of the reactive material and aggregate and backfilled with natural soils to 1 m below the soil surface. Following the completion of the wells, electric pumps and associated electrical and plumbing equipment were installed to facilitate the pumping of groundwater through the reactive media. A programmable logic controller was installed in a dedicated control panel and its operation was fully automated.

Figure 4 Large diameter PRB well system

7 Results and Discussion

Remediation performance was determined by routine sampling and analyses of groundwater from 54 wells inside and outside the remediation area for over a decade. Following the placement of the PRB wells the groundwater geochemistry has shown a change in few monitoring wells in particular increases in the total organic carbon (TOC), DO, and ORP. This can be explained by groundwater reducing conditions generate from the biodegradable products.

7.1 PRB wells coupled with the active system – groundwater hydraulics

The local hydraulic conditions and groundwater velocity that govern the performance of the PRB system for TCE removal were enhanced by the extraction and re-injection system. The limitations of aquifer hydraulic conditions were alleviated, thus facilitating the transport of contaminants to the large-diameter PRB wells (Figure 5). The DSI report for aquifer testing showed that the average hydraulic conductivity derived from the slug and aquifer pumping tests in four wells was 3.7x10-7 m/s. The hydraulic conductivity tests showed uniform values typical for clays and clayey silts, thereby showing low to very low hydraulic conductivity of the aquifer. Consequently, the aquifer can only be treated as a limited water-bearing stratum rather than a conventional aquifer. The hydraulic gradient increased considerably from the initial condition (Figure 1) with the groundwater flow as part of the connected flow towards the zone of depression (Figure 5).

Figure 5 Groundwater peizometric head during the remediation process

The locations and number of proposed extraction and injection wells increased hydraulic containment, thereby stopping the existing contamination plume from spreading any further (Figure 5), with the flow generally towards PRB wells. The re-injection of cleaned groundwater from the PTS and PRB wells at the fringe of the plume increased the hydraulic gradient in areas of high contaminant concentrations. Transport of TCE to the extraction wells was facilitated, as was reducing the spread of TCE (Figure 5). Due to the sediments' low hydraulic conductivity, the hydraulic changes through extraction and injection of groundwater were not revealed quickly. The groundwater monitoring results confirmed that an extensive increase in the hydraulic gradient was achieved with the cones of depression forming a connected drawdown, which enhanced the hydraulic containment significantly, predicted by the modelling.

7.2 Remediation performance monitoring and evaluation of the PRB wells

In general, TCE concentrations in groundwater showed significant declines in the source area over the 10-year monitoring period. The baseline TCE concentrations within the treatment area ranged from 400 to 8,890 µg/L (Figure 2). The average reductions in concentrations of TCE at the case study site during the four years, when the PTS remediation was operating, show that the average concentration at the start (Mar/2009) was 676 µg/l. The concentrations reported at the date when the PTS terminated (Mar/2013), with the same monitoring wells, was 365 µg/l. Hence the approximate reduction was 46% (Figure 6). It is recommended to combine PTS remediation techniques near the source/ high impact zones such that PTS reduce the contaminant loading on the reactive material and improve the longevity of the PRB wells.

In 2010, the monitoring network was expanded from 29 to 54 wells by the installation of additional wells close to the source areas, and led to an increase in the mean concentrations of TCE obtained in July 2010. The TCE geometric mean concentration was adopted to calculate the reduction in concentration in percentage terms, and was calculated as the difference between concentrations at start and end points divided by the average concentration at the start. As shown in Figure 6, the linear regression of the geometric mean concentration with time showed a declining trend. The contribution of rainfall infiltration to the groundwater hydraulic gradient has limited contribution to the overall groundwater table fluctuation, consequently, TCE concentration response to rainfall events as temporal variation is minimal as demonstrated in the figure 6.

Figure 6 Mean and geometric mean groundwater TCE concentrations from 2007 to 2018, with respective linear regression and monthly rainfall records (BoM, 2018).

The TCE concentrations over time for the groups of groundwater monitoring wells, based on their locations relative to the source areas and/or to the extraction/re-injection wells are shown in Figure 7. During the monitoring and site characterization period (2006 to 2008) there were significant fluctuations of TCE concentrations in all groundwater wells. Figure 7 demonstrated that following the commencement of remediation in 2009, performance of the reactive material were monitored comparing TCE concentrations of groundwater extracted from PRB wells to the concentration from the nearest monitoring well, consequently, TCE remained adsorbed on reactive media at PRB. The increases in TCE concentrations observed at the initial stage of PRB well remediation, i.e. at the monitoring wells close to the re-injection wells, may be due to relatively higher concentrations of TCE in groundwater extracted from PRB well reactive media, afterwards the concentrations dropped as time passed (Figure 7).

Figure 7 Mean groundwater TCE concentrations for groups of monitoring wells based on their locations relative to the remediation wells (extraction/re-injection wells), with respective linear regression and monthly rainfall analysis.

The optimal location of the recirculation system improved the hydraulic containment has been achieved. In addition, this has increased the hydraulic gradient in highly contaminated sectors of aquifers, so that despite low hydraulic conductivity, significant contaminant transport to the extraction wells occurs. The TCE concentrations from the monitoring wells situated away from the remediation system ("external wells") showed that the concentrations were maintained, thereby reducing the spread of the existing contamination plume (Figures 6 and 7). The modelling results indicate that in none of the scenarios did the TCE plume spread during the remediation.

Since the monitoring dataset is intrinsically heterogeneous, considering 6.5% of non-detections, non-normal distribution and temporal trends, the Mann-Kendall non-parametric statistical test was applied to the groundwater TCE concentration trends analysis (ITRC, 2013). ProUCL 5.1 software was used here (US EPA, 2016) and the results are shown in Figure 8.

Figure 8 Mann-Kendall intrawell test for non-parametric trend analysis, sorting wells based on their locations relative to the remediation wells.

As shown in Figure 8, the Mann-Kendall non-parametric statistical test for all available data reveals an overall decline, with 47% (24/51) of the wells decreasing, 8% (4/51) increasing, and 37% (19/51) no trend were observed. Four MWs (8%) did not have enough data for the statistical test ($n < 5$). The increasing trend were observed at the groundwater wells located at the end of the plume (outer side of the re-injection wells) due to the mound formed at the reinjection wells treated groundwater results in increasing trend on the outer side of the plume despite the lower concentration. This result has further strengthened our confidence in the efficacy of the remediation system.

Generally, no significant changes in the geochemistry of groundwater samples were observed before and after installation of PRB wells. In general, the TCE concentrations in groundwater showed significant declines in the source area, and furthermore, the extended plume throughout the monitoring period indicated that the remediation strategy resulted in the clean-up of the aquifers. Complementary statistical analysis was done using the same software (US EPA, 2016) to estimate site-representative mean TCE groundwater concentrations, with an upper confidence level of the 95 percentile (UCL 95), and which is comparable to the adopted site screening value of DIL (TCE = 500 µg/L) (Figure 9). The resulting plot confirms a clear decline in TCE groundwater concentrations, but the UCL 95 was still above the adopted threshold (DIL) after the last monitoring period (Oct/2017).

Figure 9 Statistical analysis of 95% n-UCL for the groundwater TCE concentration trend from 2007 to 2017

Projecting the exponential regression curve beyond the monitored period indicates the UCL 95 will achieve the target concentration for site closure (DIL) in the next 6 years. These results show that due to the limited hydraulic conditions of the aquifer that site closure can only be achieved by long-term remediation. Even with the maximum pumping and injection rates the well interference covers only a very small area.

The research project demonstrated the efficiency of the technology and it is possible to draw the following conclusions on the main advantages of this technique:

– It is very efficient to contain the plume and target specific area of remediation without disruption of land use.

- It is applicable at the sites despite the challenging hydraulic condition with lower hydraulic conductivities such as dense clay.
- If used with well calibrated groundwater modelling the technique could be used to remove contaminants from heterogeneous natural deposits.
- The technique could be used is able to treat both organic and inorganic contaminants, such as heavy metals, nitrates, etc. if appropriate reactive material is sued.
- Good cost effectiveness to treat deep aquifer.

Despite all the advantages, this technique has some limitations, which are:

- The breakthrough of the reactive material depends on the extent of the plume hence the diameter of the PRB well for civil construction.
- The necessity to apply detail site investigation to calibrate groundwater modeling for selection of PRB well locations and reinjection wells.
- Removal efficiency is significantly reduced if hydrogeochemistry is not suitable for the reactive material as well as the structure of the aquifer with large fracture rocks resulting in channel flow.

In order to guarantee efficient remediation of the techniques, it is important to implement well calibrated groundwater fate and transport modeling, and to investigate physicochemical contaminant–hydro geochemical interactions the occurrence of reverse electroosmotic flow and the influence of organic substances present in the remediated soil.

8 Conclusion

A large set of hydrogeological data was obtained and analyzed, and a review of historical and field test results, demonstrated that the hydraulic conditions at the particular study area were characterized principally as a low water-bearing aquifer. The aquifer had a very low hydraulic conductivity with the groundwater table 15m below groundwater surface. In order to evaluate the

PRB remediation technique and the impacts of hydraulic containment, a column study and a three-dimensional calibrated groundwater flow model was established.

When extraction and re-injection wells were only a short distance apart they caused extensive increases in the hydraulic gradient by the formation of connected drawdown. The recirculation of treated groundwater at the fringe of the plume in turn supports the plume being contained within the boundary of the property, in addition to contributing to increasing the hydraulic gradient towards the PRB wells. The *in situ* innovative remediation approach using large-diameter PRB wells in a coupled active system can be very cost-effective to successfully remediate contaminated aquifer with low hydraulic conductivity and low water-bearing aquifer system. The outcome of this technology were a significant reduction in the concentration of TCE. The daughter product, - 1,1-, cis-1,2- and trans-1,2- dichloroethylene was monitored and were below the screening values and no increasing trend was measured. Over six years after the implementation, no rebound has been observed and a decline in the contaminant concentration is the documented trend. This technology leads to the reduction of the groundwater TCE concentration. As part of performance evaluation of the reactive material we are acknowledged the need to undertake sampling of reactive material from the PRB wells.

The long-term monitoring data obtained as part of performance evaluation and for assessing the longevity of the reactive material indicates continuing reduction of TCE concentrations. This system is expected to continue operating in the future. Finally, the TCE concentrations declined significantly in the source area and the extended plume throughout the monitoring period and indicated that the remediation process did clean up the aquifers to some extent.

9 Acknowledgments

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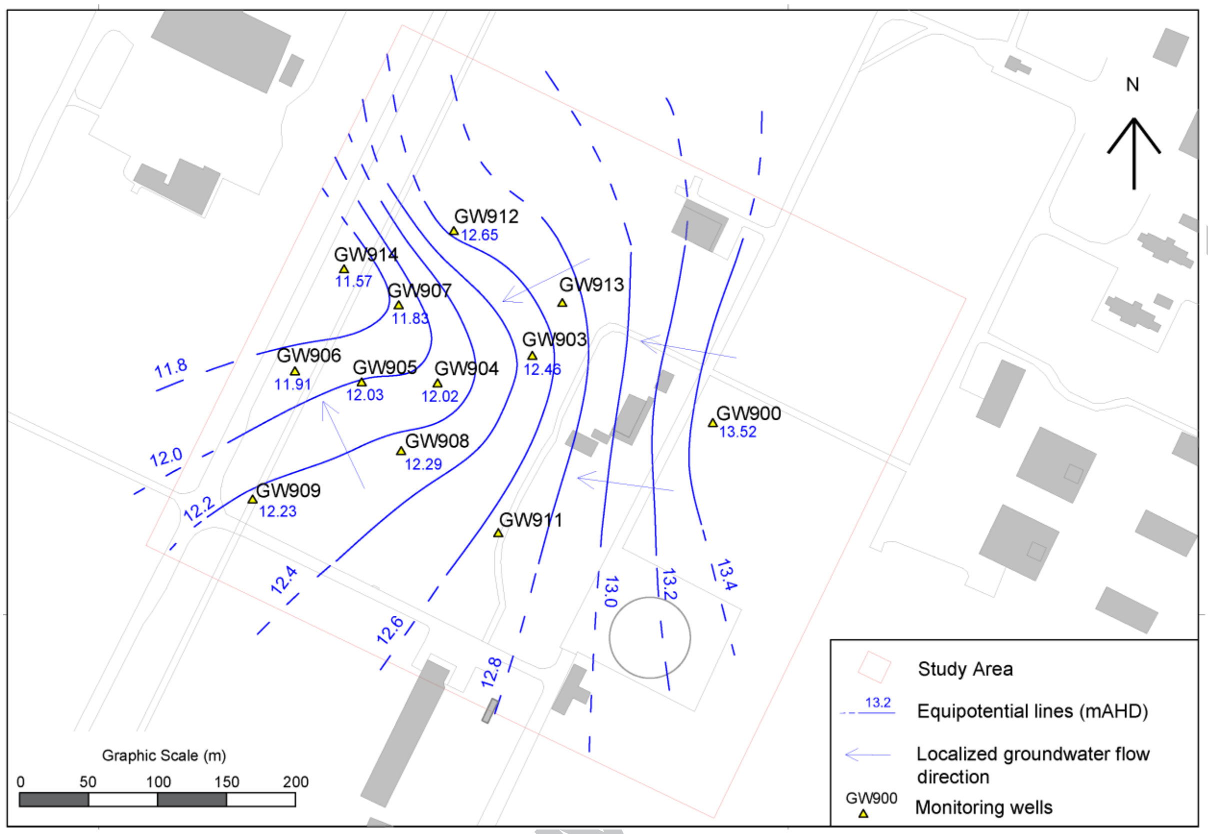
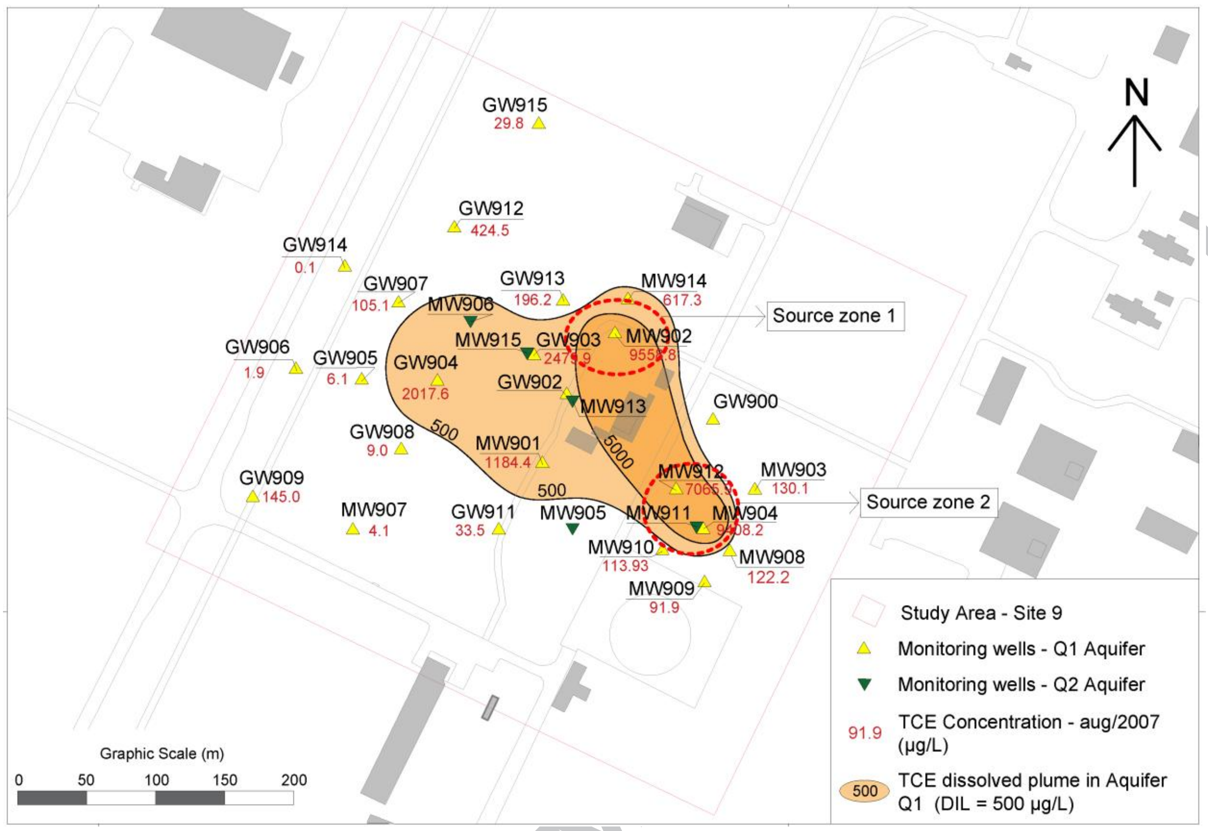
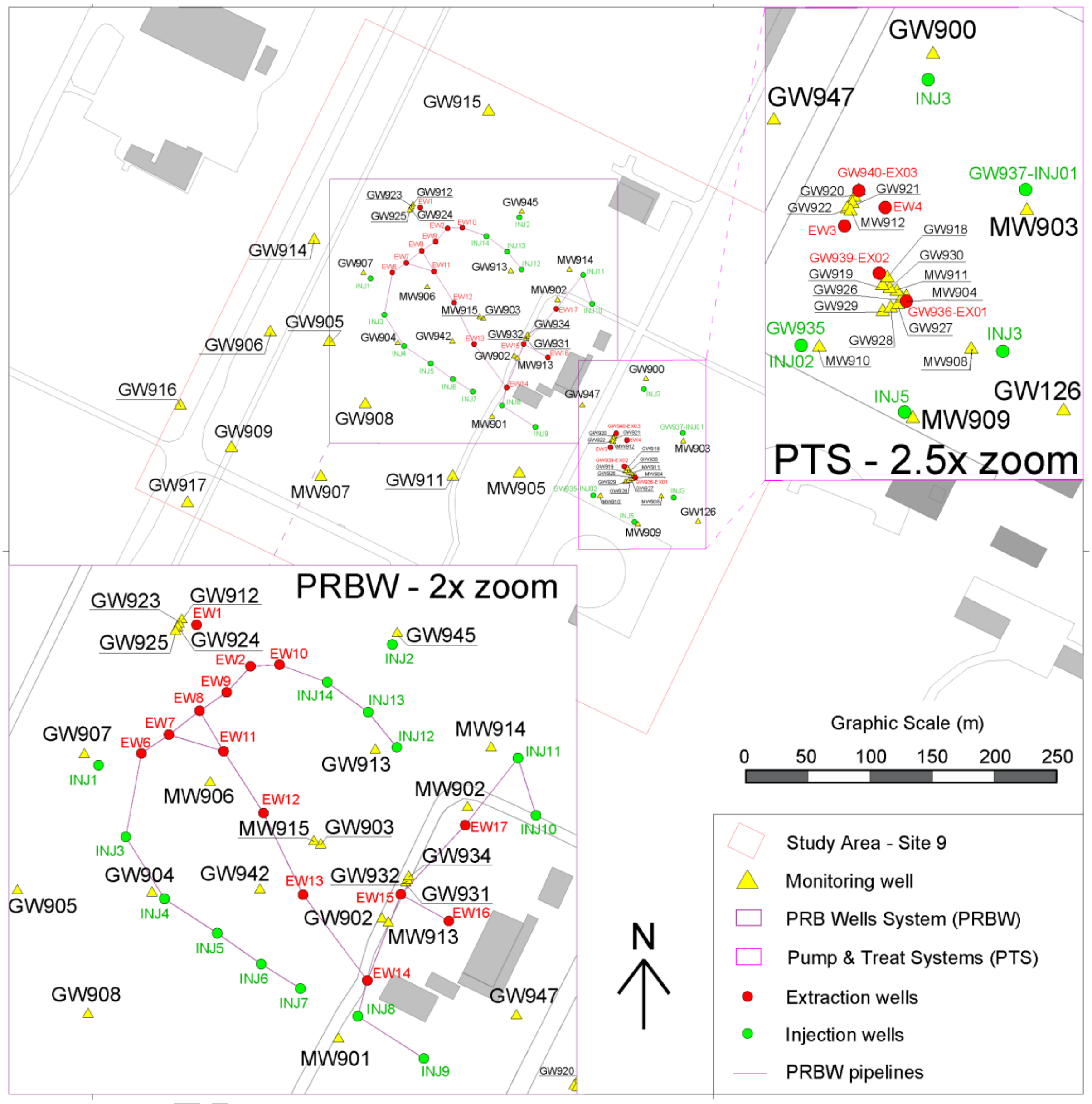
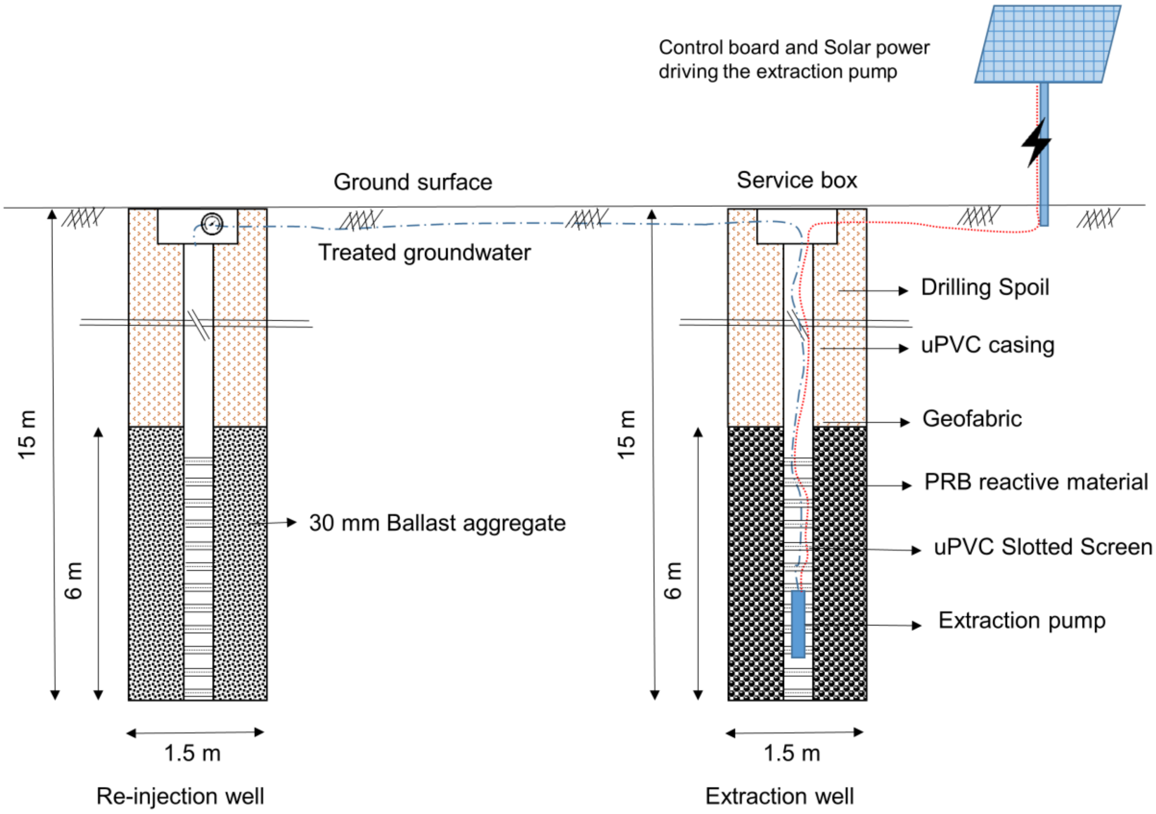
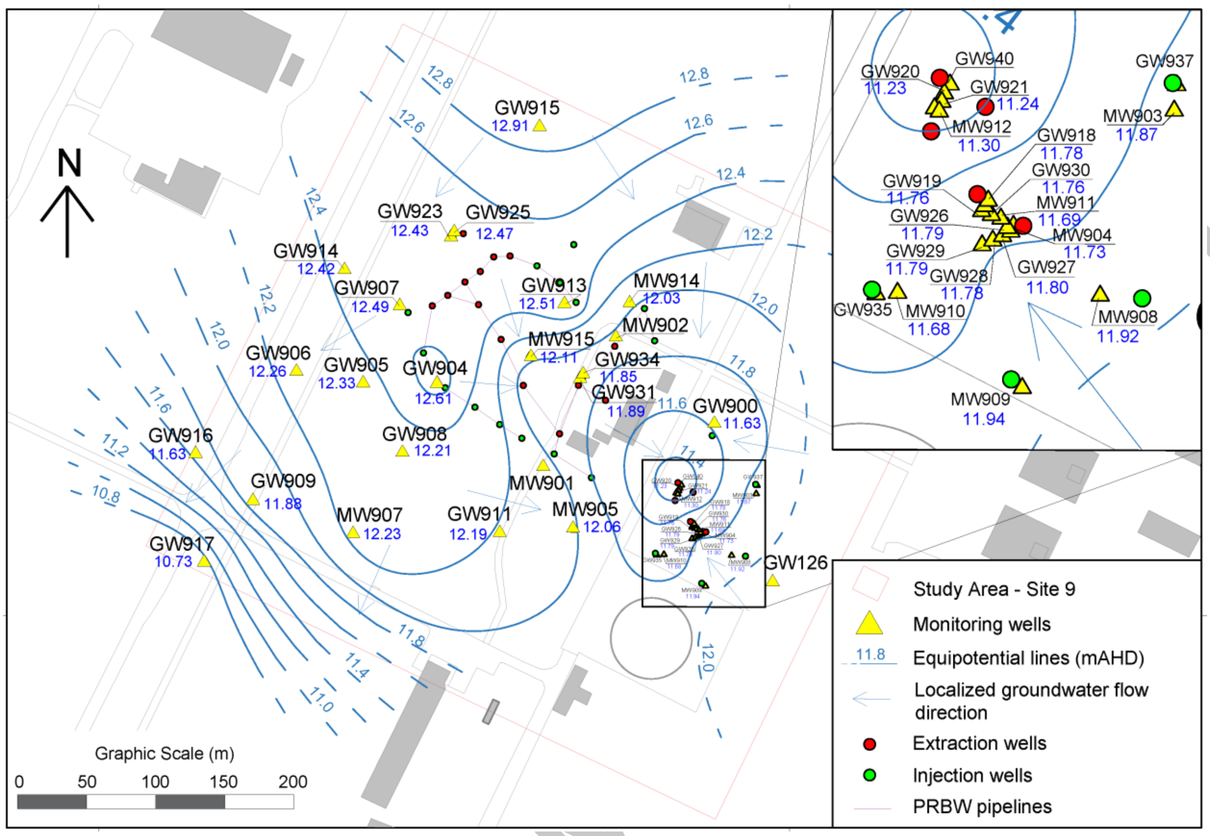

N
GW912
12.65
GW914
11.57
GW907
11.83
GW913
GW903
12.46
GW906
11.91
GW905
12.03
GW904
12.02
GW900
13.52
GW908
12.29
GW909
12.23
GW911
11.8
12.0
12.2
12.4
12.6
12.8
13.0
13.2
13.4
Graphic Scale (m)
0 50 100 150 200
Study Area
13.2
Equipotential lines (mAHD)
Localized groundwater flow direction
GW900
Monitoring wells

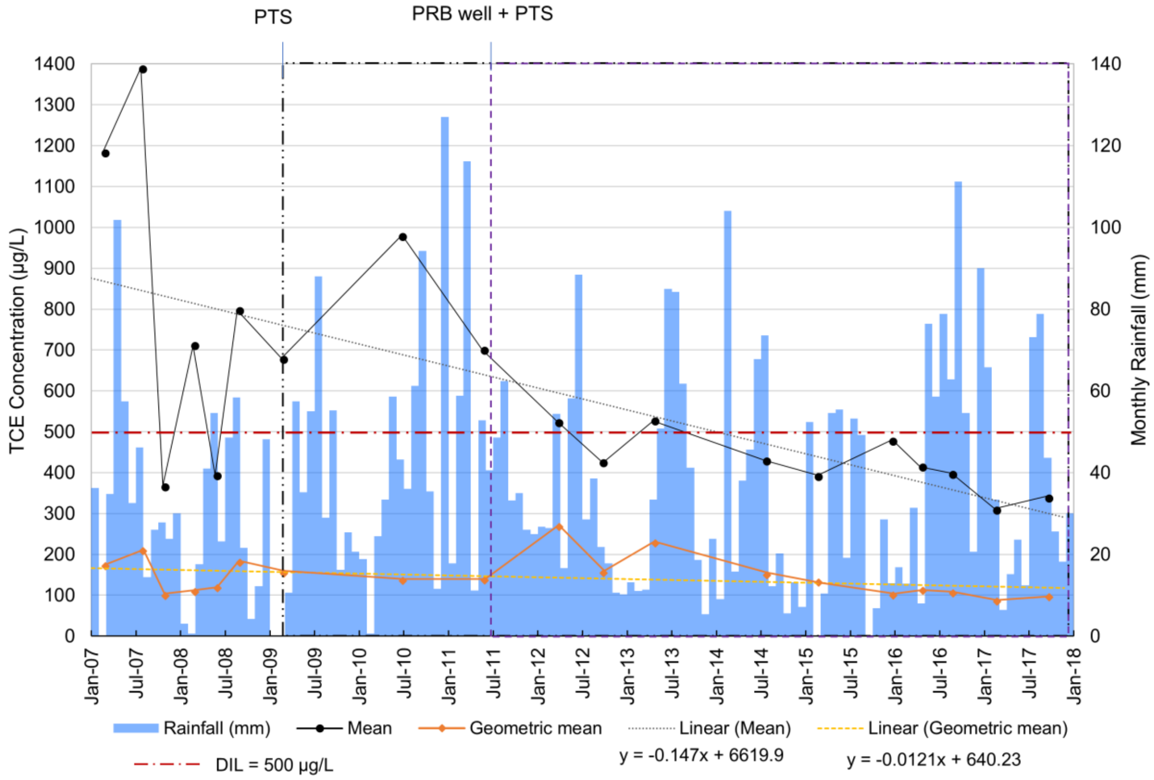

N
GW915
29.8
GW912
424.5
GW914
0.1
GW907
105.1
GW913
196.2
MW914
617.3
MW906
Source zone 1
MW915
GW903
MW902
GW906
1.9
GW905
6.1
GW904
2017.6
GW902
MW913
GW900
GW908
9.0
500
MW901
1184.4
5000
GW909
145.0
MW912
MW903
130.1
500
Source zone 2
MW907
4.1
GW911
33.5
MW905
MW911
MW904
MW910
113.93
MW908
122.2
MW909
91.9
Graphic Scale (m)
0
50
100
150
200
Study Area - Site 9
Monitoring wells - Q1 Aquifer
Monitoring wells - Q2 Aquifer
91.9
TCE Concentration - aug/2007
(µg/L)
500
TCE dissolved plume in Aquifer
Q1 (DIL = 500 µg/L)

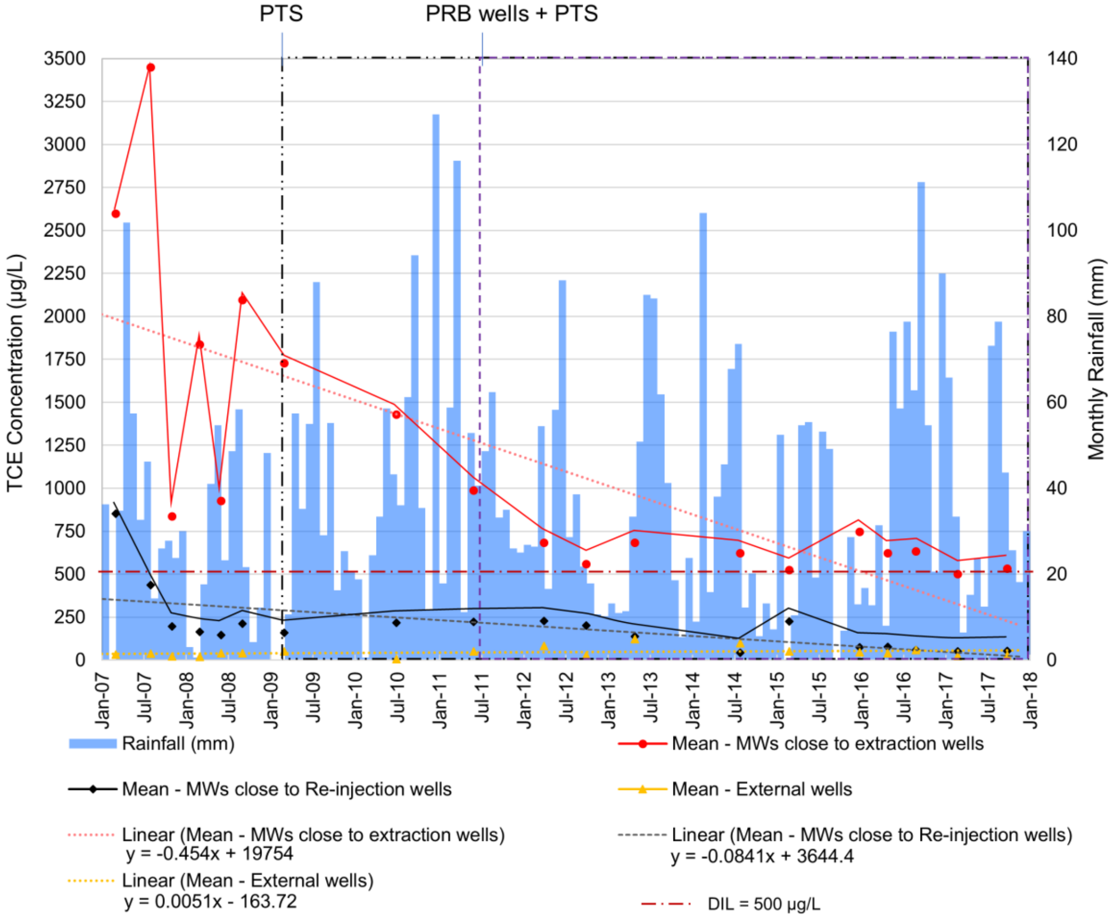


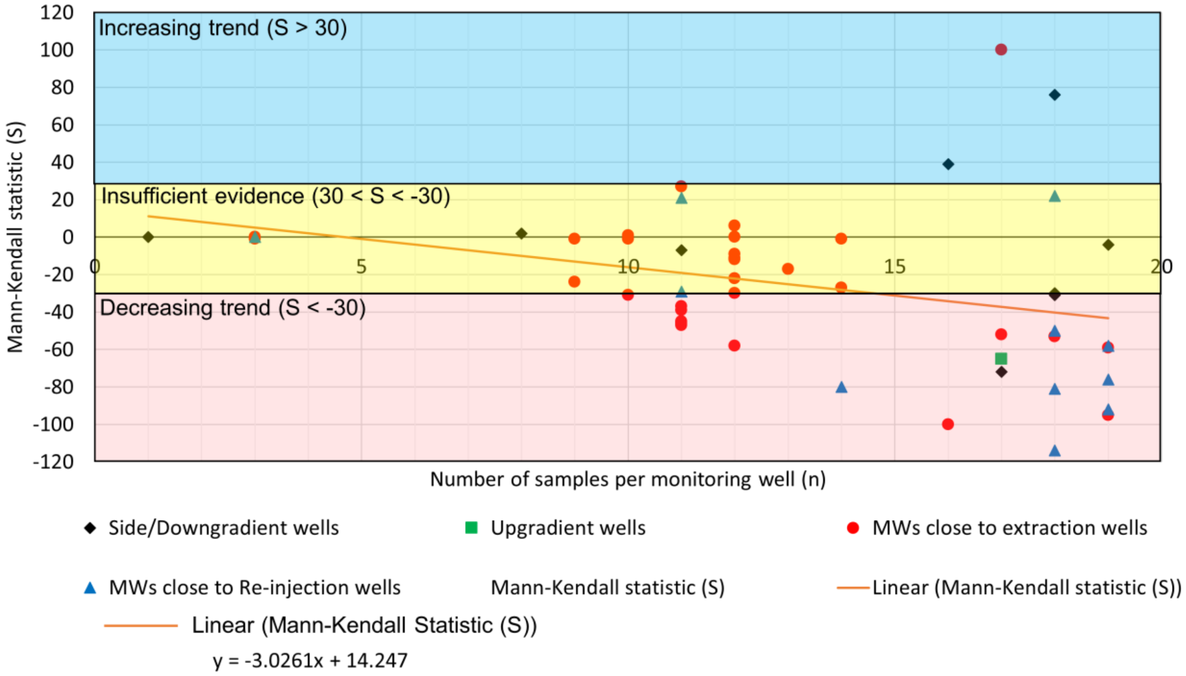
PTS - 2.5x zoom
PRBW - 2x zoom
GW900
GW947
INJ3
GW940-EX03
GW937-INJ01
GW920
GW921
GW922
EW4
EW3
MW912
GW918
MW903
GW939-EX02
GW930
GW919
MW911
GW926
MW904
GW929
GW936-EX01
GW935
GW927
GW928
INJ02
MW910
MW908
INJ5
GW126
MW909
GW915
GW914
GW905
GW906
GW916
GW909
GW908
GW917
MW907
GW911
MW905
GW923
GW912
EW1
GW925
GW924
GW945
EW2
EW10
INJ2
EW9
EW8
INJ14
INJ13
EW7
EW11
INJ12
MW914
GW907
EW6
INJ11
INJ1
GW913
MW906
MW902
EW12
MW915
GW903
EW17
INJ10
GW934
GW904
GW942
GW932
EW13
EW15
GW931
EW16
GW902
MW913
INJ4
INJ5
INJ6
EW14
INJ7
INJ8
MW901
INJ9
GW920
N
Graphic Scale (m)
0
50
100
150
200
250
Study Area - Site 9
Monitoring well
PRB Wells System (PRBW)
Pump & Treat Systems (PTS)
Extraction wells
Injection wells
PRBW pipelines


Control board and Solar power
driving the extraction pump
Ground surface
Service box
Treated groundwater
Drilling Spoil
uPVC casing
Geofabric
PRB reactive material
uPVC Slotted Screen
Extraction pump
30 mm Ballast aggregate
15 m
6 m
15 m
6 m
1.5 m
1.5 m
Re-injection well
Extraction well

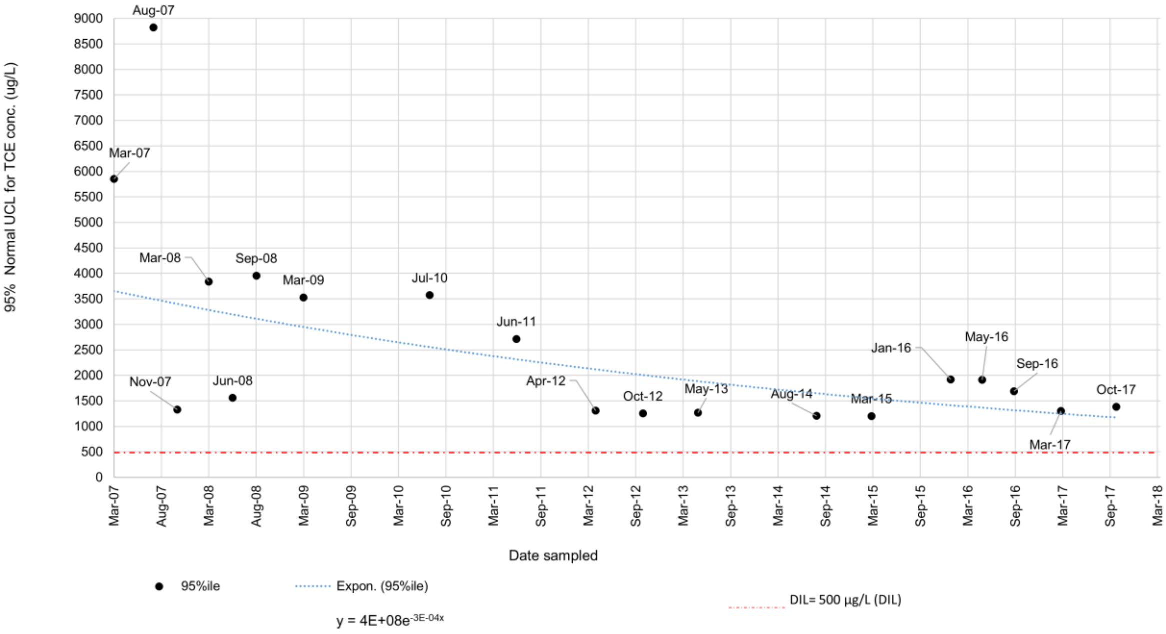

N
GW915
12.91
GW923
12.43
GW925
12.47
GW914
12.42
GW907
12.49
GW913
12.51
MW914
12.03
MW902
MW915
12.11
GW934
11.85
GW931
11.89
GW900
11.63
GW906
12.26
GW905
12.33
GW904
12.61
GW908
12.21
GW916
11.63
GW909
11.88
MW901
MW907
12.23
GW911
12.19
MW905
12.06
GW917
10.73
GW126
GW920
11.23
GW940
GW921
11.24
MW912
11.30
GW937
MW903
11.87
GW918
11.78
GW930
11.76
MW911
11.69
MW904
11.73
GW919
11.76
GW926
11.79
GW929
11.79
GW928
11.78
GW927
11.80
GW935
MW910
11.68
MW908
11.92
MW909
11.94
Graphic Scale (m)
0 50 100 150 200
Study Area - Site 9
Monitoring wells
Equipotential lines (mAHD)
Localized groundwater flow direction
Extraction wells
Injection wells
PRBW pipelines


PTS
PRB well + PTS
TCE Concentration (µg/L)
Monthly Rainfall (mm)
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
0
20
40
60
80
100
120
140
Jan-07
Jul-07
Jan-08
Jul-08
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
Jul-17
Jan-18
Rainfall (mm)
Mean
Geometric mean
Linear (Mean)
Linear (Geometric mean)
y = -0.147x + 6619.9
y = -0.0121x + 640.23
DIL = 500 µg/L


PTS
PRB wells + PTS
TCE Concentration (µg/L)
Monthly Rainfall (mm)
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
140
120
100
80
60
40
20
0
Jan-07
Jul-07
Jan-08
Jul-08
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13
Jan-14
Jul-14
Jan-15
Jul-15
Jan-16
Jul-16
Jan-17
Jul-17
Jan-18
Rainfall (mm)
Mean - MWs close to extraction wells
Mean - MWs close to Re-injection wells
Mean - External wells
Linear (Mean - MWs close to extraction wells)
y = -0.454x + 19754
Linear (Mean - MWs close to Re-injection wells)
y = -0.0841x + 3644.4
Linear (Mean - External wells)
y = 0.0051x - 163.72
DIL = 500 µg/L



Increasing trend (S > 30)
Insufficient evidence (30 < S < -30)
Decreasing trend (S < -30)
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
Mann-Kendall statistic (S)
0
5
10
15
20
Number of samples per monitoring well (n)
Side/Downgradient wells
Upgradient wells
MWs close to extraction wells
MWs close to Re-injection wells
Mann-Kendall statistic (S)
Linear (Mann-Kendall statistic (S))
Linear (Mann-Kendall Statistic (S))
y = -3.0261x + 14.247


95% Normal UCL for TCE conc. (ug/L)
Date sampled
95%ile
Expon. (95%ile)
y = 4E+08e-3E-04x
DIL= 500 µg/L (DIL)
Mar-07
Aug-07
Nov-07
Mar-08
Jun-08
Sep-08
Mar-09
Jul-10
Jun-11
Apr-12
Oct-12
May-13
Aug-14
Mar-15
Jan-16
May-16
Sep-16
Mar-17
Oct-17

Highlights

- Low permeability aquifers pose a challenge to in situ remediation
- An innovative remediation technology for low permeability aquifers is presented
- Employing coupling remediation techniques minimize cost and time for clean up