Tampere University of Applied Sciences

Applicability Analysis of Permeable Reactive Barriers for the Treatment of Groundwater in Orivesi

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BACHELOR'S THESIS

May 2019

Degree Programme in Environmental Engineering

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Degree Programme in Environmental Engineering

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Applicability Analysis of Permeable Reactive Barriers for the Treatment of Groundwater in Orivesi.

Bachelor's thesis 33 pages, appendices 2 pages
May 2019

This study was aimed to examine the overall application possibility of constructing and operating Permeable Reactive Barrier (PRB) for remediation of chlorinated solvents in groundwater. RESET project, initiated by Finnish Environmental Institute (SYKE), was the reference study for PRB construction, applications and monitoring data interpretation for remediation of chlorinated solvents in Orivesi aquifer contaminated with trichloroethene (TCE) and tetrachloroethene (PCE). Finnish by-product metal Iron, known as Zero valent Iron (ZVI), was studied for the treatment of TCE and PCE in the PRB constructed in Orivesi site.

The materials for site information and PRB construction was provided by SYKE. The various tests including slug test, packer test, tracer test and column test were researched and included in the study which define the groundwater flow, hydraulic conductivity, contaminant distribution and other variable factors affecting the construction and applications of PRB. Graphical interpretation of TCE, PCE, Vinyl Chloride (VC) and cis 1,2-dichloroethene (DCE) was done to interpret the long term remediation of groundwater with PRB.

Finnish geological and climatic conditions posed some limitations for the construction and applications of PRB. Bed rock fracture zones, glaciofluvial deposits and change in groundwater temperature created difficulties in estimation of barrier configurations and positions. The remediation of TCE and PCE was seen decreasing with increase in VC concentration in treated groundwater.

The TCE and PCE remediation was successful to some extent where the concentrations in treated groundwater dropped below limit values. The discussion included possible solutions for the improvement of barrier performance in long term use with multiple barrier system including sand filter wall. Comparative study of chemical injection process with PRB showed possibility of PRB use might be more efficient in long term use with advance research and hybrid technology developments.

Key words: groundwater remediation, permeable reactive barrier, chlorinated solvents

CONTENTS

ABBREVIATIONS AND TERMS

PRBs	Permeable Reactive Barriers
TCE	Trichloroethene
PCE	Polychloroethene
SYKE	Suomen Ympäristö keskus (Finnish Environment Institute)
ZVI	Zero Valent Iron
DCE	Cis-1,2-dichloroethylene
VC	Vinyl Chloride
DO	Dissolved Oxygen

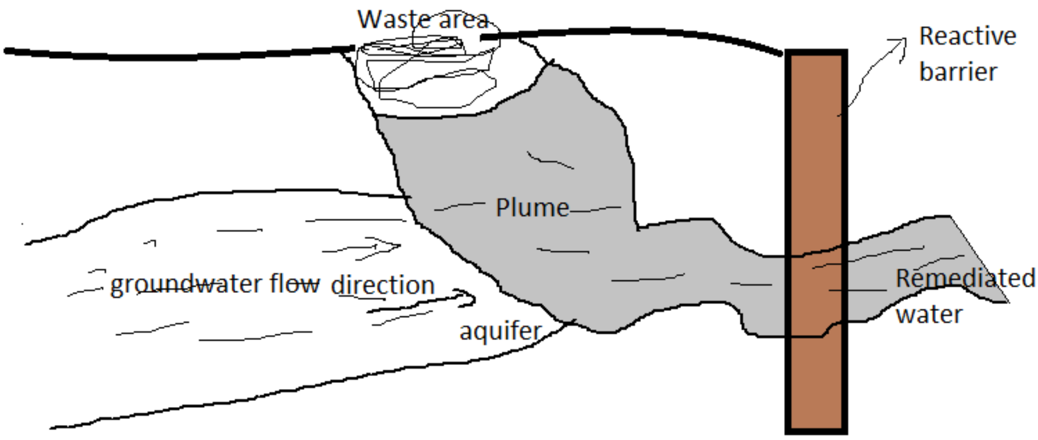
1 INTRODUCTION

In situ remediation is basically remediation process that deals with the remediation of soil and water on the site without excavation of contaminated soil or water off from the site of contamination (Gaurina-Medjimurec, 2014).
Permeable Reactive barriers (PRB) is an in-situ remediation process for contaminated groundwater. PRBs are basically a wall consisting of certain type of permeable reactive materials, which oppose the contaminated groundwater flow. The contaminated groundwater while passing through the wall is remediated through chemical, physical or biological process, depending upon the contaminants and the reactive material chosen. (Vidic & Pohland, 1996).
Trichloroethene (TCE) and tetrachloroethene or polychloroethene (PCE) are the most common chlorinated solvents found in groundwater which has adverse effects on human health. TCE and PCE are carcinogenic and can reach to human through evaporation from soil surface or through groundwater consumptions. These chemical compounds are man-made compounds and is widely used for industrial manufacturing in removing grease and paints. (Bove, Shim & Zeitz, 2002).
RESET project is a groundwater remediation project initiated by Finnish Environment Institute (SYKE), to study the effects of Nordic geological and climatic conditions on the performance of PRBs for the remediation of chlorinated solvents in Finnish groundwater. This project is also aimed to study the cost-effective reactive medium for PRBs using suitable industrial by-product materials.
This thesis is aimed to contain overall facts and researches, including the remediation data analysis, for a thorough applicability analysis of PRBs for remediation of chlorinated solvents in Finnish groundwater.

2 Theoretical Background

2.1 Permeable Reactive Barriers

Permeable Reactive Barriers are ongoing research based technology that is hoped to eradicate the ex-situ remediation process for groundwater remediation. The PRBs are simple structure built on ground opposing the groundwater force so that no external force or energy is required to push the contaminants to reactive medium for the contact and reaction. (Gavaskar, 1999).



PICTURE 1. Permeable reactive barriers (Environment Protection Agency, US, 2012, modified.)

Picture 1 shows the simplest structure and site information for the application of PRBs. The picture has an aquifer where the contaminants are being deposited and a plume that has mobile contaminants along with the groundwater flow. The plume is directed towards the PRB constructed in funnel and gate system opposing the flow where the contaminants come in contact with the reactive medium for the remediation to occur.

2.1.1 Reactive materials and PRB designs

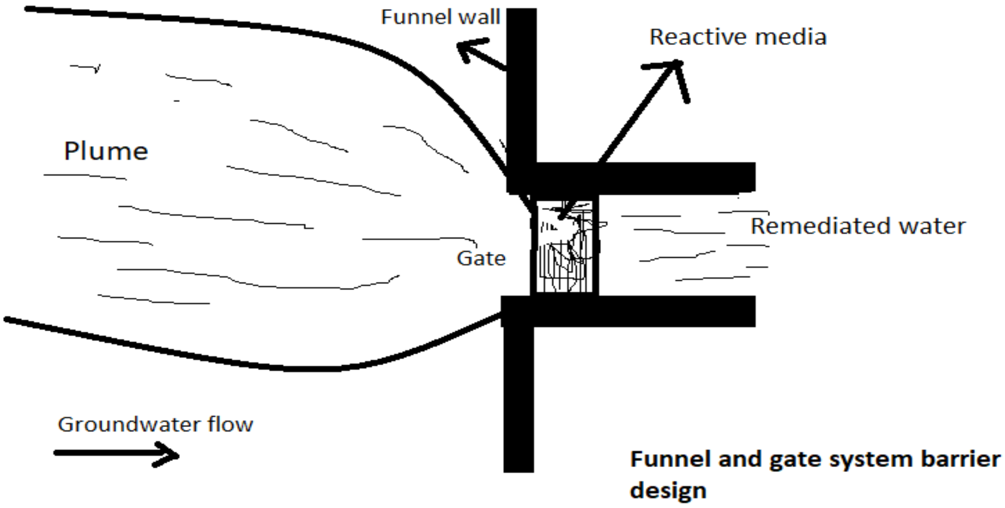
There are various different reactive reagents that can be used for the water remediation process with the PRBs. The reagents used for the water remediation depends on the types of contaminants, physical and chemical characteristics of contaminants. The PRB design depends on the site characterisations including the water flow direction, chemical mobility in water, concentration of contaminants, climatic conditions and geological and topographical parameters. (Vidic et al., 1996.)

TABLE 1: Reactive materials used in PRBs (Vidic et al., 1996, modified)

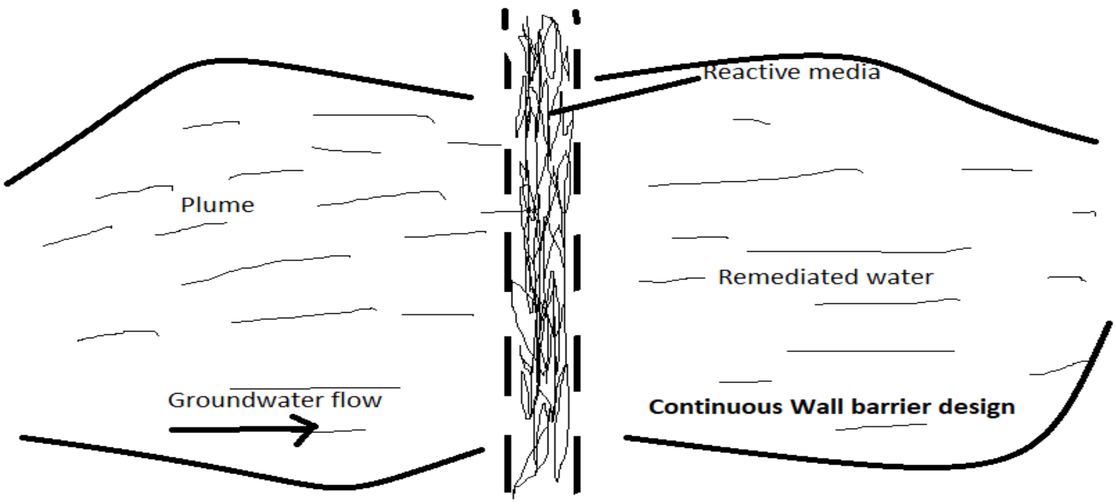
Contaminants	Barrier types	Reactive Media
Organics: • TCE, PCE, DCE, BTEX • nitrobenzene • DCA, TCA • PCBs, PAHs	***Degradation***	• Zero-valent iron • Iron (II) porphyrins • resting-state microorganisms • oxygen releasing compounds • dithionite
	Sorption	• zeolite • surfactant modified sillicates • organobentonites • activated carbon
Inorganics: • heavy metals (Ni, Pb, Cd, Cr, V, Hg) • radioactive (U, Ra, Sr, Cs, Tc) • nitrate	***Sorption***	• peat • ferric oxyhydroxide • bentonite • zeolites and modified zeolites • chitosan beads
	Precipitation	• hydroxyapatite • zero-valent iron • dithionite • lime or limestone
	Degradation	• saw dust

ZVI is the most common reactive material used in PRBs, as it is considered to be very versatile in remediation of organic contaminants through reduction and precipitation.

The very common designs of PRBs are Funnel-Gate design and Continuous system design (Thiruvenkatachari, Vigneswaran & Naidu, 2008). The PRB design depends on the site characterisations and requirements.



PICTURE 2: Funnel and Gate system (ITRC Mining Waste Team, 2005, modified.)



PICTURE 3: Continuous wall barrier design (ITRC Mining Waste Team, 2005, modified.)

Funnel and Gate system has a permeable section through which the plume passes through and comes in contact with the reactive medium. Also, there is a rigid solid wall through which water cannot pass but it directs the plume towards the permeable section of the wall. Whereas the continuous wall system has its whole section permeable, covering the whole plume area for the water to pass through it, without any solid walls. (Bronstein, 2005.)

2.1.2Zero Valent Iron (ZVI) for remediation of Chlorinated Solvents

Zero valent Iron is granular iron dust with a zero valency, which has highest number of orbiting electrons in the outermost shell, making it a rich electron donor. So, ZVI is also a very strong reductive agent and it reduces the organic and inorganic contaminants such as TCE and PCE dissolved in water. (Thiruvenkatachari et al., 2008.)
TCE and PCE under the reduction when in contact with ZVI degrade to simpler compounds like Ethane and Ethene. (Gavaskar, 1999.)

$$3Fe^0 + C_2HCl_3 + 3H^+ \rightarrow 3Fe^{2+} + C_2H_4 + 3Cl^- \quad (1)$$

Through a hydrogenolysis pathway, *Cis*-1,2-dichloroethylene (DCE) is an intermediate product before TCE and PCE degrades completely to Ethane and Ethene. But in some very rare case, DCE might degrade to Vinyl Chloride (VC) which both are very slowly degraded. But hydrogenolysis pathway does not occur over 95% in most cases, so mostly beta-elimination pathway reduces TCE to ethane and ethane with very quick degradable intermediates like acetylene. (Gavaskar, 1999.)
Higher metal contaminants present in water like chromium and uranium can be precipitated and removed. The dissolved oxygen (DO) and carbonates present in groundwater might react and even corrode the ZVI which is disadvantage if the groundwater contains high concentration of DO and carbonates. Being a highly reducing agent, ZVI even reduces the water. (Gavaskar, 1999.)

$$2Fe^0 + O_2 + H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (2)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (3)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + OH^- \quad (4)$$

These types of precipitation carbonates and corrosion of reactive Iron could cause problems in barrier efficiency in the remediation process by reduction in hydraulic conductivity and loss of reactive surface which in turn let the contaminated water to pass through the barrier untreated. (Gavaskar, 1999.)

3 RESET Project

RESET project is a test project for granular iron barrier for the remediation of chlorinated solvents in groundwater under Nordic climatic and geological conditions. Also the project was initiated to test the industrial by product iron for the reactive media in the barrier. Granular iron dust also known as Zero Valent Iron (ZVI) was a main reactive medium used for the test. Permit application and initial site surveys were conducted by SYKE in 2003-2004. The long term PRB applicability monitoring has been ongoing since 2006. (Eskola, Hjorth &Tuominen, 2007.)
Test site for the PRBs was chosen to be an aquifer in a residential area of Orivesi (longitude 24˚21' 32" East, latitude 61˚39' 28" North) has been contaminated with tetrachloroethene (PCE) and trichloroethene (TCE), released from a dry cleaner that was in operation until 1989 (Kivimäki, Nystein, Reinikainen, Tuominen, Eskola, Järvikivi, Hjorth & Karhu, 2006).

3.1 Site descriptions

An aquifer in the residential area of Orivesi, which had a dry cleaner (working until 1989) which inappropriately disposed chlorinated solvents (TCE and PCE) to groundwater, was chosen as a test site for the pilot project during the application period. The Orivesi aquifer is a shallow aquifer with gravely and sandy soil compositions of about maximum 15m thickness comprising also partial clay layers. The bed rock consists of both minor and extensive fractures and is made up of mostly granodiorite and mica schists. Multilevel monitoring wells along the groundwater flow direction for continuous water monitoring were built with multiple material testing like packer test, tracer test and slug tests followed by multiple geological surveys. MINDFLOW simulation helped determine the barrier dimensions. (Kivimäki et al., 2006.)

3.2 Barrier Design and applications of PRBs

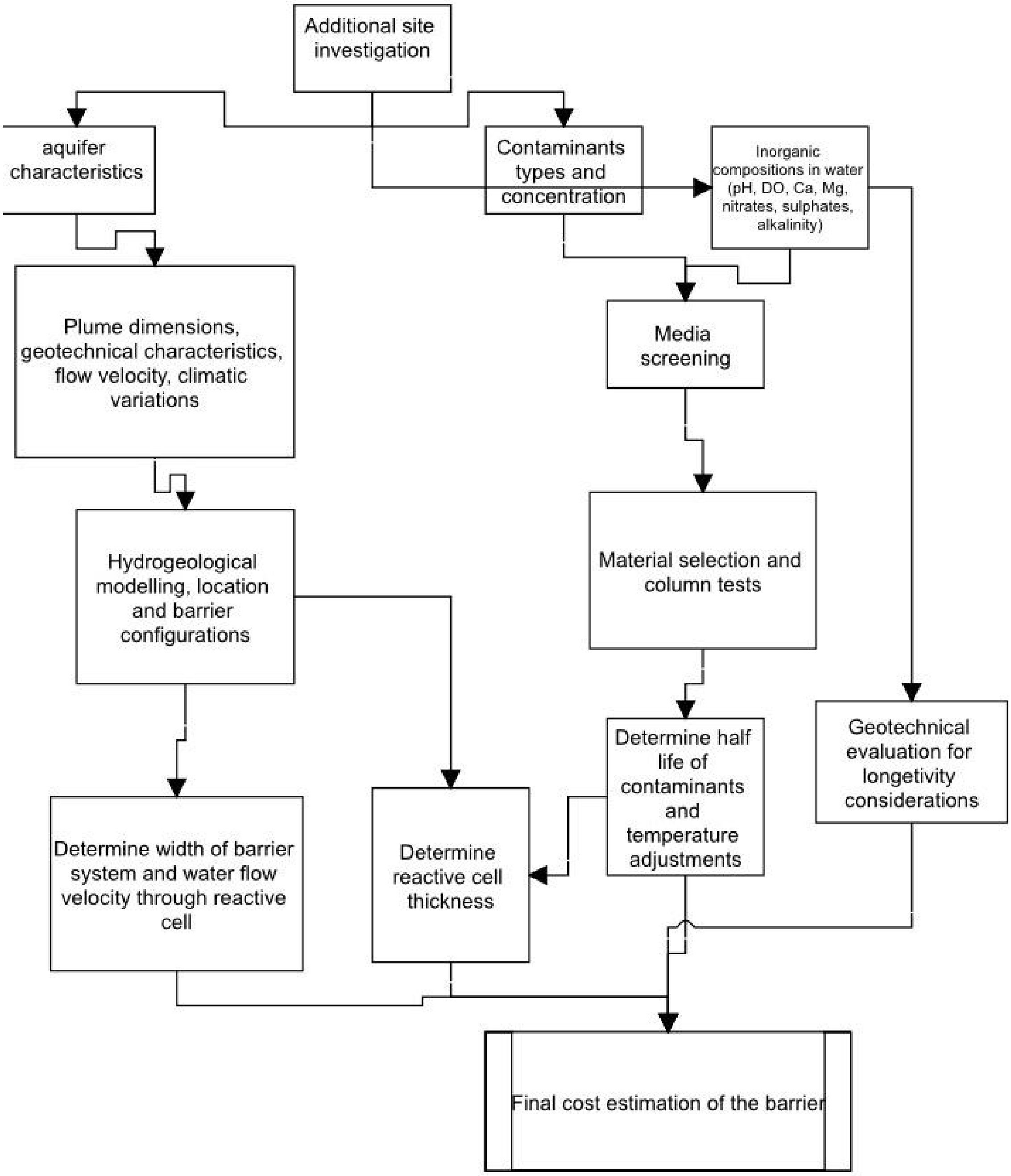
3.2.1 Preliminary site assessment

Preliminary site investigations include basic steps of identifying the major contaminants in the groundwater and determining the contaminants distribution, which ultimately give an idea for suitable reactive medium for the remediation process.

Also, initial measurements of the groundwater velocity is a part of preliminary investigations of the targeted site. The groundwater flow direction and velocity has a direct effects on the barrier design and whole remediation process. The fast flow of groundwater has less residence time in the reactive medium which leads to the thicker width of the barrier resulting in increased cost for the construction of the barrier, whereas, slow and stable flow of groundwater prevents the contaminants to react with the reactive medium.

Topographical and geological investigations are to be assessed during the preliminary investigations because these factors leads to a thorough planning for the constructions of the barriers. Large sediments and underground rock configurations might limit the cost efficiency and time for the construction of the barrier. (Gavaskar, 1999.)

Preliminary site assessment progresses to additional site characterisation comprising of other major steps on planning and building the PRB.



PICTURE 4: Site assessment process for designing a PRB (Gavaskar, 1999, modified.)

Flow chart as shown in Picture 4, is a step wise interpretation of full scale site characterisation that is done for the proper site characterisation, that is in turn giving the whole cost estimation and PRB design configuration.

3.2.2 RESET project Site characterisation and material test

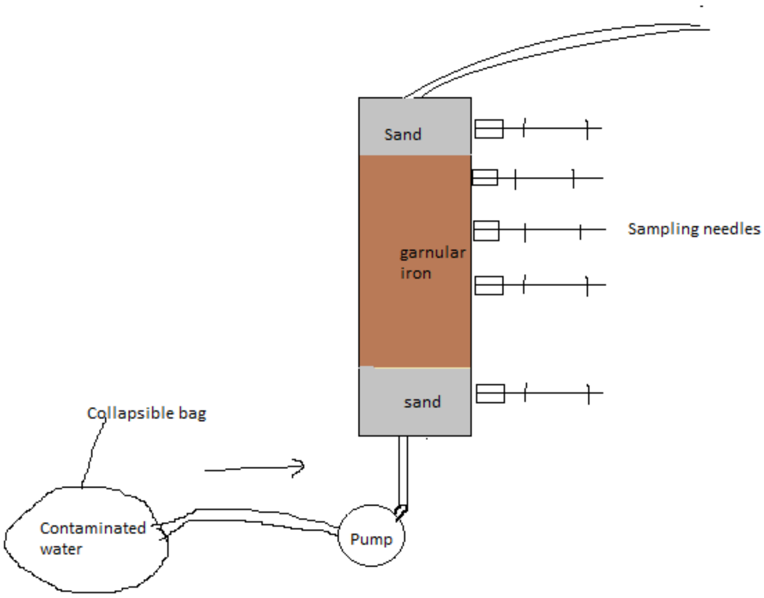
Site investigations and material test for the project was done in 2003 to 2005, which included general preliminary site investigations under Finnish geological surveys and additional site investigations. Geological site characterisations including unconsolidated deposits and heterogeneity was done by aeromagnetic measurements, ground penetrating radar, seismic refraction surveys and electrical resistivity soundings. The results showed that the mineralogical compositions of the debris to be granitic composed of SiO_2, MgO, Al_2O_3, Na_2O, K_2O and FeO, with about 72% of SiO_2. (Kivimäki et al., 2006.)

Slug test is basically done to estimate the hydraulic conductivity based on the Bouwer and Rice algorithm around the monitoring wells, by penetrating the unconfined aquifers. It is done by quick removal of certain volume of water from the well and measuring rate of water level rise in the well. It can also be done by adding a certain volume of water (slug) to the well and measuring the rate of water level fall in the well. The rise or fall rate of water level in well determine the hydraulic conductivity. (Bouwer, 1989.)
The slug test is initiated by rapid raise or lowering of the water level with minimal noise into the water level readings. Solid slug, bailer or pneumatic pressurization techniques are few ways of slug test initiation. But pneumatic technique is preferred, due to its instant noise reduction after the test is started. Also, solid slug and bailer can be used for initiation but the sensors and cables blockage should be clearly avoided. (Butler, 1998.) The measurement techniques can be manual tape measurement with electric water level sounders or pressure transducers with data logger for accurate readings.

Packer test helps to determine variability of wells or boreholes, intersecting different hydrogeological units, such as hydraulic properties and water quality in the aquifer. It isolates a part of borehole for sampling of fluid in it. The test can be carried out in open boreholes which are stable boreholes without falling rocks or soil disturbing the rocks. Or, it cab ne done through cable drilling rods in unstable boreholes. In open boreholes single or double packer test is possible whereas cable assembly drill rods need double packer tests. It includes measurement of pressure build up and water flow rate over a time period. Various tests are included in packer tests which gives the conductivity, flow rate and pressure references from the hydrogeological perspective of the groundwater. Rock configurations and fracture zones interaction with the groundwater is identified with the ***injection test****s,* where the water is injected with certain pressure in static groundwater level and the final steady water flow condition is then recorded. In Confined or trapped groundwater conditions known as artesian conditions, ***Discharge tests*** are done, where natural pressure response is monitored after shut in decays with respect to time. ***Shut-in recovery tests,*** are followed immediately after the discharge tests are done recording the pressure build up over time. These tests finally compile the hydraulic conductivity results of the groundwater including information on the hydrogeological conditions of the site. (Yihdego, 2016.)

Tracer test is a simple technique of estimating water flow and aquifer properties by simply adding traceable chemical compounds into the groundwater flow system. Before the test is started tracer selection where the used tracers have specific properties required for accurate tracing. The tracer is injected rapidly starting at a point in the water flow and traced on the other point in the direction of groundwater flow with respect to time. Tracer should not have any effects on transport properties of the water regarding density and viscosity. Different types of tracers are; *conservative tracer,* which does not include phase shifts except for occupying the volume in water whereas *partitioning tracer* test include compounds undergoing phase change which has longer residence time in water than in conservative tracers. Other tracers like radioactive compounds can also be used. The tracer might undergo chemical leaching in water so they should be extracted back from the water. Mostly tracer tests involve one or more injection wells depending upon the variable flow conditions and multiple extraction wells. Tracer tests include qualitative test regarding fluid sources, recharge or discharge locations and hydraulic conductivity. For the test, the required tracer compounds are injected to the water rapidly with minimum time taken for injection. The chase fluid is then injected to the water so that the extraction of tracer becomes easier as the chase fluid indicates the end of tracer in water. The tracer flow from point A to point B with respect to time gives the estimated flow values at different monitoring points. The flow geometry distribution helps estimate the pore space underground, flow path distribution and flow resistances giving the quantitative figures for the site characterisation. (Shook, Ansley & Wylie, 2004.)

Number of boreholes drilled followed by X-Ray fluorescence spectrometry was used in determination of bedrock constituents and fracture zones. Also, Specific analyser namely LECO 2000 analyser was used for the determination of Total carbon, TOC (total organic carbon) and nitrogen and sulphur contents. All these tests showed that the sand and gravel deposits covering the bedrock with an elongated fractures expanding from northwest to the southeast of the aquifer. The hydraulic conductivity from the slug tests was estimated to be ranging from $6x10^{-6}$ to $3x10^{-3}$ ms^{-1}, whereas the tracker test gave an estimation of linear groundwater flow velocity to be about 1.2 to 2.3 metres per day in the direction of southeast from the aquifer. (Kivimäki et al., 2006.)



PICTURE 5: Column test for estimation of degradation rates and material reliability (Gavaskar, 1999, modified)

For the materials to be used in PRB in Orivesi aquifer, column test is a very reliable test procedure for determining the half-life of contaminants, reactivity of material used for remediation and also to determine precipitates and excess compounds formed during the remediation process. The groundwater flow rate

is maintained as to that of the site while passing the water through the closed collapsible bag (to prevent the external aeration) to maintain accuracy.
In the RESET project material test was done preliminarily with five domestic by product Iron and four commercial reactive Iron and with several column tests finally domestic by product Iron (different granular sizes named as A and B) was used for further evaluation and evaluation was done under two different temperatures, 24°C and 7°C.
The half-life for PCE and TCE degradation at 24°C were found to be 0.9 hours and 1.2 hours respectively for Iron A. For Iron B at 24°C, half-life of PCE and TCE was found to be about 2.8 hours and 2.5 hours respectively. Since Iron B showed greater value of half-life for both the contaminants degradation, Iron A was finally chosen for the field use in Orivesi site PRB. Tests also showed that the formation of VC and DCE was negligible, lower water temperature did not make big difference in the half-life value of both contaminants and hazardous side product leaching from the reaction was way lower in concentration. The PCE and TCE initial concentration in the monitoring well close to the dry cleaner were 5600µg l^{-1} and 280µg l^{-1}, respectively. PRB was then built where the PCE concentrations fell under the range of 530µg l^{-1} and 990µg l^{-1} and also, it was noted that the bedrock fracture zone was not present in the area for assuring the plume does not escape untreated.

TABLE 2: Temperature correction factor regarding half-life of contaminants for Iron A (Kivimäki et al., 2006, modified.)

Temperatures	**Half-life of PCE (h)**	**Half-life of TCE (h)**
24°C	0.9 ± 0.1	1.2 ± 0.1
7°C	1.5 ± 0.1	2.1 ± 0.2
Temperature correction Factor	1.6 ± 0.1	1.7 ± 0.1

The spot for the PRB to be constructed was selected from all the geophysical investigations, contaminants characterisation and tests and material tests. The chosen spot has an average groundwater velocity of approximately 3.0 md^{-1}, concentrations of PCE and TCE about 990µg l^{-1} and 130µg $l^{-1}$and half-life of PCE 4.9h with temperature correction factor of 1.6h. The calculations regarding the water flow rate and half-life of contaminants showed the required residence time of flowing contaminated water volume about 60h. The target concentration of both contaminants after the remediation is aimed to be 0.5µg l^{-1} or lower. Finally, the PRB was constructed with funnel-gate system design consisting bentonite geotextiles along with clay layers. Continuous trench cavity (12.5m x 4m x 2.5m dimensions) filled with 125 m^3 of granular ZVI. The trench included a monitoring well (2m diameter and 14m depth) for groundwater regulations and continuous monitoring. (Kivimäki et al., 2006.)

4 Data interpretation for chlorinated solvents and comparative study

The monitoring data for the chlorinated solvents for Orivesi aquifer was extracted from open-data system, Finland under POVET database uploaded by Finnish Environment Institute (SYKE). The data for the chlorinated solvents in RESET project were monitored through two major monitoring wells. Monitoring well **HP505PE** is monitoring the concentration of chlorinated solvents (PCE, TCE, VC and cis-DCE) before the groundwater enters the PRB. Monitoring well **HP503PE** is monitoring the concentrations after the groundwater exists the PRB.

4.1 Concentration of chlorinated solvents in groundwater before entering the reactive barrier

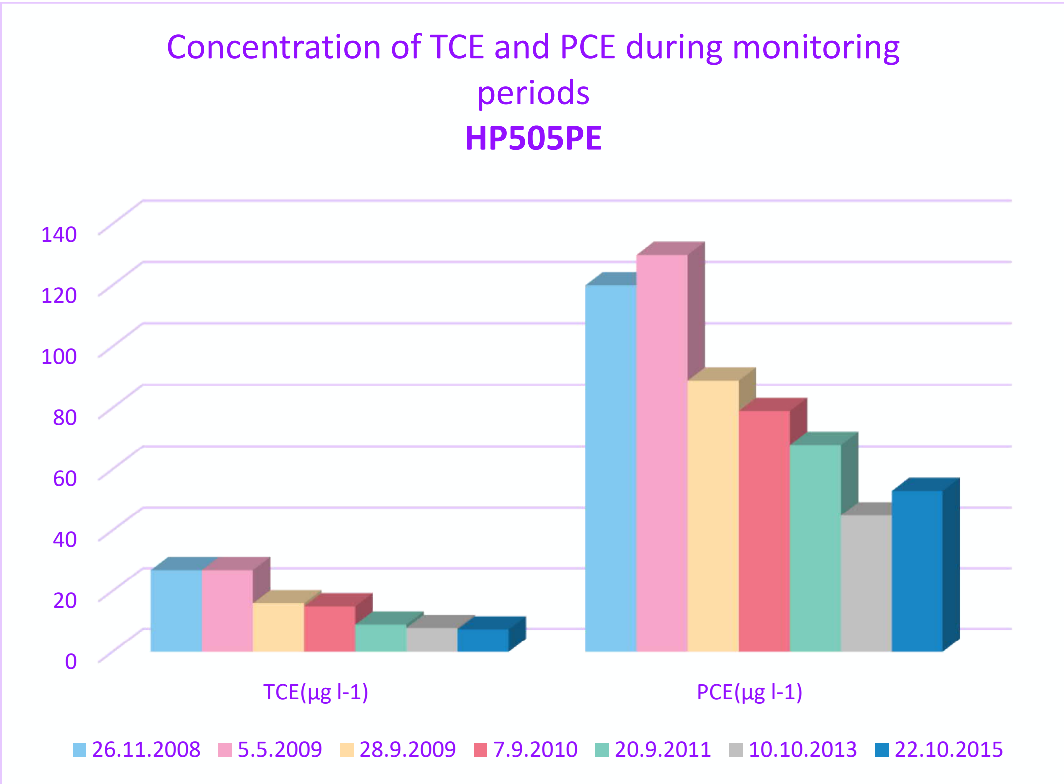


FIGURE 1: Concentration of TCE and PCE during monitoring periods in Orivesi groundwater before entering the PRB.

TABLE 3: Limit values and treatment goal for chlorinated solvents in Orivesi groundwater (Eskola et al,. 2007).

Contaminants	WHO limit values (μg l^{-1})	treatment goal (μg l^{-1})
PCE	40	<5
TCE	70	<5
VC	0,3	-
cis-DCE	50	-

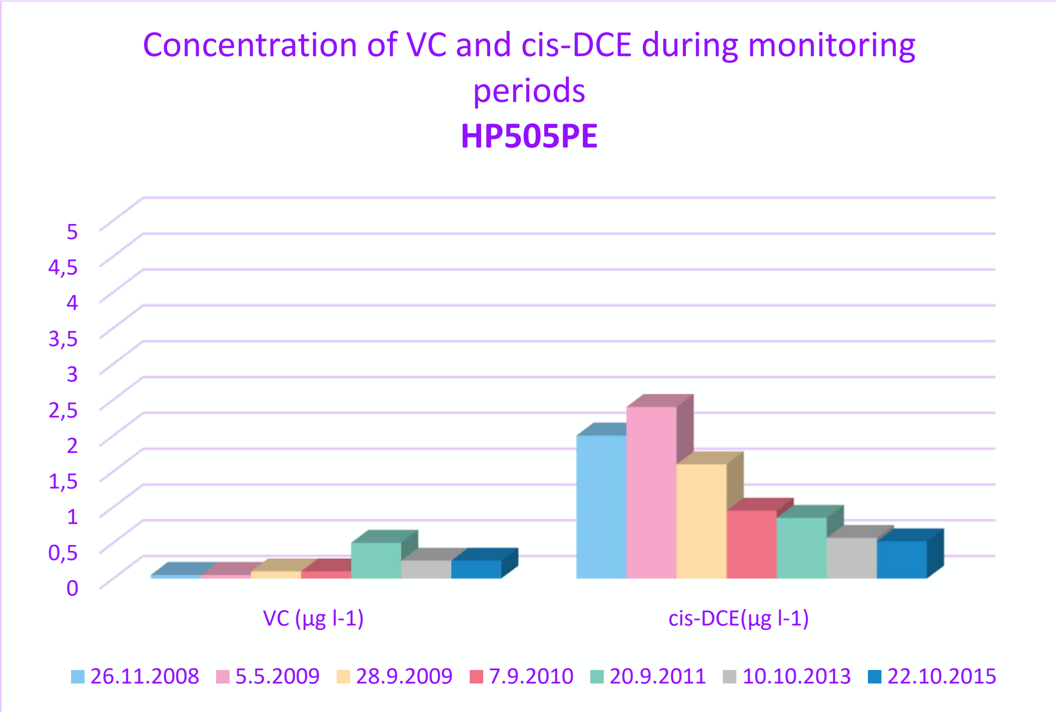


FIGURE 2: Concentration of VC and cis-1,2 DCE during monitoring periods in Orivesi groundwater before entering the PRB.

Figure 1 shows the graphical representation of TCE and PCE concentrations in the groundwater during the yearly monitoring of the water remediation project in Orivesi. The representation is done according to the table presented in appendix (1) of this thesis report. Figure 1 bar graph, in comparison to the WHO limit values as in Table 3, shows that the concentrations of TCE is under the human safety limit but PCE concentrations are way above the limit values during the monitoring periods. The target concentrations of PCE and TCE after remediation through PRB is under 5 μg l^{-1} for both contaminants according to Table 3.

Similarly, in Figure 2, the graphical representation of VC and cis-1,2 DCE is done according to the table in appendix (1). Here in Figure 2, the concentrations of VC and DCE are way lower than the WHO limit values (Table 3). The cis-DCE is the dissociation products of PCE and TCE. Whereas when the dissociation goes through hydrogenolysis pathway cis-DCE dissociates to VC, which is an intermediate product which dissociated very slowly (Gavaskar, 1999).

4.2 Concentration of chlorinated solvents in groundwater after exiting the reactive barrier

The chlorinated solvents PCE and TCE in Orivesi groundwater is targeted to be remediated by the PRB constructed using by-product metal Iron. The graphical representation of concentrations of PCE and TCE is presented in Figure 3, which is a representation from the monitoring data table in appendix (2).

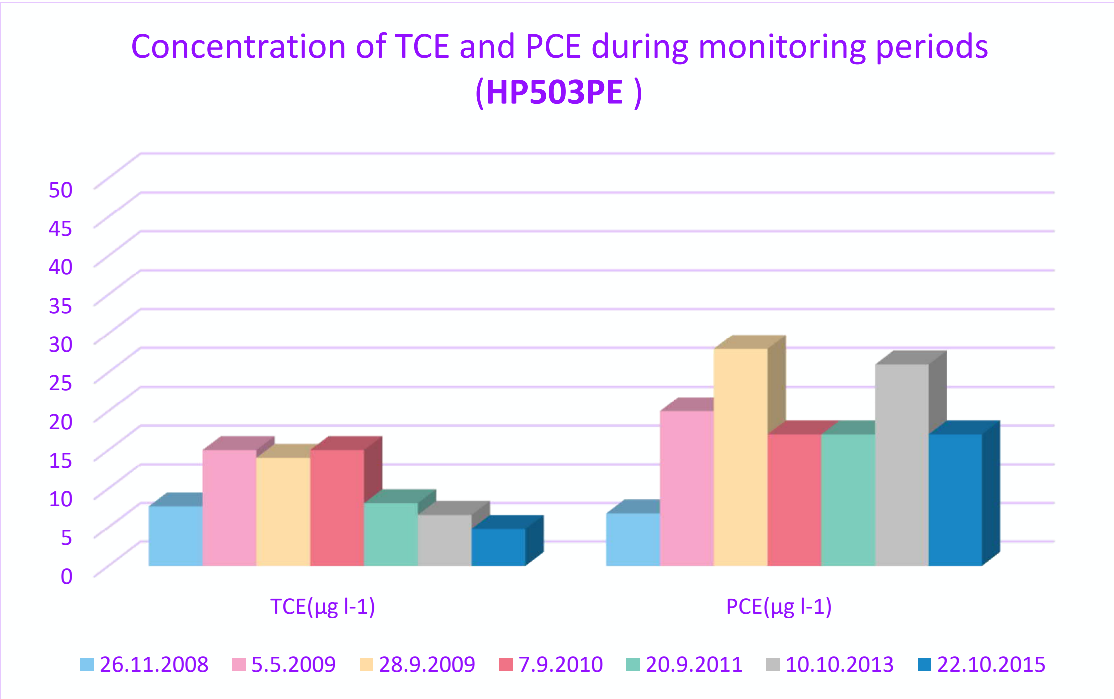


FIGURE 3: Graphical representation of TCE and PCE concentrations in groundwater after exiting the reactive barrier.

The concentrations of PCE and TCE has dropped below the WHO limits (Table 3) as seen in Figure 3. The TCE concentrations were already low according to Figure 1 but the high concentration of PCE (Figure 1) has gradually dropped after passing through the PRB according to Figure 3. The concentration values, in the beginning of monitoring period, after the groundwater has passed through the barrier has shown great possibility of remediation where both PCE and TCE concentrations were dropped below target limits. But in further years the remediation rate is under WHO limits but has not dropped to target limit (Table 3). The reason for this could be the decrease in Iron reactivity and less residence time for the contaminants.

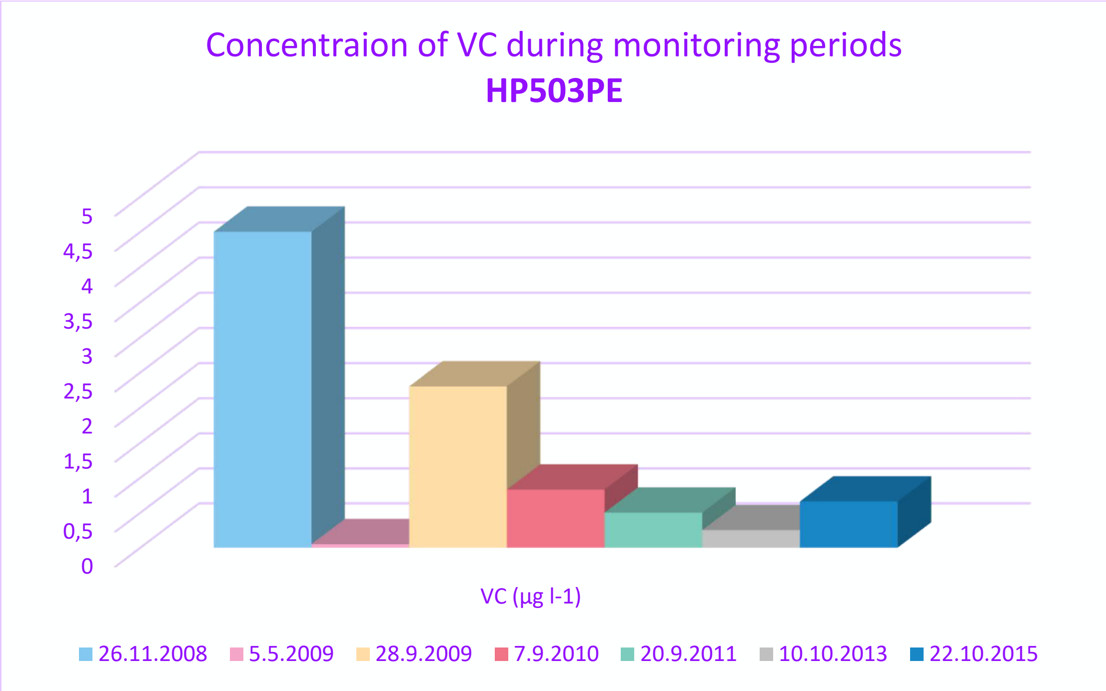


FIGURE 4: Concentration of VC in groundwater after exiting the reactive barrier

Although the concentrations of PCE and TCE has dropped below the WHO limits (Figure 3), concentration of VC in most of the monitoring periods has increased way above the WHO limits (Figure 4). According to 26.11.2008 monitoring data (appendix 2), the concentration of VC is highest, but gradually dropping since 2009 monitoring periods. But the concentrations still is higher than limit value. The reason might be iron passivation in long term use, mineral and biomass accumulation preventing the solvents from complete dissociation through beta-elimination which might have lead DCE through hydrogenolysis resulting in formation of VC.

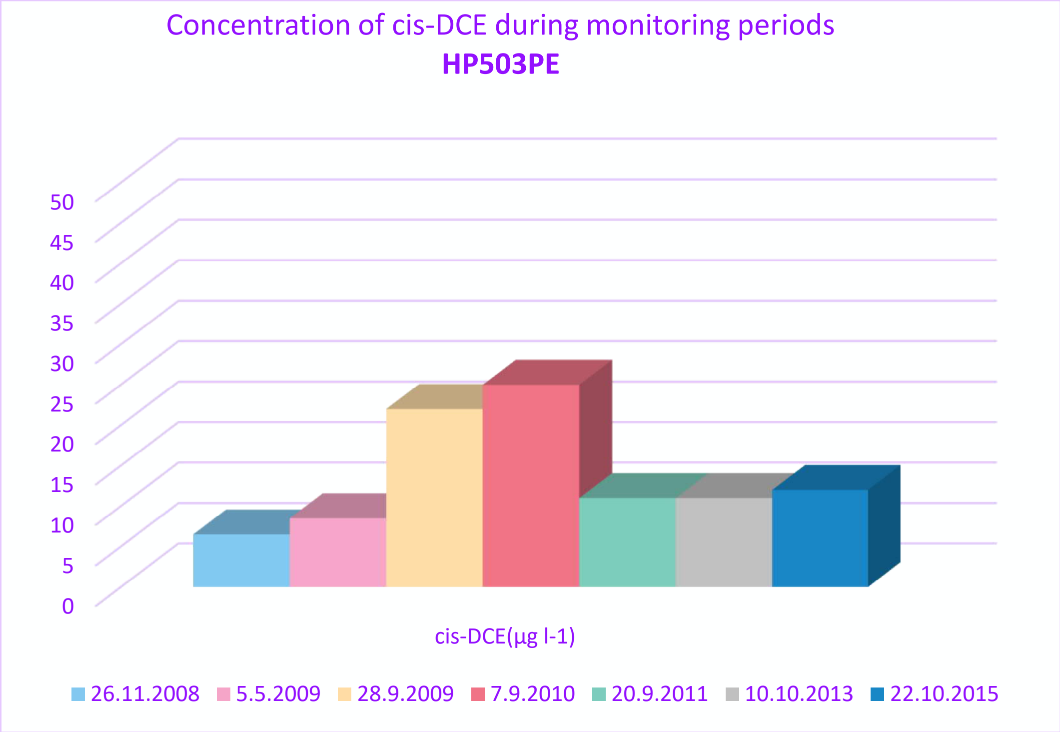


FIGURE 5: Concentration of cis-1,2 DCE in groundwater after exiting through reactive barrier

Figure 5 shows the greater concentration of cis-1,2 DCE than in Figure 2 but the concentration, even though increasing, is still under the WHO limit.
The higher value of cis-1,2 DCE might be because of the low oxygen levels and high Iron concentration which triggered reactions similar to that in the reactive barrier. But could not dissociate completely due to less residence time. (Eskola et al., 2006.)

The actual concentration values for Figure 1 & 2 are in the table in Appendix 1 and for Figure 3 & 4 are in the table in Appendix 2.

4.3 Comparative study of In-situ Chemical injection process with PRB

In-situ chemical injection remediation process is basically process where the remediation of contaminated groundwater is done by injecting tested chemicals to remediate the targeted contaminants at targeted points (Yin & Allen, 1999). This process includes the injection of many different chemicals for the remediation process which includes liquid oxidant injections, gaseous oxidants and reductant injections, chemical flushing with surfactants, foams, cosolvents, etc. The chemical injection process has basically four different processes namely;

1) Oxidation by injection of liquid oxidants for the remediation
2) Reduction by liquid reductant barrier
3) Reduction and Oxidation via gaseous reductants and oxidants injection
4) Colloidal Zero Valent Iron (ZVI) injection for reductive barrier

For **Oxidation by injection of liquid oxidants**, site investigations are done to identify contaminants distribution and mobility including all kinds of geophysical investigations followed by suitable oxidant selection via extensive lab and column tests. The oxidants like Potassium Permanganate, Hydrogen Peroxide along with Iron (II) and Ozone are chosen depending on the contaminants and lab tests which are then injected directly to the groundwater or soil through drilled holes or wells at targeted point. Liquid oxidants can also be injected using hydraulic fracturing technique but it requires more detailed site characterisation because of its risks to the geophysical impacts on the environment. (Yin et al., 1999.)

Reduction by liquid reductant barrier or Colloidal ZVI injection, has the same remediation reactive which occurs in PRBs and site characterisation and investigation is quite similar to the PRBs. Except, liquid reductant barrier might need more lab and material testing and chemical withdraw well also needs to be modelled. The main difference of these chemical injection process and PRB is that PRB needs excavation of some part of the site for the construction of the physical reactive barrier whereas injection does not require physical wall construction or excavation but need the withdraw well and precise regular monitoring. (Yin et al., 1999.)

Gaseous Oxidants and reductants injection, is also a possible way of treatment but a very secure and well monitored injection and airtight gas extraction system should be constructed which requires extensive research on system engineering and monitoring and site assessment. Gas like Hydrogen sulphides and ozone are used as reductant, which are highly toxic in case of leaking to environment. (Yin et al., 1999.)

TABLE 4: Comparison of Chemical injection process with PRB.

Topics of comparison	**Chemical injection**	**PRB**
Contaminants treated	Most of the organic and inorganic contaminants are treated with oxidation and reduction but adsorption and precipitation might not be possible with liquid and gaseous injections.	Organic contaminants like TCE, PCE, PAHs, etc. and inorganic contaminants heavy metals, nitrates and radioactive compounds can be treated via degradation, adsorption and precipitation using suitable solid materials (Table 1).
Site investigations	Requires proper geophysical investigations. Extensive additional characterisation for identifying injection points placements and withdraw points. Large contaminated areas can be considered for remediation process.	Requires proper geophysical site investigations for placement and construction of barrier, barrier modelling and material selection. Very large area of contamination might require multiple barrier construction and more site characterisation.
Material tests	Proper lab tests, column tests and leaching tests and by product gas filter and chemical extraction tests	Proper column tests including leaching tests
Modelling and construction on site	Excavation is minimum. Chemicals injected through drilled holes or wells, so no extensive modelling required but in case of liquid chemical extraction proper monitoring and extraction points to be built. For gas injection a well-engineered system is should be designed for leakage prevention.	Excavation is required for the wall construction. Results from site characterisation and material tests define the dimensions and design of the barrier. The constructed barrier does not need extraction wells in most cases.
Efficiency	Quick and very efficient for contaminant treatment. Target limit can be reached fast with regular monitoring and proper chemical injection. Construction might be cost efficient but chemical and monitoring in long-term can be very expensive.	Slow and steady process, target limit might get tampered during long-term use due to de creasing reactivity. Construction costs are higher but materials and long-term use is very cost efficient.

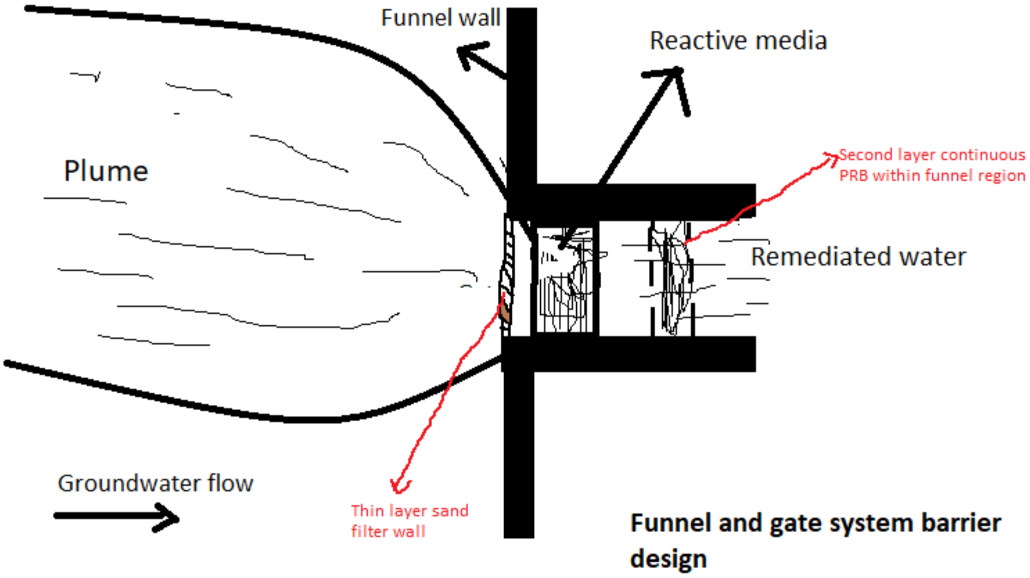
5 DISCUSSION

The applications of Permeable Reactive Barrier with ZVI as a reactive media for the remediation of TCE and PCE was studied which included the site characterisation and investigation of groundwater contaminated site in Orivesi, Finland. The construction of PRB, material selection and test, monitoring data interpretation for long-term remediation process of PRB constructed during RESET project, initiated by Finnish Environment Institute, is presented in this study. Also, a general comparative study of Chemical injection remediation process with PRB was done. All, these studies contribute to the final analysis of the applications of PRB for remediation of chlorinated solvents (TCE and PCE) in Orivesi groundwater. Furthermore, possibility of applications and improvement of PRB's remediation efficiency with minimum cost can be discussed for the conclusive analysis of this study, which might help for the better and efficient in-situ remediation of chlorinated solvents in Finnish groundwater in Future.

The data interpretations in Figure 1, 2, 3, 4 and 5 shows that the PCE and TCE which are the major chlorinated solvents targeted to remediate were successfully remediated and concentrations dropped below the limit values presented in Table 3. In 2006, analysis done by Finnish Environment Institute, the results showed that the PRB successfully remediated TCE and PCE and the value dropped below 5 µg l^{-1}, without any increment in VC concentration (Eskola et al., 2006). But in long term use the target concentrations has never been reached. Instead, according to Figure 4, the VC concentration in groundwater has increased above the WHO limit value and also the increment in concentration of cis-1,2 DCE is seen which in Iron passivation conditions might result in increment in VC concentration in groundwater.

The reason for this kind of decreasing efficiency of PRB in long term use might be due to the mineral deposits, nitrates and sulphate precipitates, carbonates and DO corroding the Iron. Mineral deposits and precipitates prevent the proper contact of contaminants with the Iron. High hydraulic due to fracture zones and galciofluvial deposits in Finnish land might also cause the problems in constructing desired reactive zone and thickness for proper water passage through PRB, resulting in lower efficiency. (Eskola et al., 2006.)

The possible solution for the improvement of barrier efficiency can be a multi-layer barrier system along with thin sand filter wall at the entrance of the gate. The solution is represented in Picture 6 below.



PICTURE 6: Addition of thin layer sand filter wall and continuous barrier to funnel gate design. (ITRC, Mining Waste Team, 2005, modified.)

The sand filter layer in the gate as shown in Picture 6 is a possible way to filter minerals, precipitates and biomass from entering the reactive zone which might contribute in preventing the early Iron passivation and corrosion. Whereas, also in Picture 6, the second layer continuous mini PRB might give the contaminants more residence time to dissociate completely through beta-elimination which helps decreases the possibility of increase in VC and cis-1,2 concentration in remediated water. Also, this improvisation might be useful in long term use of PRB to bring high TCE and PCE concentrations down to target limits.

Comparative study of chemical injection process with PRB showed that there are more similarities regarding reduction processes that both remediation process go through like both processes require proper site characterisation and investigations. Chemical injection process, although possess less construction work in comparison to PRB construction, can be used in wider contaminants remediation for quicker results. But on the other hand PRBs can be also a better solution in shallow aquifers and regular geophysical conditions.

TABLE 5: Final Discussion regarding the PRB applications

Discussion Topics	Points of discussion	Discussion and Analysis
TCE and PCE remediation in Orivesi	Was it successful?	It looks quite successful as the contaminants' concentration dropped down below limit values.
Possible problems in Orivesi PRB case	Increase in VC concentration, target limit values for TCE and PCE not achieved, why?	Mineral, precipitates and biomass deposits preventing required contact of contaminants and Iron. Decrease in Iron reactivity due to corrosion and high hydraulic.
Possible solutions	Is it possible to improve the efficiency? How?	Might be possible with slight improvisation with barrier design and technical researches. One possible solution is represented in Picture 5.
Comparison with Chemical injection process	Which is more applicable? Why?	Cost estimation PRB with multiple barrier system might be lower in case of long term use and large site remediation. But remediation efficiency of chemical injection is higher. PRB is applicable for particular contaminants while chemical injection remediates wide range of contaminants. For shallow aquifer in normal geographical and climatic conditions PRB is more applicable in long term use and is cost efficient.

More technical research is needed for field scale improved applications of PRB. But in general conditions (climatic and geographic), it is one of the most cost efficient and long-term remediation process. With improved technical barrier design and hybrid remediation process (for example: chemical injection and PRB used together), with proper monitoring and lab research PRB might be the future of in-situ groundwater remediation.

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APPENDICES

Appendix 1. Table for concentration of Chlorinated solvents monitored from the well HP505PE. (Water before entering the barrier)

Date	VC (µg l-1)	cis-DCE(µg l-1)	TCE(µg l-1)	PCE(µg l-1)
26.11.2008	0,05	2	27	120
5.5.2009	0,05	2,4	27	130
28.9.2009	0,1	1,6	16	89
7.9.2010	0,1	0,95	15	79
20.9.2011	0,5	0,85	9	68
10.10.2013	0,25	0,57	7,9	45
22.10.2015	0,25	0,52	7,4	53

Appendix 2. Table for concentration of Chlorinated solvents monitored from the well HP503PE. (Water after exiting the barrier)

Date	**VC (µg l-1)**	**cis-DCE(µg l-1)**	**TCE(µg l-1)**	**PCE(µg l-1)**
26.11.2008	4,5	6,5	7,7	6,8
5.5.2009	0,05	8,5	15	20
28.9.2009	2,3	22	14	28
7.9.2010	0,83	25	15	17
20.9.2011	0,5	11	8,1	17
10.10.2013	0,25	11	6,6	26
22.10.2015	0,66	12	4,8	17