Assignment 3 for ENVT 5503 Weng Mun Ong 24188697

Part 1 – Time series analysis

1. Introduction

Dichloromethane (DCM) is a common groundwater pollutant among chlorinated solvents. As a dense non-aqueous phase liquid (DNAPL), DCM tends to accumulate with other chlorinated organic compounds in aquifers (Hermon et al., 2018; Lucas & Jauzein, 2008). At the Yvelines district in Paris, high concentrations of DCM had been detected in groundwater at P site. This contamination was sourced from the past spills and disposal events of chlorinated solvents into a pit near the site (Lucas & Jauzein, 2008).

A pump-and-treat technology was implemented at P site as a remediation action to prevent DCM from spreading and removal of the DCM mass in the groundwater (Langwaldt & Puhakka, 2000; Lucas & Jauzein, 2008). Analysis of the time series of DCM levels is crucial for maintaining groundwater quality in Yvelines. For irregular time series data over three years, advanced functions such as the R zoo package is needed to provide better performance. Monitoring the trend of this time series provides understanding into monotonic changes whether DCM concentrations are increasing or decreasing to assess natural attenuation following the pump-and-treat well (Western Australian Government, 2023). A forecast model for future DCM concentrations is also necessary to predict possible mitigation needs. Therefore, this report aims to: 1) model the DCM time series across spatial and temporal scales; 2) identify the trend in DCM concentrations to assess the groundwater quality; 3) implement forecast model for future remediation actions.

2. Methods

The data collection of DCM concentrations was conducted from a monitoring station at the P site in Yvelines from January 1994 to May 1997. The original data on DCM concentrations was imported into R 4.3.3 for analysis (Lucas & Jauzein, 2008). The likely trajectory of groundwater DCM concentrations at the Yvelines site was assessed using time series models for trend and forecast analysis (Rate, 2024a) from R packages. A time series plot of the DCM concentrations was created with the zoo package due to the irregular time series of DCM concentrations.

Before conducting trend and forecast analysis, a power transformation (0.5) of the original data was applied based on a visual variance check to result in an easy reading of the DCM, comparing the untransformed, power-transformed, and $\log_{10}$-transformed data. The Augmented Dickey-Fuller Test was used to evaluate the stationarity of the time series. To estimate the trend period and slope for the trend line of DCM concentrations whether positive or negative, the Mann-Kendall Test and Sen's slope from the trend package (Gilbert, 1987) were performed in R. The trend was visualised using Locally Estimated Scatterplot Smoothing (LOESS) (Rate, 2024a).

For forecasting the future DCM concentrations for the original time series, an autoregressive integrated moving average (ARIMA) model was developed using the forecast package. Since there was no seasonality in the time series (estimated frequency of one), the non-seasonality model was developed easier. The parameters for the number of autoregressive predictors(p), differencing steps(d)and moving average predictors(q) values were determined using the auto.arima function, aiming for the lowest AIC and ensuring the confidence intervals did not include zero. The forecasted time series for DCM concentrations was plotted using ggplot2 package based on non-seasonal model.

3. Results

The time series plot of DCM concentrations for approximately 3.25 years is shown in Figure 1. The highest concentration (424278 µg/L) was recorded in 1994, while the lowest concentration (504 µg/L) occurred in 1997. The noticeable fluctuations during the first two years are plotted in Figure 2. There were relatively minimal changes in DCM concentrations after 1996 and the residual DCM concentrations mostly remained below 10000 µg/L. However, there is a sudden increase in DCM levels at the end of 1996.

For the trend analysis of the power-transformed (0.5) DCM concentrations, both trend tests resulted in p-values below 0.05 with S and Sen's slope values of -1.57×10^4 and -2.21, respectively. The results indicate a significant negative trend over the 3.25 years (Figure 2 and Table 1).

In forecasting the DCM concentrations for approximately 90 % of the length of the original time series, the ARIMA (2,1,2) model was used based on the lowest Akaike Information Criterion (AIC) value with 1928.52 and all confidence intervals excluding zero to achieve the forecast model's suitability (Table 2). The future projection for two additional years (Figure 3) suggests that residual DCM concentrations will remain in the groundwater. However, the wide shaded areas indicating the confidence intervals suggest a high level of forecasting uncertainty.

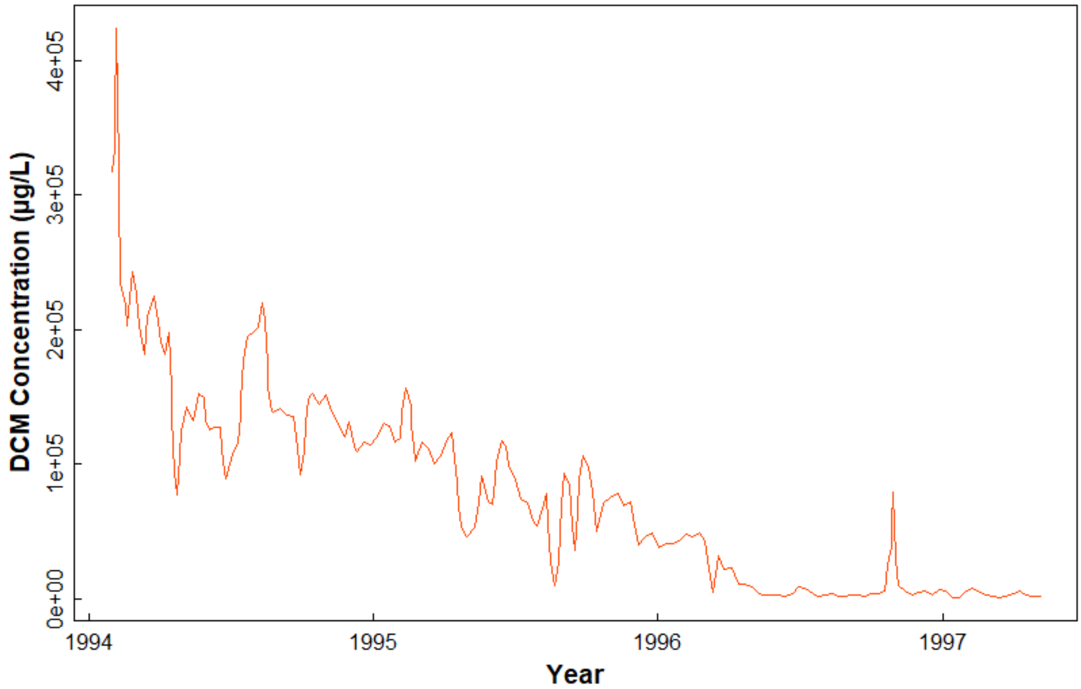

Figure 1 Plot of DCM concentrations time series data in approximately 3.25 years using zoo package.

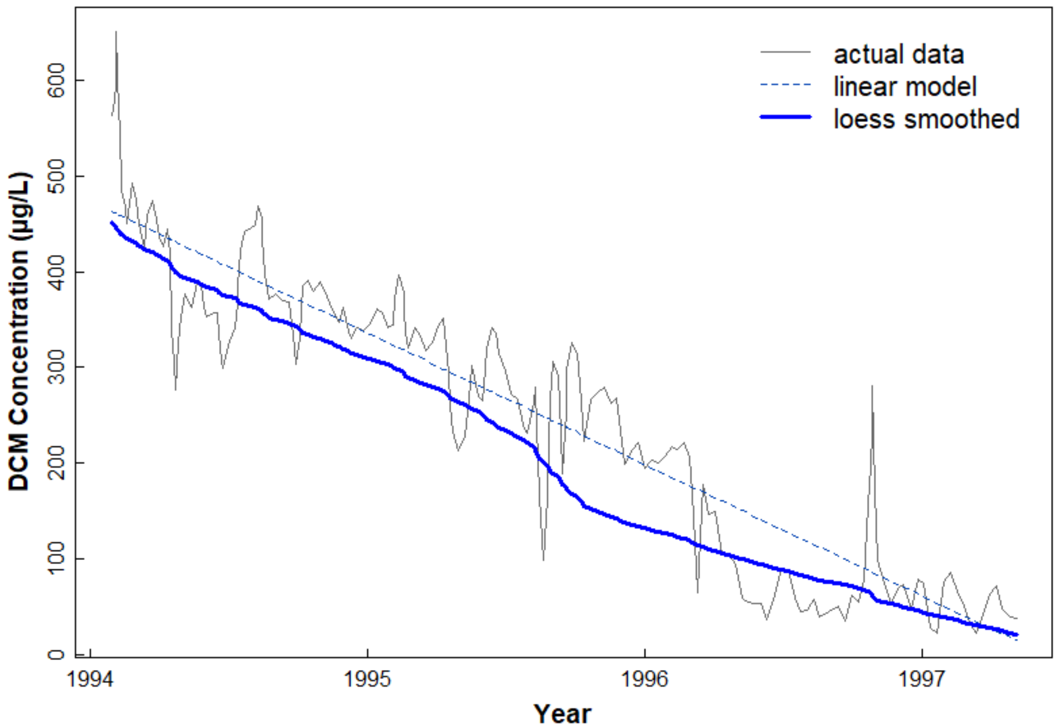

Figure 2 Plots of DCM concentrations time series data (0.5 power transformed) and the trend in approximately 3.25 years represented using a loess smoothing model.

Table 1 Summary of stationarity and trend analysis for DCM concentrations after 0.5 power transformation.

Analysis Type	Test	Metric	Value
Stationarity	Augmented Dickey- Fuller Test	p-value	0.0314
Trend	Mann-Kendall Test	p-value	$<2.20\times 10^{-16}$
		S	-1.57×10^{4}
	Sen's slope	p-value	$<2.20\times 10^{-16}$
		Sen's slope	-2.21

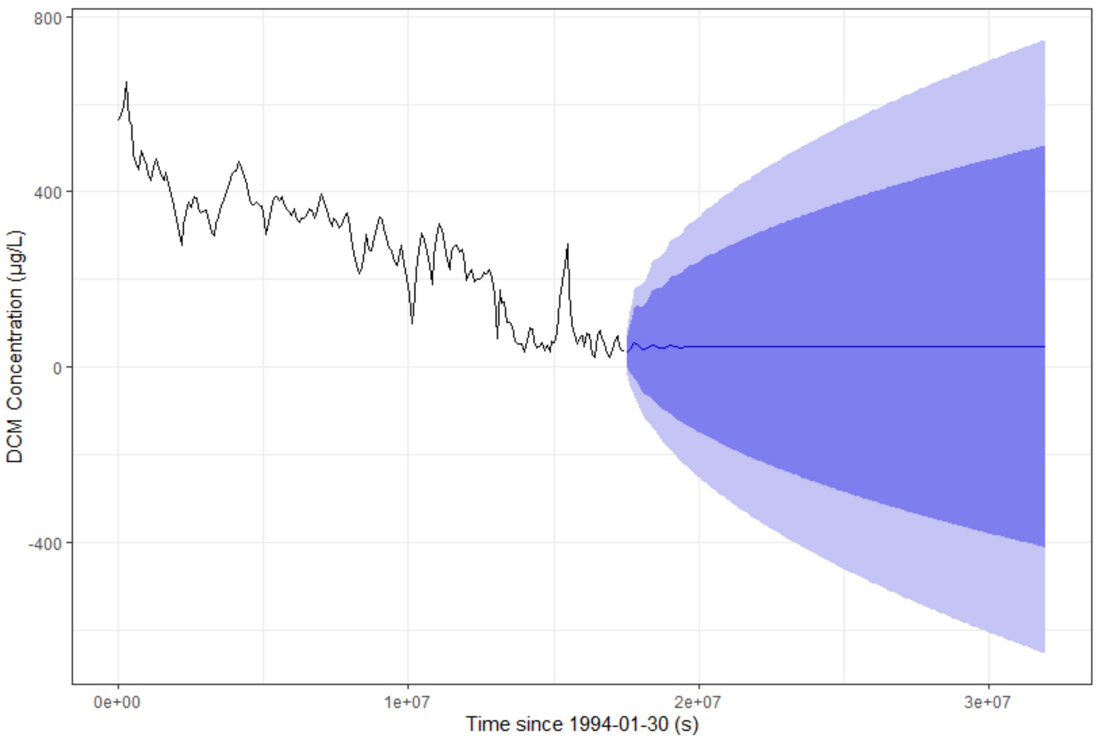

Figure 3: Powe transformation time series(zoo) with forecast no seasonality (estimated frequency is 1).

Table 2 The 2.5 % and 97.5% confidence intervals for the parameters of c (2,1,2) model with 1928.52 AIC.

C (2,1,2)	2.5%	97.5%
ar1	1.012	1.356
ar2	-1.023	-0.698
ma1	-1.264	-0.799
ma2	0.463	0.932

*ar: auto-regression coefficients; ma: moving average coefficients.

4. Discussion

According to time series data from 1994 to 1997, DCM concentrations at the P site monitoring station in Yvelines declined by approximately 99 %. Since DCM poses risk to the ecosystem in groundwater, a negative trend in its concentrations through the analysis of Mann-Kendall test and Sen's slope indicates an improvement in groundwater quality at the site (Western Australian Government, 2023). This decline supports the significance of a negative trend in the natural attenuation of DCM concentrations.

The notable reduction in DCM concentrations could be contributed by the pump-and-treat well, hydraulic protection from river and the aquifer's high permeability (Lucas & Jauzein, 2008). However, since the pump-and-treat well was stopped usually, it may explain the smaller variance in DCM concentrations during the latter half of the period (Lucas & Jauzein, 2008). Consequently, the natural attenuation and the river's hydraulic protective actions likely played major roles in decreasing DCM concentrations.

Despite the 99% decrease over 3.25 years, residual DCM concentrations showed minimal change in the final year. It might be potentially due to low DCM concentrations sustaining in the groundwater. A concentration spike with highest concentration in 78565 µg/L in from four detected times was recorded in late October. The DCM concentrations were quickly dropping to 9651 µg/L within a week, likely due to a temporary influx of DCM along the aquifer and operation of the pump-and-treat well at that period.

Forecast results suggest that residual DCM concentrations will persist in the groundwater over the next three years, indicating the need for enhanced remediation actions. Further studies should investigate the integrated mitigation strategies such as a combination of in *situ* bioremediation (Hermon et al., 2018) with pump-and-treat systems. However, the alternative models should be considered to support the predictions due to the significant uncertainties in current forecasting model.

5. Conclusion

In conclusion, the time series analysis of DCM concentrations at the P site in Yvelines from 1994 to 1997 demonstrates a notable improvement in groundwater quality in DCM concentrations and a significant negative trend from square root transformation by using zoo and trend packages in R 4.3.3. The pump-and-treat well effectively reduced DCM concentrations. Further studies on integrated remediation measures are recommended to prevent future DCM accumulation. The modifications to forecast models could help reduce uncertainty in future predictions.

Part 2 – Simulation of a permeable reactive barrier using Hydrus-1D

1. Introduction

Perfluorooctanoic acid (PFOA) is an emerging contaminant (EC) from the group of per- and polyfluoroalkyl substances (PFAS). It is mainly used in fire-fighting foams and stain-resistant products (Cheng et al., 2008; Wang et al., 2024). The strong persistent ability of PFOA in the environment leads to bioaccumulation in groundwater over long periods (Cheng et al., 2008). This persistence is due to the highly stable C-F bond in PFOA (127 kcal mol^{-1}) and makes it hard to be degraded (Wang et al., 2024). Therefore, PFOA in groundwater poses risks to ecosystems and human health.

Therefore, the implementation of effective remediation strategies to remove PFOA from groundwater is important to mitigate environmental concerns. Permeable reactive barrier (PRB) technology is an effective approach to remove the contaminants in groundwater. PRB is a subsurface wall containing reactive materials, such as zero-valent iron (ZVI, Fe^0). PRB intercepts and treats the contaminants by transforming them into less harmful compounds (Faisal et al., 2018). ZVI is an eco-friendly reactive material and has shown efficiency in removing PFOA from groundwater through defluorination (Liu et al., 2020). In a brief, this report aims to simulate PFOA concentrations in groundwater over a temporal scale of 300 days, with and without the implementation of a ZVI-PRB using Hydrus-1D modelling software.

2. Methods

The simulation models were developed using HYDRUS-1D to simulate the concentrations of PFOA in groundwater, both with and without a permeable reactive barrier (PRB). Input parameter values were identified before initiating the simulations and are listed in Table 3. Two soil materials were selected to represent the aquifer of groundwater and the ZVI-PRB. A flow path of 30 m was chosen to indicate the groundwater flow, with a simulation period of 300 days and six print times to track the changes in PFOA concentration. Given the variety of soil types encountered in the groundwater, Sandy Clay was selected to represent the aquifer for the simulation models (Ajayi & Umoh, 1998). The parameters for water flow and solute transport in Sandy Clay were applied with default values by Hydrus-1D.

The values for the adsorption isotherm coefficient (Kd) and first order rate coefficient (Alpha) for PFOA passing through the ZVI-PRB were referenced from an article (Wang et al., 2024). The initial PFOA concentration of 1 mg/L was chosen based on the same article (Wang et al., 2024). A summary of the parameters' values for water flow, solute transport, and reaction based on the article is presented in Table 4. To simulate the concentration of PFOA without the ZVI-PRB in another simulation model, Kd and Alpha values were set to zero in the solute transport parameter settings.

For the simulation models, a 3 m thick ZVI-PRB was specified in the material distribution (Jiang et al., 2023) with the distances from13.5 m to 16.5 m for two material indices to define the soil profile. The initial water contents in the models were set to 0 cm for the saturation zone (Rate, 2024b). After setting up the graphic editor and finalising all parameters in Hydrus-1D, the models were successfully developed. The simulation results were then imported into R for data analysis where graphs were generated to illustrate the changes in the concentrations of PFOA over time.

Table 3 General simulation parameters for the modelling of PFOA concentrations in groundwater using Hydrus-1D.

Parameters	Terms	Values
Geometry Info	Length(m)	30
	Number of soil materials	2
Time Information	Final Times (days)	300
Print Information	Number of Print Times	6 (Default)
Solute Transport	Mass unit	g
	Pulse Duration(days)	30
Solute Transport Boundary Conditions	Boundary Conditions(mg/L)	1
Soil Profile- Graphic Editor	Water Condition	0
	Material Condition	2
	Thickness of PRB (m)	3 (13.5 – 16.5)

Table 4 Simulation parameters with the variables of groundwater aquifer and ZVI-PRB for the modelling of PFOA concentrations in groundwater using Hydrus-1D.

Parameters	Terms	Groundwater	ZVI-PRB
Water Flow	Soil Catalogue	Sandy Clay	ZVI-PRB
	Residual soil water content, Qr [-]	0.1	0.0524
	Saturated soil water content, Qs [-]	0.38	0.5013
	Alpha (soil water retention) [1/m]	2.7	4.56
	n (soil water retention) [-]	1.23	3.0374
	Saturated hydraulic conductivity, Ks [m/days]	0.0288	21.6
Solute Transport	Bulk Density	1500000	1130000
	Dispersion	0.1	0.0048
	Fraction	1	0.48
Solute Transport and Reaction	Kd for contaminants(m^3/g)	0	420000
	Alpha(h^{-1})	0	0.26

3. Results

The simulation models for PFOA in groundwater with and without the permeable reactive barrier (PRB) are presented in Figures 4 and 5, respectively. The higher concentrations observed at 50 and 100 days show the transport of PFOA within the first 10 m of the groundwater flow path. At 100 days (green dotted and dashed line), the concentration of PFOA decreases to 0 mg/L after passing through the ZVI-PRB, located at the end of the flow path. The PFOA concentration at 200 days gradually drops to 0 mg/L as the plume reaches and passes through the ZVI-PRB along the flow path with approximately 14 m. At 250 days, the concentrations of PFOA drop below 0.1 mg/L with the ZVI-PRB adsorbing the residual and resulting in no detectable PFOA in the groundwater after 250 days. The graph of sorbed concentration over time (Figure 4, right) shows a peak around 15 m and indicates the effectiveness of the ZVI-PRB in adsorbing PFOA. There are small overlaps in the peak of sorbed concentrations at 150, 200, and 250 days which demonstrates the consistent adsorption using the ZVI-PRB over time. After 15 m, the sorbed concentration are zero.

Figure 5 shows the flow path of PFOA in groundwater over 300 days. The concentration of PFOA decreases with increasing distance along the groundwater flow path without ZVI-PRB. There are the larger differences in PFOA concentrations observed during the first three stages, while smaller differences observed in the last three stages. Without the application of the ZVI-PRB, PFOA remains present in the groundwater throughout the simulation.

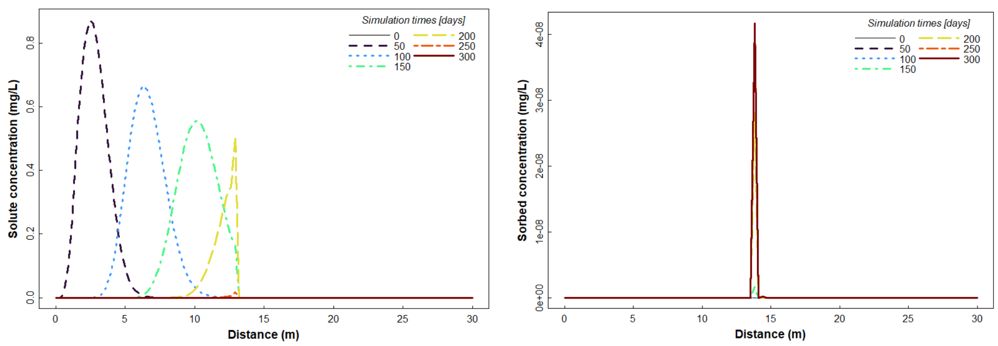

Figure 4 The concentration of PFOA after 300days simulation (left) and sorbed concentration (right) with the implementation of ZVI-PRB

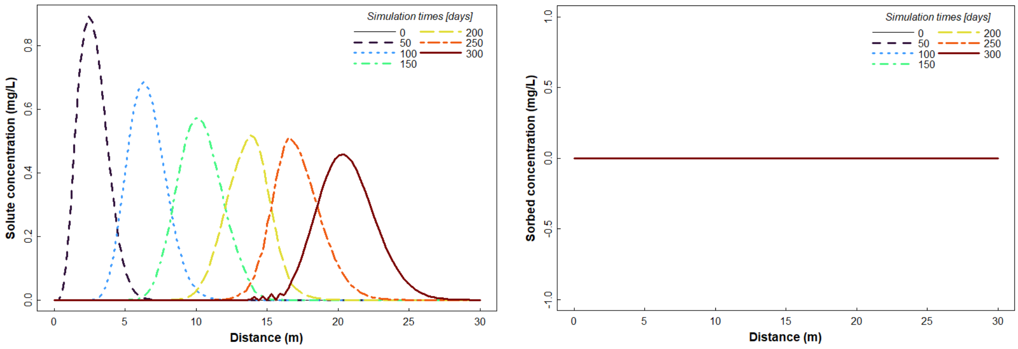

Figure 5 The concentration of PFOA after 300days simulation (left) and sorbed concentration (right) without the implementation of ZVI-PRB

4. Discussion

The gradual decrease in PFOA concentrations in the simulation models after passing through the ZVI-PRB at 13.5 m of groundwater flow path demonstrates the high effectiveness of the permeable reactive barrier (PRB) with the reactive material of zero-valent iron (ZVI). The sorbed concentration results indicates PFOA in the groundwater is fully captured by the ZVI-PRB and does not transport to further distance. These results indicate the potential of ZVI-PRB technology as an efficient remediation measure to remove 1 mg/L PFOA along a 30 m groundwater flow path with sandy clay aquifer. According to the site investigations' health-based guideline values in Australia, the acceptable PFOA levels for recreational and drinking water are 0.56 µg/L and 10 µg/L, respectively (Australian Government Department of Health, 2022). Consequently, 1 mg/L of PFOA in groundwater which exceeds the recreational water quality guideline can be completely removed within 300 days with the application of ZVI-PRB. The removal process of PFOA is achieved through the defluorination of PFOA into smaller compounds by ZVI. However, there are some challenges remain due to the time-consuming problem of the remediation process and the various of soil types in groundwater such as Sand, Silt Sand, and Sandy Loam with different hydraulic conductivity in simulation models of ZVI-PRB. Thus, further studies with the modification of these models by exploring different soil types and shorter final times to optimise the effectiveness of ZVI-PRB. Additionally, the combination of ZVI-PRB with microbial remediation which could remove PFOA in shorter period (Wang et al., 2024) gives a novel direction for future research.

5. Conclusion

In conclusion, this report demonstrates the effectiveness of ZVI-PRB in decreasing the PFOA concentrations in groundwater (Sandy Clay) within 300 days with 6 print times by simulating the models under the presence and absence of ZVI-PRB in Hydrus-1D. The models achieve the removal of PFOA below the health-based guidelines for recreational and drinking water in Australia. The parameters of the groundwater aquifer and ZVI-PRB were referred to in the articles mentioned before. Future studies on the different soil types of aquifers and the integration of bioremediation with ZVI-PRB can be conducted to shorten the final times of ZVI-PRB applications.

6. Reference

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