Statistical Analysis of the Effect of Water Table Fluctuation and Soil Layering on the Distribution of BTEX on Soil and Groundwater Under Anaerobic Condition

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Abstract

Crude oil, gasoline, and diesel fuel spills pollute groundwater in many coastal areas. BTEX is a hydrocarbon of concern due to its high-water solubility, which allows it to spread widely in the subsurface environment. The mobile phase of LNAPLs percolates through porous soil and accumulates above the water table. Subsurface geological, pollutant morphology, and hydrogeologic site features make natural attenuation difficult to understand. Texture and vertical spatial variability affect soil hydraulic properties and water and contaminant distribution in soil profiles. Changes in rainfall strength and frequency and increased water demand may increase groundwater level oscillations in the next century. Five sets of columns, including one soil column and one equilibrium column, were operated for 150 days. One of the columns was operated under a steady state condition (S), and four columns under transient water table condition. The stable column (S), and the Fluctuating column 1 (F1) contain homogenized soil, while the fluctuating columns 2, 3, and 4 contains heterogenous soil. ORP values at the middle of the columns varied cyclically with WTF. EC values affected greatly by fluctuation and temperature and the statistical test p-value $3.119e^{-10} < 0.05$ implying that there are statistical differences between EC values of these columns. On the other hand, pH for the five columns were fluctuated in the same range (P-value $0.3694 > 0.05$). Soil layering affects the attenuation of BTEX, as the peak concentrations for benzene occurred at second imbibition cycle for the homogeneous soil, while for the heterogeneous soil occurred between second and fourth imbibition cycles.

Keywords: BTEX; Groundwater; Water table fluctuations; soil hydrogeochemistry

1. Introduction

Groundwater pollution is common in coastal areas and it is caused by the accidental spilling of petroleum products such as crude oil, gasoline, and diesel fuel (Huang et al., 2021). Certain compounds in LNAPL, such as benzene, have a negative impact on the environment and human health. (Cavelan et al., 2022; Sookhak Lari et al., 2018). Because of this, BTEX is among the hydrocarbons of highest concern (Chompusri et al., 2002). After LNAPL spilled, the mobile phase infiltrates through the soil and collects at the top of the water table. A considerable fraction of pollutants may be residualized as LNAPL ganglia by capillary pressures or sticking to soil grains (Cavelan et al., 2021). When the water table decreases, the mobile LNAPL goes down with it, which results in a redistribution of the LNAPL and a rearrangement of the partitioning of LNAPL components across various phases (Cavelan et al., 2022).

Remediation strategies for polluted aquifers and the natural attenuation mechanisms of hydrocarbons in the source zone and groundwater plumes have been studied extensively (Sihota et al., 2016). Due to factors such as subsurface geological and microbiological heterogeneity, pollutant morphology and type, and hydrogeologic features of a site, all of which influence the amount and rate of NSZD depletion (Sookhak Lari et al., 2018; Van De Ven et al., 2021; Zanello et al., 2021). Texture and vertical spatial heterogeneity affect soil hydraulic properties and water and pollutant distribution in soil profiles. Depending on soil hydraulic properties, the hydraulic relationship between surface soil and groundwater can fluctuate while the water table depth remains constant (Li et al., 2014).

Subsurface biogeochemical cycling and pollutant and nutrient are regulated by soil hydrological oscillations (Zhang & Furman, 2021). Dissolution, volatilization, and transverse migration of dissolved LNAPL components are restricted in stable water table conditions due to the slow vertical dispersion and diffusion of dissolved LNAPL compounds (Cavelan et al., 2022; K. Gupta et al., 2019). The movement of water table results in the movement and distribution of LNAPLs, particularly in the vertical direction (Alazaiza et al., 2021). Moreover, successful remediation planning is heavily reliant on our understanding of the aquifer's structure (i.e., porosity and permeability) (Di Palma et al., 2017). Temperature variations, pH fluctuations, changes in water table dynamics, and changes in soil moisture content are often what distinguish difficult contaminated areas (Haberer et al., 2015).

Few studies have been conducted to investigate the mass transfer of NAPLs in the capillary fringe in the presence of dynamic boundary conditions; however, these studies are uncommon. There is a lack of research that focuses on the alteration of redox conditions and the soil geochemical properties under these conditions (J. Y. Lee et al., 2001; Rühle et al., 2015; Zhou et al., 2015). In this experiment, the distributions of hydrocarbon pollutants and hydrogeochemical parameters were investigated in five columns polluted with petroleum hydrocarbons (BTEX) under anaerobic conditions, and the analysis carried out using Kruskal wallis test for the individual parameters and Kendall correlation to find if there any connection between the hydro-chemical properties and BTEX concentrations in the columns.

2. Materials and Methods

Five sets of columns, including one soil column and one equilibrium column, were built. One of the columns was operated under a steady state condition (S), and four columns were operated under transient water table condition in a range of soil surface (0 cm) to -40 cm. The stable column (S), and the Fluctuating column 1 (F1) contain homogenized soil, while the fluctuating columns 2, 3, and 4 (i.e., F2, F3, and F4) contains heterogenous soil. Moreover, the fluctuating columns 3 and 4 (i.e., F3, and F4) has higher temperature to represent groundwater temperature in the state of Qatar (Ahmad et al., 2020; Ngueleu et al., 2018).The water level in the equilibrium columns was used to manage the imposed water regime, and the water level in the equilibrium column was determined by pump channel. The soil for this study was collected from Sumaysima beach in Qatar's eastern suburb of Doha (25°34'26.4"N 51°29'15.7"E). This location demonstrates the ongoing interplay between seawater and groundwater, as seen by the oscillation of the water table (Ngueleu et al., 2019). The synthetic influent solution was prepared by mixing Milli-Q water with background nutrients such as $MgCl_2$ (89 mg L-1), KCl (24 mg L-1) Calcium chloride (243 mg L-1) and NaCl (1300mg L-1). During the first 24 hours of the experiment, the pump channel A was used to fill the equilibrium columns with the synthetic groundwater. 2 L Tedlar bags filled with argon gas was connected to the equilibrium columns to offer hydraulic elements of water fluctuation and collect gas samples. The anaerobic conditions were achieved by continuously purging the equilibrium columns to a DO concentration < 0.8 mg L-1.

3. Results and Discussion

3.1 Hydro-chemical properties

The average porosity of the soil in the groundwater level column, S, F1, and F2 were 22%, 22%, and 22%, respectively. ORP values at the middle of the columns fluctuated during the experiment, while for the bottom of the columns a drop in ORP values occurred in F1, F2, and F3 between 30 and 40 days, and for S and F4, the decrease in ORP values occurred at 70 and 150 days, respectively. This suggests that circumstances conducive to anaerobic respiration have developed in each and every soil column (Ismail et al., 2020; Shafieiyoun et al., 2020; Meng et al., 2021). The results of the statistical test for the middle of S, F1, and F2 showed that the p-value is equal to 0.6771 which is > 0.05, which implies that there is no significant difference between the ORP values, while the p-value for ORP values at the bottom of the columns is equal to 0.0649 which is > 0.05 implies that there is no statistical difference between the columns. This finding implies that ORP values statistically didn't change either with water table fluctuations or due to soil heterogeneity. Haberer et al., (2012), Rezanezhad et al., (2014), Wang et al., (2014), and Meng et al., (2021), they demonstrated that the ORP measured at a particular depth varies cyclically with the fluctuations of the water level.

At the middle of the columns, EC for the stable column S was fluctuated in a lower range than F1, while F1 started at 5000 mS cm^{-1} and decreased to ~ 4000 by the end of the experiment. while comparing the fluctuating columns F1 and F2 to observe the influence of soil layering, these two columns have an inverse effect on the EC values as F1 started at higher concentration and decreased, while F2 started at a lower concentration and increased. The p-value for the EC values at the middle of the columns is equal to $1.7971e^{-05}$ which < 0.05 implying that there are statistical differences between EC values at the middle of these columns. Atekwana and Atekwana (2010) reported that changes in pore fluid conductivity can be caused by both hydrologic and microbiological process. The hydrological process such as advective flow due to water table fluctuation.

The initial sulfate concentrations at the middle of all columns are 100, 282, and 134 mg L^{-1} for S, F1, and F2, respectively. For the stable column S no change in sulfate concentration were detected during the experiment, while for the fluctuating column F1, the concentration of sulfate increased with the first imbibition cycle and by the end of the experiment decreased by 75% of the initial concentration. Moreover, for the fluctuating columns F2, the concentration of sulfate increased after the second imbibition cycle and decreased by 34% of the initial concentration. The increase in sulfate concentration occurs due to the movement of sulfate to the middle of the column with the water table.

The effect of water table fluctuation is observed by comparing the columns S and F1, significant reduction occurs in F1 as compared with S. Comparing the columns F1 and F2 would provide insight into the effect of soil layering, as the reduction in sulfate concentration is greater in F1 than in F2. The p-value for at the middle of the columns S, F1, and F2 is found to be equal to $2.2516e^{-04}$ which < 0.05 implying that there are statistical differences between sulfate concentrations during the experiment between the columns and the water table fluctuations and soil heterogeneity has effects on sulfate concentrations.

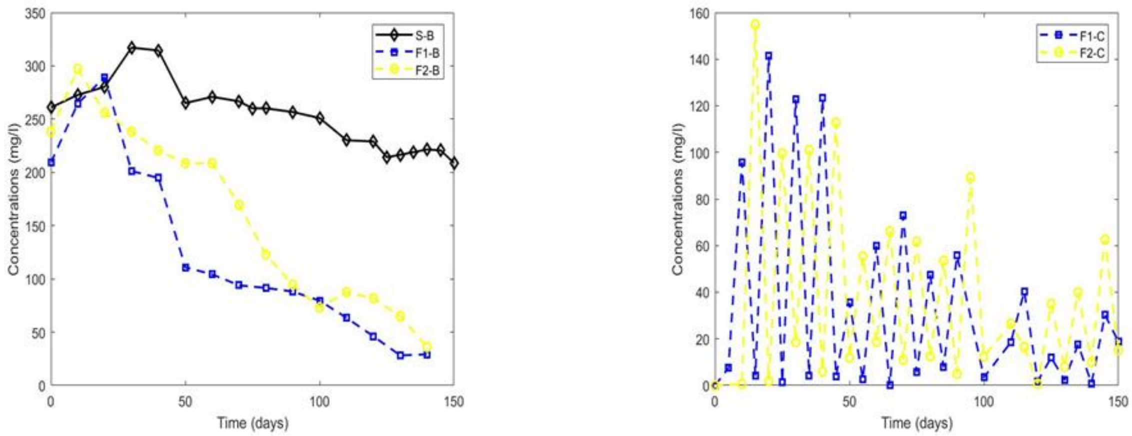

Fig. 1: Benzene concentrations at the middle and the bottom of the columns S, F1, and F2

3.2 Correlation between the Hydro-chemical Parameters of Dissolved Organics

For the experimental condition, LNAPLs which refer to benzene and toluene were under completely saturated condition in the stable column (S). Whereas the conditions of the LNAPLs in the fluctuating columns (F1& F2) were continuously cycling between being saturated and unsaturated. The Kendall tau correlation test is used to test the correlation between the concentration of hydro-chemical indicators (ORP, EC, and sulfate concentrations) and the concentration of benzene and toluene.

The concentrations of benzene and toluene are found in Figure 1 and figure 2. For ORP, both S and F1 columns have positive moderate correlation with benzene, while for toluene, it is a positive weak correlation. It implies that water table fluctuations didn't affect the ORP values between the two homogenized soil columns in the presence of LNAPLs. For EC, benzene and toluene correlation in the column S in not statistically significant, while in the column F1, the correlation is positive strong and moderate, for benzene and toluene, respectively. For the sulfate concentrations with benzene between stable and fluctuating homogenized soil, the correlation is positive strong and very strong in the columns S and F1, respectively. For toluene, the correlation is weak and strong in S and F1, respectively. These differences occurred as a result of BT dissolution due to water table fluctuation while at the same time sulfate is accumulated at the middle (depth B) of the column by the moving synthetic groundwater from the bottom of the columns to the top due to sampling. This argument can be supported by the decrease in sulfate concentrations at the bottom (depth C) of the stable column. It may be validated by examining the sulfate concentration pattern in the stable column with the concentrations of Ca^{2+} and Mg^{2+} concentration patterns. In a study that was quite similar to this one, Rezanezhad et al., (2014) found that the solid-phase concentrations of elements such as iron, manganese, and others are higher in the first 30 centimeters of the stable column, but decrease with increasing depth. The increase in benzene concentration can be a result of its high dissolution rate and higher solubility in water (Kim et al., 2008; Njobuenwu et al., 2005), which occurs due to increase contact time. This correlation may possibly be a consequence of increased biodegradation and natural attenuation at this location of the column, particularly when it is accompanied with a positive correlation with ORP and a negative correlation with DIC.

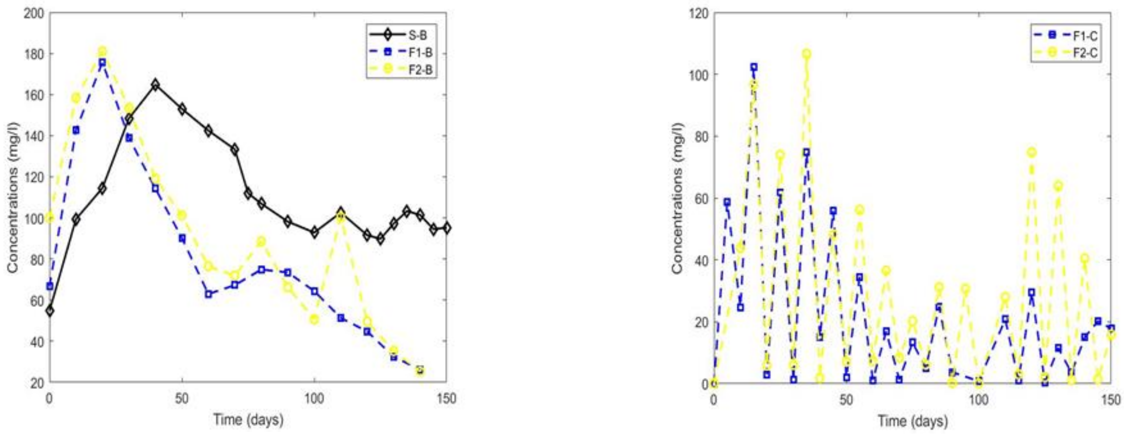

Fig. 2: Toluene Concentrations at the middle and the bottom of the columns S, F1, and F2

Between the two fluctuating columns, F1 and F2, for ORP in both F1 and F2 has positive moderate correlation with benzene and toluene. This may imply that soil heterogeneity didn't affect ORP values. For EC, benzene has strong positive correlations in F1, while it is negative strong in F2. Same for toluene, the correlation with EC, is moderate positive in F1, but it is moderate negative in F2. The correlations between Benzene and sulfate concentrations are positive, very strong and positive moderate, respectively. For toluene, it is strong and moderate for F1 and F2, respectively. Soil homogeneity varies between the two columns, with homogenized soil found in F1 and heterogeneous soil in F2. By comparing solely homogeneous and heterogeneous soil (F1, and F2), it can be observed that homogeneity has a greater impact on the dissolution of benzene and toluene and the flow of sulfate through the column, particularly in the layered column F2 where injected layer has a low permeability. Johnston and Trefry (2009) demonstrates that the layer variability has an influence on the initial vertical distribution of LNAPL, while the source zone layer does not have such a significant influence on the LNAPL recovery rate. Rather, the most influential factors are media properties around the water table that are farther from the well.

The soil texture and vertical spatial variability is significantly impact soil hydraulic characteristics and the distribution of water and contaminants throughout the soil profile (Johnston & Trefry, 2009; Li et al., 2014). When the fluctuating water table moved to the upper and lower portions of the column during the imbibition and drainage cycles, it redistributed LNAPLs and sulfate vertically, which explains their concentration increase at the second and third imbibition cycles for the fluctuating columns. Kehew and Lynch (2011) stated that sulfate can be carried as far as 1.75 meters below the water table. Numerous scholars have explained how variations in groundwater level affect the vertical mobility and spatial distribution of NAPLs within an aquifer (Alazaiza et al., 2020; Kehew & Lynch, 2011; Lee et al., 2001; Van De Ven et al., 2021).

4. Conclusion

ORP values in the middle columns varied cyclically with WTF and promoting reducing conditions, but statistically it has similar correlation in term of water table fluctuations and soil heterogeneity. EC values was affected greatly by water table fluctuation, as well as soil heterogeneity in the presence of benzene and toluene. The sulfate concentrations reduction in homogenized soil is greater than layered soil, and it reduces the correlation between LNAPLs and sulfate concentrations. The association between BTEX and sulfate concentrations, when combined with a positive correlation with ORP and a negative correlation with DIC, may indicate an increase in natural attenuations in the fluctuating columns.

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Cite as: Reem Ismail R. & Al Raoush R., "Statistical Analysis of the Effect of Water Table Fluctuation and Soil Layering on the Distribution of BTEX on Soil and Groundwater Under Anaerobic Condition", *The 2nd International Conference on Civil Infrastructure and Construction (CIC 2023)*, Doha, Qatar, 5-8 February 2023, DOI: https://doi.org/10.29117/cic.2023.0185