

Article

Mechanisms of Non-Aqueous Phase Liquid Retention in Low-Permeability Aquifer Lenses: Effects on Contaminant Remediation

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Abstract: The residual non-aqueous phase liquid (NAPL) within low-permeability lenses of aquifers is a major contributor to “tailing”, a phenomenon that complicates the remediation of NAPL-contaminated sites. A fundamental challenge in addressing this issue is the lack of understanding of the primary controlling factors and underlying effects of NAPL residuals in these aquifer lenses. This study aims to identify the key factors and mechanisms affecting NAPL residuals in low-permeability lenses through a series of experimental approaches. These include soil column simulation experiments on NAPL residuals in various low-permeability lenses, adsorption experiments on aquifer and lens particles, pore mercury intrusion testing, and particle size distribution analysis. The experiments provided valuable data on residual NAPL saturation S_R , particle adsorption capacity, particle size, gradation, and pore size and distribution in different lenses. Using a mass conservation approach, the particle adsorption contributed less than 0.5% to the total NAPL residuals, while retention accounted for more than 99.5%, highlighting that retention is the dominant mechanism governing NAPL persistence in these lenses. The mechanism underlying this result was further clarified through an analysis of particle size characteristics. Correlation analysis was conducted to examine the relationships between residual NAPL and macropore porosity ($n_{\max}$, diameter > 60 μm), mesopore porosity (n_{mid} , diameter = 30~60 μm), and small pore porosity ($n_{\min}$, diameter < 30 μm). The results demonstrated that mesopores exhibited the strongest correlation with NAPL retention, due to their pronounced capillary action and sufficient storage capacity for NAPL.

Keywords: aquifer; low-permeability lens; NAPL residuals; particle adsorption; retention; pore diameter



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1. Introduction

In recent years, the increased utilization of organic chemical products has led to a significant influx of organic compounds into the subsurface environment during processes such as refining, storage, transportation, and usage [1–4]. Among these compounds,

petroleum and petroleum-based chemical pollutants frequently manifest in water as non-aqueous phase liquid (NAPL) [5–7]. NAPL can be classified into two categories according to their density. One category is Light Non-Aqueous Phase Liquids (LNAPLs) with a density less than that of water. Common LNAPLs include diesel, benzene, xylene, etc. The other category is Dense Non-Aqueous Phase Liquids (DNAPLs) with a density greater than that of water. Common DNAPLs include tetrachloroethylene, chlorinated organic solvents, etc. NAPL pollutants are characterized by their high toxicity, chemical stability, and resistance to degradation [8–10], which contributes to their prolonged persistence in subsurface soil and water environments, thereby posing significant threats to both ecological and human health. During the remediation of NAPL-contaminated sites, it has been observed that the “tailing” phenomenon, resulting from residual NAPL in low-permeability lenses (a low-permeability lens refers to a geological body whose permeability is poorer than that of the surrounding aquifer media and whose volume is much smaller than that of the aquifer) of aquifers (Figure 1), is a primary factor contributing to the failure of pollution treatment efforts [11–14]. Therefore, it is imperative to identify the key controlling factors and mechanisms that affect the presence of residual NAPL in low-permeability lenses of aquifers to enhance the effectiveness of NAPL pollution remediation strategies.

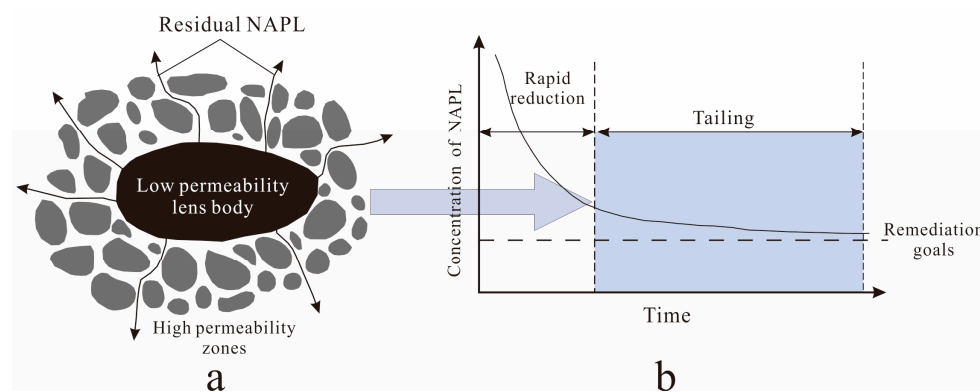


Figure 1. Residual NAPL in low-permeability lens body (a) leads to “tailing” (b).

To investigate the effect of aquifer lenses on NAPL residuals, researchers both domestically and internationally have undertaken a series of studies. The findings suggest that NAPL residuals in aquifers are primarily composed of pore retention and particle adsorption [15–17]. The particle size of the lens plays a significant role in affecting NAPL residuals: in fine-grained media, coarser lenses facilitate NAPL migration, thereby reducing residuals; conversely, in coarse-grained media, finer lenses impede migration, resulting in increased NAPL residuals [18–20]. Additionally, alterations in the pore structure of the lenses also affect NAPL residuals. Smaller pores elevate the critical displacement pressure, hindering water flow from overcoming capillary forces to penetrate low-permeability regions. In these zones, residual NAPL aggregates form NAPL-contaminated areas, consequently increasing NAPL residuals [21–26].

In summary, NAPL residuals in aquifers are affected by particle adsorption and pore retention mechanisms. Variations in NAPL residuals are associated with the grain size and pore characteristics of aquifer lenses. However, the extent to which NAPL residuals are sensitive to particle adsorption and pore retention, as well as the underlying mechanisms driving these effects, remain inadequately understood. To investigate this issue, this study designed soil column simulation experiments that varied permeability coefficient ratios K_{mn} , which represent the ratio of the permeability coefficient of the aquifer medium to the lens. By modifying the permeability of the lenses, this study simulated aquifers containing different lens types to examine the variations in NAPL residuals under diverse

lens conditions. Additionally, particle adsorption experiments were conducted to quantify the maximum adsorption capacity of the lenses for NAPL. Utilizing the law of mass conservation, this study calculated the sensitivity ranking of NAPL residuals in relation to particle adsorption and pore retention, thereby identifying the primary factors that control NAPL behavior in aquifer lenses. Furthermore, particle size distribution experiments and mercury intrusion tests were performed to ascertain the grain size and pore characteristics of both aquifers and lenses. By integrating the influence rankings of particle adsorption and retention on residual NAPL, correlation analysis was employed to elucidate the mechanisms that affect NAPL residuals in aquifer lenses.

2. Materials and Methods

To achieve the objectives of this study, a series of experiments were designed, including soil column simulation experiments, particle adsorption experiments, mercury intrusion porosimetry, and particle size analysis. Furthermore, a standard curve for NAPL concentration was established based on experimental measurements. The materials and methods employed in each experiment are detailed below.

2.1. Soil Column Simulation Experiment

2.1.1. Experimental Materials

No. 0 diesel is a non-toxic and easily accessible LNAPL. Its properties, such as density, viscosity, solubility, etc., are similar to those of common NAPL pollutants like xylene, crude oil, and aviation kerosene. So, in this experiment, non-toxic and available No. 0 diesel was utilized as a substitute for NAPL pollutants. The properties of the diesel are summarized in Table 1. To prevent microbial degradation from affecting the experimental results [27], white quartz sand with low clay content was selected to simulate the aquifer medium. This sand was procured from Henan Minghai Environmental Technology Co., Ltd. (Zhengzhou City, Henan Province, China) and underwent sterilization at high temperatures (105) prior to its application. The physical properties of the quartz sand are outlined in Table 2.

Table 1. Physicochemical properties of diesel used in NAPL experiments.

Viscosity (mPa·s)	Surface Tension (mN·m)	Liquefied Density ρ_o (g/mL)	Boiling Point (°C)	Octane Number
287	2.68	0.83	180–360	40–55

Table 2. Physical and permeability characteristics of quartz sand used in NAPL simulations.

Medium ID	Particle Size D (mm)	Bulk Density ρ (g/cm ³)	Permeability Coefficient K (m/d)	Permeability Coefficient Ratio K_{mn}	Porosity n (%)
No. 1 quartz sand (simulating aquifer)	0.25–4.00	1.53	137.84	1	42.85
No. 2 quartz sand (simulating low-permeability lens body)	0.09–1.75	1.61	30.04	5	41.07
No. 3 quartz sand (simulating low-permeability lens body)	0.063–1.00	1.69	12.45	11	40.67
No. 4 quartz sand (simulating low-permeability lens body)	0.063–0.75	1.69	5.93	23	40.61
No. 5 quartz sand (simulating low-permeability lens body)	0.053–0.425	1.73	2.78	50	40.59

The experimental setup included a HACH DR3900 spectrophotometer, an emulsifier, a HACH DRB200 digester, 500 mL beakers, pipettes, and HACH reagent tubes.

2.1.2. Experimental Apparatus and Design

In this study, soil column simulation experiments were employed to investigate the variations in NAPL residuals under varying conditions by modifying the permeability, size, and hydraulic gradient of the lens. The soil column was constructed from polymethyl methacrylate (PMMA), measuring 95 cm in height and 7 cm in diameter, with a maximum filling height of 75 cm. A sampling port and a downstream head measurement device were installed at the base of the column, while an inlet connected to a constant-head water supply was positioned 10 cm from the top (Figure 2a). The lens was designed with a diameter of $\phi = 3.5$ cm and a height of $h = 20$ cm, taking into account the dimensions of the soil column, the flow characteristics of liquids within the column, and the effect of the lens on NAPL residuals. Based on the permeability coefficients of the media in Table 2, five levels of K_{mn} were established at 1, 5, 11, 23, and 50. Previous research indicates that the hydraulic gradient of groundwater in plain areas typically ranges from 1‰ to 12‰ [28,29]. For the permeability coefficients of the media utilized in this experiment, the flow velocity was set at 0.14 cm/min to facilitate monitoring; the filled soil column is shown in Figure 2b. A comprehensive overview of the experimental design is summarized in Table 3.

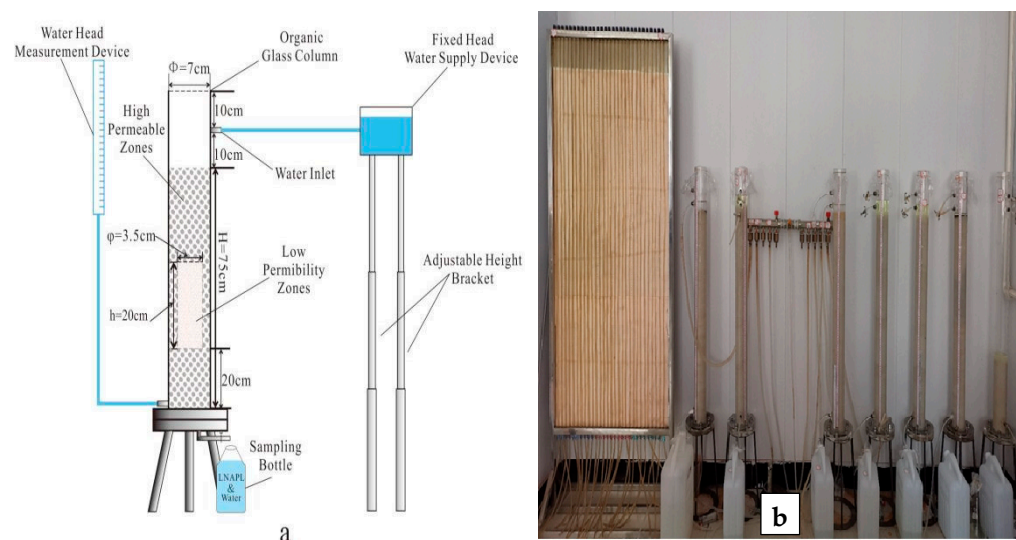


Figure 2. Schematic diagram of filling soil column (a) and photos of completed filling (b).

Table 3. Experimental design for soil column simulations of NAPL residuals.

Experiment ID	Aquifer Particle Size (mm)	Lens Particle Size (mm)	Permeability Coefficient Ratio K_{mn}	Lens Size $\Phi/\phi \times h$ (cm $\times$ cm)	Lens Volume $V_t/$ (cm ³)	Groundwater Flow Velocity V (cm/min)	Aquifer Mass m_w (g)	Lens Mass m_t (g)
1	0.25–4.00	0.25–4.00	1	3.5 $\times$ 20	192.325	0.14	4119.61	294.26
2	0.25–4.00	0.09–1.75	5	3.5 $\times$ 20	192.325	0.14	4056.32	309.64
3	0.25–4.00	0.063–1.00	11	3.5 $\times$ 20	192.325	0.14	4018.11	325.04
4	0.25–4.00	0.063–0.75	23	3.5 $\times$ 20	192.325	0.14	4216.24	324.29
5	0.25–4.00	0.053–0.425	50	3.5 $\times$ 20	192.325	0.14	4055.37	332.70

Following the completion of the packing process, NAPL was introduced from the top of the column with the assistance of a glass rod to facilitate the flow. Liquid samples were collected from the sampling port located at the bottom of the column, and the injection of NAPL was halted once the collected liquid was entirely composed of NAPL. At this

juncture, the total volume of NAPL injected into the plexiglass column (V_0) was recorded. Subsequently, the constant head water supply apparatus was activated, and the experiment commenced in accordance with the design in Table 3. Samples were taken from the sampling port at the base of the soil column, and the volume of the effluent was documented. The concentration of NAPL in the effluent was measured at various time intervals (NAPL concentration determination method in Section 2.5) until a steady concentration was achieved, at which point the experiment was complete. The total volume of NAPL discharged (V_c) was calculated utilizing the mass conservation principle. Residual NAPL saturation (S_r) in each soil column was determined using Equation (1) [30–32].

$$S_r = \frac{V_0 - V_c}{V} \times 100\% \quad (1)$$

where V represents the total pore volume, V_0 represents the total volume of NAPL injected into the plexiglass column, and V_c represents the volume of NAPL discharged.

2.2. Adsorption Experiment

2.2.1. Experimental Equipment and Materials for Adsorption Experiments

The materials and equipment utilized in the adsorption experiment comprised a THZ-82 constant temperature water bath oscillator (Figure 3), 250 mL stoppered Erlenmeyer flasks, quartz sand (Table 2), a HACH DR3900 spectrophotometer, and an FA2004N electronic balance.

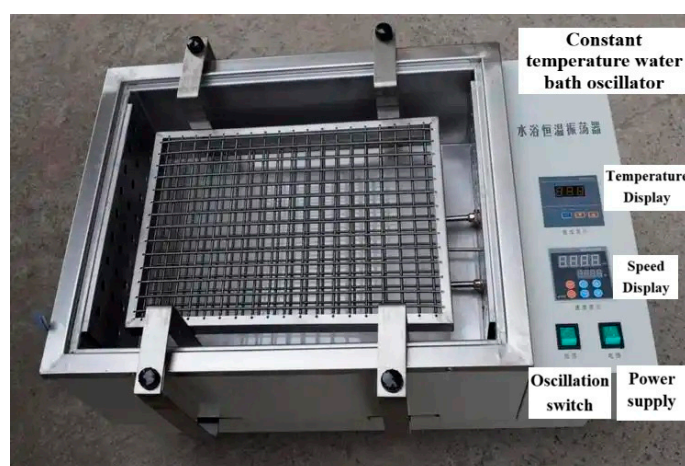


Figure 3. Image of THZ-82 thermostatic oscillator used in adsorption experiments.

2.2.2. Experimental Design for Adsorption Experiments

1. Adsorption Equilibrium Time

In the work of Xia et al. [33], the adsorption kinetics experiments revealed that NAPL is adsorbed by fine micro-sized sand aggregates in less than 24 h. To ensure the accuracy of the data obtained, the adsorption time between quartz sand and NAPL solution in this study was established at intervals of 1 h, 3 h, 6 h, 9 h, 12 h, 24 h, and 48 h. A total of 150 mL of NAPL solution was measured using a graduated cylinder and subsequently added to seven stoppered Erlenmeyer flasks, labeled 1 through 7. The thermostatic water bath oscillator was set to the desired temperature and oscillation frequency, with a preheating period of 20 min following stabilization of the water temperature at 20 °C, after which the flasks were placed into the oscillator. Subsequently, 3 g of quartz sand was introduced into each flask, and the water bath oscillator was activated. One flask was removed from the oscillator at each of the specified time intervals: 1 h, 3 h, 6 h, 9 h, 12 h, 24 h, and 48 h. For the determination of NAPL concentration (NAPL concentration determination

method in Section 2.5), 2 mL of the middle-layer solution was extracted from each flask. A curve depicting the relationship between NAPL concentration (C) and time (t) was plotted. The experiment was concluded when the slope of the curve stabilized, indicating that the medium had reached adsorption equilibrium.

2. Theoretical Maximum Adsorption Capacity

A series of NAPL solutions with varying concentration gradients, including the maximum NAPL concentration observed at the conclusion of the soil column experiment, was prepared. For each concentration, 150 mL of NAPL solution was transferred into a 250 mL stoppered Erlenmeyer flask. The temperature and oscillation frequency of the thermostatic water bath oscillator were adjusted, and once the water temperature stabilized at 20 °C, the flasks were placed into the oscillator for a preheating period of 20 min. Subsequently, 3 g of quartz sand was added to each flask, and the oscillator was activated. Oscillation was ceased once the adsorption equilibrium time was attained. A 2 mL sample from the middle layer of each solution was extracted, and NAPL concentration was determined (NAPL concentration determination method in Section 2.5). The adsorption capacity of each medium was calculated using the mass conservation method, and an isothermal adsorption curve was plotted and fitted. Utilizing the packing mass of the lens in Table 3 and NAPL concentration at the conclusion of the soil column experiment, the maximum adsorption capacity of each lens for NAPL was calculated.

2.3. Mercury Intrusion Porosimetry

2.3.1. Experimental Equipment and Materials for Mercury Intrusion Experiment

The mercury intrusion porosimetry test was conducted at Qinghai University, and experiment was MicroActive Autopore V 9620 mercury intrusion porosimeter, produced by Micromeritics, Norcross, GA, USA (Figure 4). The principal materials employed in the experiment comprised quartz sand, with its specifications and physical properties in Table 2, as well as an FA2004N electronic balance.

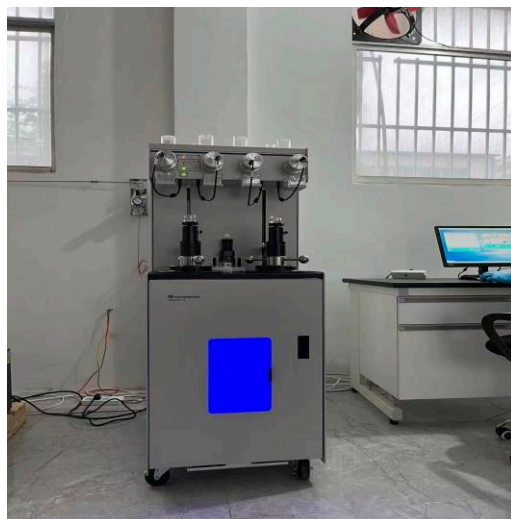


Figure 4. Image of mercury intrusion porosimeter for pore structure analysis.

2.3.2. Experimental Design for Mercury Intrusion Porosimetry

According to the principles of mercury intrusion porosimetry [34,35], the testing process begins with mercury entering larger pores at a specified pressure. The porosimeter measures these larger pores. As the pressure is incrementally increased, mercury progressively penetrates smaller pores, thereby facilitating the determination of pore size and the characteristics of pore volume distribution within the sample.

To measure the pore size distribution of each lens, a predetermined amount of quartz sand was accurately weighed and subsequently placed into 5 cc sample tubes. Mercury intrusion experiments were performed to ascertain the pore size distribution of each sample.

2.4. Particle Size Analysis

2.4.1. Experimental Apparatus and Materials for Particle Size Analysis

The primary apparatus utilized for particle size analysis comprised sieves with varying mesh sizes and a Mastersizer 3000 laser particle size analyzer (The Mastersizer 3000 laser particle size analyzer is produced by Malvern Instruments Limited in Malvern, UK). The principal materials employed in this analysis included quartz sand, with the specifications and physical properties in Table 2, as well as an FA2004N electronic balance.

2.4.2. Particle Size Analysis Design

The analysis boundaries were established utilizing both the sieving method and the laser particle size analyzer, tailored to the characteristics of the media under investigation. For the aquifer media, specifically Quartz Sand 1, which exhibits relatively large particle sizes, the sieving method was employed. A sample weighing 50 g of Quartz Sand 1 was accurately measured using a balance and subsequently placed in a series of sieves arranged in descending order of mesh size, from top to bottom. The sieves were subjected to horizontal shaking to facilitate the measurement of the mass of quartz sand retained on each sieve. A particle size distribution curve was generated based on the mass percentage of quartz sand corresponding to various particle sizes, thereby yielding the results of the particle size analysis. In contrast, for Quartz Sands 2, 3, 4, and 5, the particle size distribution was determined through the use of a laser particle size analyzer. The percentage of particles within each size range was quantified, and cumulative particle size curves were constructed to derive the particle size analysis results.

2.5. NAPL Concentration Determination

The liquid collected in the sampling bottles from the soil column simulation experiment comprised a mixture of NAPL and water. To accurately quantify NAPL concentration in the effluent, a standard curve correlating NAPL concentration with chemical oxygen demand (COD_{Cr}) was developed by preparing standard solutions [36]. Subsequently, NAPL concentration in the effluent was determined using this standard curve.

2.5.1. Experimental Apparatus and Materials for NAPL Concentration Determination

HACH DR3900 spectrophotometer (The HACH DR3900 spectrophotometer is produced by Hash Corporation in Loveland, CO, USA), an emulsifier, HACH DRB200 digester, 500 mL beakers, pipettes, and HACH reagent tubes.

2.5.2. Establishment of Standard Curve

The procedure for establishing the standard curve was conducted as follows: Eight NAPL–water mixed solutions were prepared, exhibiting concentration gradients of 20 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L, 800 mg/L, and 1200 mg/L, with each solution having a volume of 500 mL in separate beakers. The emulsifier speed was set to 5000 r/min, and each solution was emulsified from low to high concentration for a duration of 3 min. Following the emulsification process, 2 mL of each sample was extracted using a pipette and transferred into HACH COD_{Cr} tubes containing potassium dichromate as the indicator. The samples were then digested at a temperature of 150 °C for 2 h utilizing a HACH DRB200 digester. After digestion, the tubes were allowed to cool to room temperature, and the COD_{Cr} values of the samples were measured using a spectrophotometer.

A standard curve correlating the concentration of NAPL with COD_{Cr} was established using the aforementioned procedure (Figure 5). The fitted equation is expressed as $C_{sj} = 0.9754 C_{cs} + 33.555$, where C_{sj} represents NAPL concentration in the prepared solution and C_{cs} represents NAPL concentration as determined by the spectrophotometer. The correlation coefficient (R^2) was 0.987, indicating a strong degree of correlation and thereby validating the feasibility of utilizing COD_{Cr} measurements to quantify diesel concentration. All experiments conducted for the determination of NAPL concentration in this study adhered to this method for NAPL quantification.

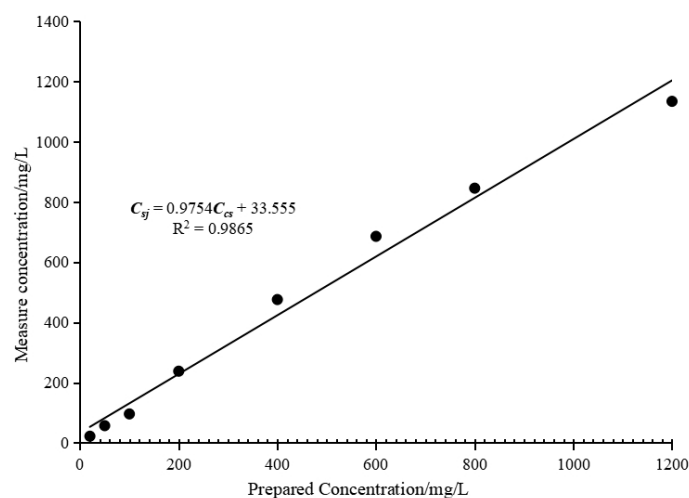


Figure 5. NAPL relationship between NAPL concentration and COD_{Cr} for quantification.

3. Results

3.1. Soil Column Experiment Results

3.1.1. Experimental Results of Soil Columns with Different K_{mn}

Following the conclusion of the soil column simulation experiments, the residual saturation of NAPL in each experimental group S_r , the residual saturation of NAPL in the lens S_R , and the concentration of NAPL in the solution of each experimental group C_D are summarized in Table 4.

Table 4. Results of soil column simulation experiments for NAPL residuals.

Experiment No.	Permeability Coefficient Ratio K_{mn}	Residual NAPL Saturation S_r (%)	Residual NAPL Saturation in Lens S_R (%)	NAPL Concentration in Effluent C_D (mg/L)
1	1	8.54	8.54	17.9
2	5	8.71	11.19	22.3
3	11	9.09	17.20	27.2
4	23	9.93	30.46	29.7
5	50	10.22	35.05	34.2

3.1.2. Relationship Between Overall S_r and K_{mn}

Low-permeability lenses significantly affect the overall S_r of NAPL within the medium. The data obtained from the soil column simulation experiments (Table 4) illustrate the relationship between S_r and K_{mn} (Figure 6).

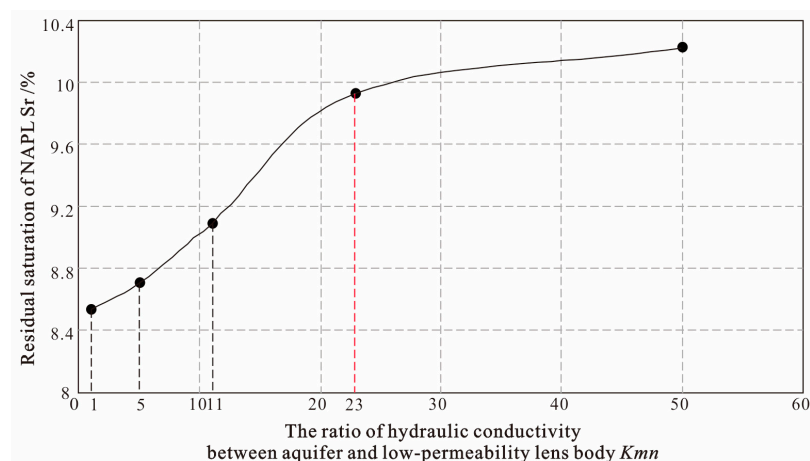


Figure 6. Relationship curve between NAPL residual saturation (S_r) and permeability coefficient gradient (K_{mn}).

As shown in Figure 6, S_r tends to increase with an increase in K_{mn} . However, when K_{mn} surpasses 23, the slope of the curve exhibits a reduction in steepness. For $K_{mn} < 23$, variations in K_{mn} exert a more significant impact on S_r compared to the range where K_{mn} is between 23 and 50.

According to existing studies, NAPL residuals in aquifers characterized by lenses predominantly arise from adsorption and entrapment processes. To investigate the sensitivity of NAPL residuals to particle adsorption and pore entrapment within low-permeability lenses, a series of particle adsorption experiments were conducted on both the aquifer and the lenses. The results of these experiments are detailed in Section 3.2.

3.2. Adsorption Experiment Results

3.2.1. Adsorption Equilibrium Time

Utilizing five types of quartz sand (1, 2, 3, 4, and 5) as adsorbents, an NAPL solution with a concentration of 35.2 mg/L was formulated, informed by the results from the soil column experiment (Table 4). An adsorption kinetics experiment was subsequently performed, and analysis of the adsorption kinetics curve (Figure 7) revealed that the time required to reach adsorption equilibrium was 24 h.

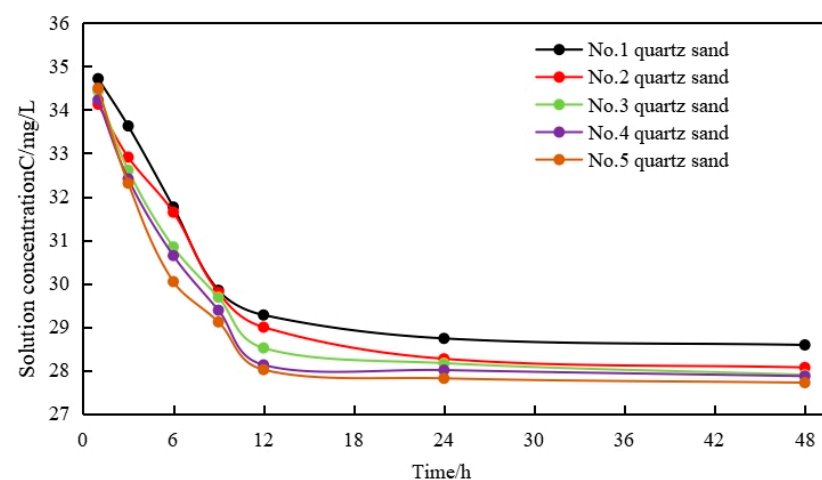


Figure 7. Adsorption kinetics curves of different quartz sands.

3.2.2. Maximum Adsorption Capacity

Isothermal adsorption experiments were conducted over a duration of 24 h, utilizing varying concentrations of NAPL solutions. Figure 8 illustrates the isothermal adsorption

curves corresponding to each individual medium. To ascertain the theoretical maximum adsorption capacity of each medium, a Langmuir-type equation was employed, which delineates the relationship between the theoretical maximum adsorption capacity of the particle surface (y , $\mu\text{g/g}$) and the equilibrium solute concentration (C_P , mg/L) in the solution. All experimental data were analyzed using the Langmuir adsorption model, and the isothermal adsorption equilibrium equations for the two different media are presented in Table 5. The NAPL concentration in the solution, as recorded upon the completion of the soil column experiment C_D (Table 4), represents the equilibrium concentration. The y of the quartz sand particle surfaces was determined by substituting the corresponding C_D into the adsorption equilibrium equation.

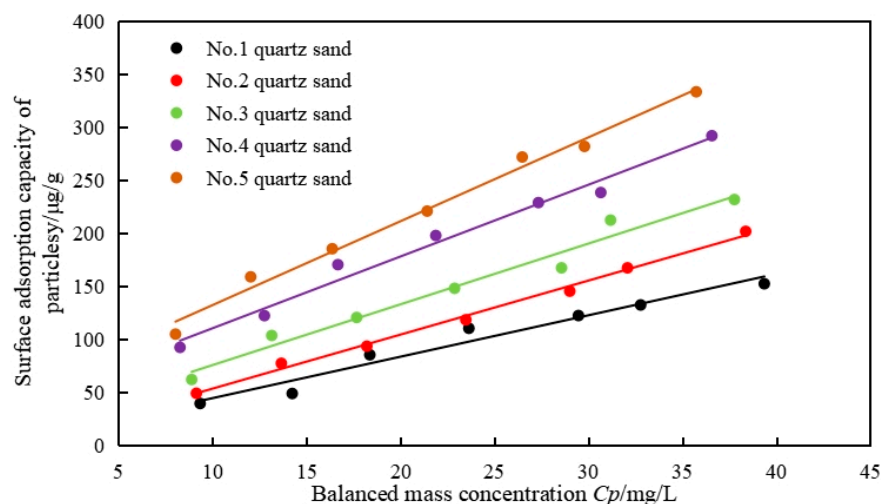


Figure 8. Isothermal adsorption curves of various quartz sands.

Table 5. Adsorption isotherm equations for quartz sands of varying particle sizes.

Medium	Langmuir	Correlation Coefficient (R^2)	Equilibrium Concentration C_D (mg/L)	Theoretical Maximum Adsorption Capacity y ($\mu\text{g/g}$)
No. 1 quartz sand	$y = 3.906 \times C_P + 5.5742$	0.9893	17.9	75.297
No. 2 quartz sand	$y = 5.093 \times C_P + 2.6649$	0.9826	22.3	107.228
No. 3 quartz sand	$y = 5.729 \times C_P + 18.499$	0.9717	27.2	156.936
No. 4 quartz sand	$y = 6.766 \times C_P + 42.869$	0.995	29.7	208.288
No. 5 quartz sand	$y = 7.907 \times C_P + 53.288$	0.9604	34.2	297.091

Based on the theoretical maximum adsorption capacity y in Table 5, in conjunction with m_t (Table 3) and ρ_o (Table 1), the maximum adsorption capacity in the lens body S_c can be determined as follows:

$$S_c = \frac{y \times m_t}{10^6 \times \rho_o} \quad (2)$$

Based on S_R in Table 4, the porosity n in Table 2, and the lens body volume V_t , the residual amount of NAPL in the lens body S_t can be determined. The equation for this calculation is given as follows:

$$S_t = S_R \times n \times V_t \quad (3)$$

The proportion of the adsorption quantity in relation to the residual amount of NAPL within the lens body is $\frac{S_c}{S_t} \times 100\%$, and the percentage of the retention amount in relation to the residual amount of NAPL within the lens body is $100\% - \frac{S_c}{S_t} \times 100\%$. The results of the aforementioned calculations are outlined in Table 6.

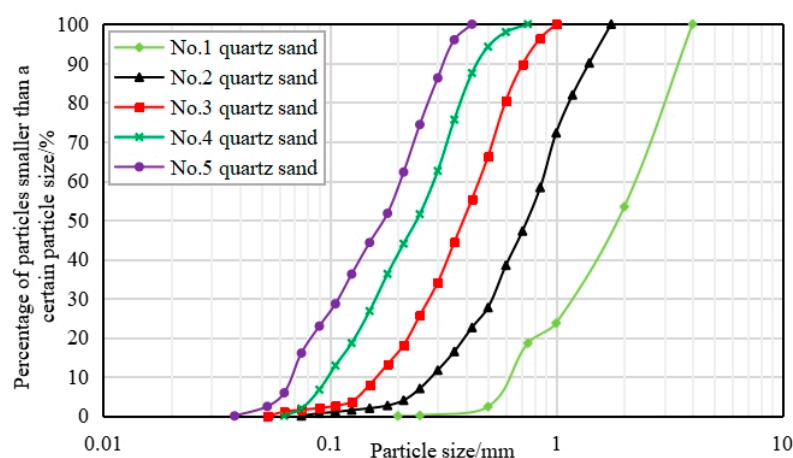
Table 6. Summary of NAPL residual quantities, adsorption, and retention in low-permeability lenses.

Experiment Number	NAPL Residual Amount in Lens Body S_t (mL)	Maximum Adsorption Amount of NAPL in Lens Body S_c (mL)	Percentage of Adsorption Amount in NAPL Residual Volume (%)	Percentage of Retention Amount in NAPL Residual Volume (%)
1	7.038	0.027	0.38	99.62
2	8.841	0.040	0.45	99.55
3	13.456	0.061	0.45	99.55
4	23.793	0.082	0.34	99.66
5	27.361	0.119	0.43	99.57

As shown in Table 6, the maximum adsorption capacity of NAPL by low-permeability lens body particles constitutes only 0.45% of the total residual volume of NAPL, whereas the retention capacity accounts for over 99.5% of the total NAPL residual volume. Therefore, retention emerges as the primary factor affecting NAPL residuals within the low-permeability lens body of the aquifer. The adsorption of NAPL by particles is affected by both particle size and specific surface area. To further investigate the relationship between particle size and NAPL adsorption, particle size distribution tests were conducted.

3.3. Particle Size Distribution Results

Figure 9 depicts the cumulative particle size distribution curves for each type of quartz sand, as derived from the results of the particle size distribution experiment. Table 7 summarizes the average particle diameter, uniformity coefficient C_u , and curvature coefficient C_s for each type of quartz sand, as determined from the cumulative distribution curve.

**Figure 9.** Cumulative curve of particle distribution.**Table 7.** Particle size and distribution metrics for quartz sand types.

Medium No.	Average Particle Diameter D_{50} (mm)	Uniformity Coefficient C_u	Curvature Coefficient C_s
No. 1 quartz sand	1.80	3.77	1.03
No. 2 quartz sand	0.75	3.15	1.14
No. 3 quartz sand	0.39	2.94	1.04
No. 4 quartz sand	0.24	3.13	1.11
No. 5 quartz sand	0.18	3.01	1.03

The average particle size is a physical parameter that characterizes the overall dimensions of particles within a given medium. C_u and C_s serve as indicators of the distribution of various particle sizes. A C_u value of less than 5 signifies a relatively uniform distribution of particles, while a C_s value between 1 and 3 suggests that there are no missing

particle sizes within the specified range. As shown in Table 8, the particle sizes of different quartz sands in the lenses exhibit variability. However, the values of C_u and C_s remain notably similar.

Table 8. Proportions of pore categories in quartz sand samples.

Medium No.	The Proportion of Macropores n_{max} (%)	The Proportion of Mesopores n_{mid} (%)	The Proportion of Small Pores n_{min} (%)
No. 1 quartz sand	91.83	5.35	2.82
No. 2 quartz sand	86.12	10.64	3.24
No. 3 quartz sand	69.29	25.25	5.46
No. 4 quartz sand	36.04	56.11	7.85
No. 5 quartz sand	9.98	63.1	26.92

The difference between low-permeability lenses and aquifer media is primarily attributed to the permeability coefficient. The pore characteristics serve as a direct factor affecting the disparity in permeability, which in turn affects the retention of residual NAPL. To investigate the mechanisms underlying residual NAPL retention in lenses, mercury intrusion experiments were performed, and the results are presented in Section 3.4.

3.4. Mercury Intrusion Experiment Results

3.4.1. Pore Distribution of Each Low-Permeability Lens Body

The cumulative pore size distribution curves are presented in Figure 10, where the horizontal axis represents the pore diameter and the vertical axis denotes the volume fraction of pores with diameters smaller than a specified value. An analysis of these curves reveals that the pores in quartz sands 1, 2, 3, 4, and 5 are predominantly concentrated within the diameter range of 20 μm to 300 μm . Notably, quartz sand 1 exhibits the highest curve among all the samples, indicating that it possesses the largest pore sizes across the various diameter ranges when compared to the other groups of quartz sands.

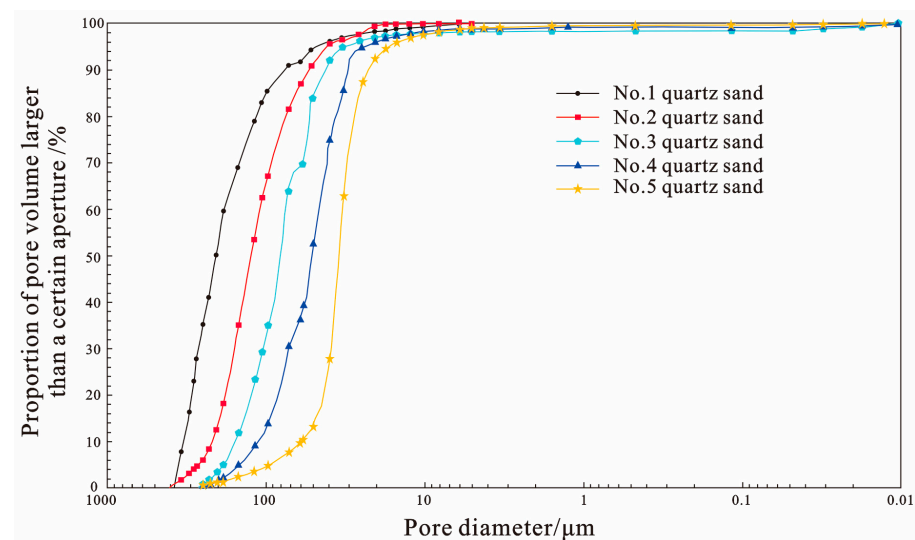


Figure 10. Cumulative curve of pore diameter distribution.

Huang et al. [37] suggested that pores with diameters ranging from 0 μm to 30 μm are classified as storage pores, which encompass bound water pores. Pores with diameters between 30 and 100 μm are identified as capillary pores, whereas pores exceeding 100 μm exhibit minimal capillary force and are categorized as gravity water pores. Thomasson [38] revealed that when pore diameters surpass 60 μm , the capillary forces diminish, resulting in these pores showing characteristics typical of gravity water pores. Consequently,

pores are categorized into three classifications based on their diameters: macropores (diameter $> 60 \mu\text{m}$), mesopores (diameter $= 30\sim 60 \mu\text{m}$), and small pores (diameter $< 30 \mu\text{m}$). The proportions of the pore volume of each type are outlined in Table 8.

3.4.2. Experimental Results

To elucidate the mechanism by which a low-permeability lens affects residual NAPL, a correlation analysis was conducted between the porosity of the aforementioned pore types and S_R of both the aquifer and the lens body (Figure 11).

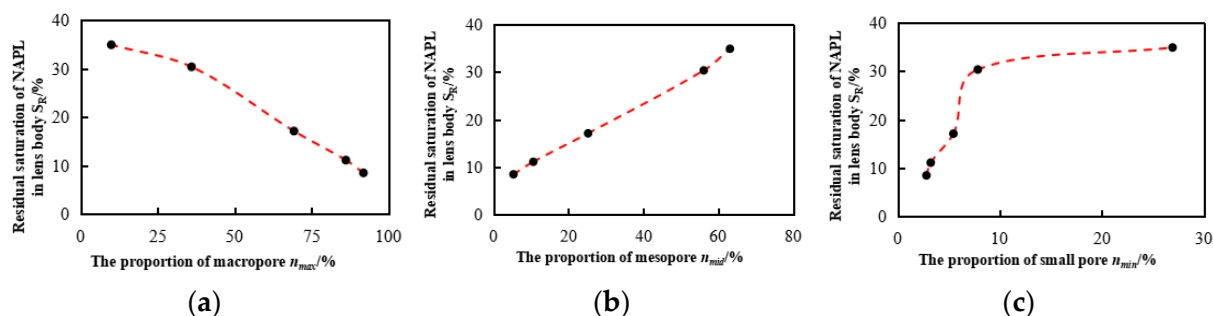


Figure 11. The variation curve of residual saturation S_R of lens body with the proportion of various pore volumes. NOTE: (a) is the variation curve of S_R with macropore porosity, (b) is the variation curve of S_R with mesopore porosity, and (c) is the variation curve of S_R with small pore porosity.

As shown in Figure 11, the S_R of the aquifer and lens body exhibits a negative correlation with the proportion of macropore volume (n_{max}). Specifically, when the volume fraction of macropores surpasses 36.04%, the slope of the curve increases, resulting in an accelerated rate of change in S_R (Figure 11a). Conversely, S_R shows a positive correlation with the proportion of mesopore volume (n_{mid}), exhibiting an approximately linear increase (Figure 11b). Additionally, S_R is positively correlated with the small pore volume (n_{min}). Notably, when n_{min} is below 7.85%, the slope of the curve also increases, which contributes to a heightened rate of change in S_R (Figure 11c).

4. Discussion

4.1. Effects of Particle Adsorption on NAPL

Based on y in Table 6 and the average particle diameter (D_{50}) in Table 7, a curve illustrating the relationship between theoretical maximum adsorption capacity and particle size was generated (Figure 12). The data indicate that the adsorption capacity diminishes as particle size increases, conforming to a power-law function. The ability of quartz sand to adsorb NAPL in solution can be attributed to the similarity in the double electric layer structure present on the surfaces of both quartz sand and NAPL particles. Upon contact, a common counter-ion layer is established. Given the substantial disparity in particle size and mass between the two, the attractive force of the common counter-ion layer is adequate to facilitate the adherence of dissolved NAPL to the surfaces of quartz sand particles, thereby forming a relatively stable structure [39–41]. Therefore, water flow alone is insufficient to completely separate these entities, enabling quartz sand particles to effectively adsorb dissolved NAPL.

The observed decrease in adsorption capacity, which follows a power-law function as particle size increases, can be attributed to the relationship between the adsorption of soluble NAPL by quartz sand and the specific surface area of the particles. Specifically, a larger specific surface area correlates with a greater quantity of NAPL that can be adsorbed. The specific surface area increases exponentially as particle size decreases [42–44]. Therefore,

smaller particles exhibit higher adsorption capacities, and y can be represented in the form of a power-law function.

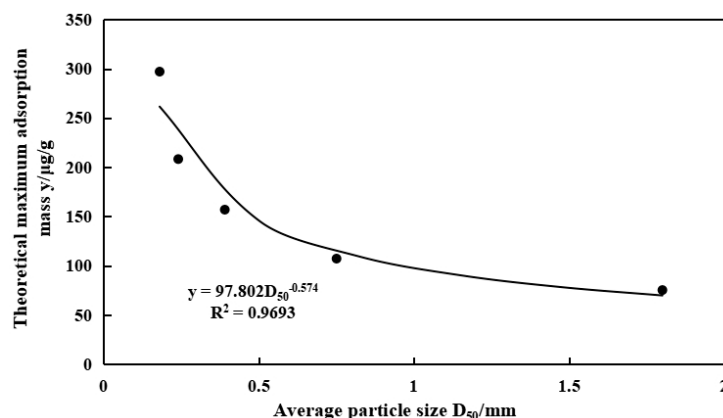


Figure 12. The variation law of adsorption capacity with particle size.

This study elucidates that the adsorption capacity of quartz sand particles for NAPL is relatively limited for the following reasons: 1. The water solubility of NAPL is exceedingly low, with concentrations typically in ppm range. As a result, the maximum adsorption of NAPL onto quartz sand particles is constrained. 2. This study utilized high-purity quartz sand, primarily composed of silicon dioxide, which possesses a crystalline structure and a smooth surface with few active adsorption sites. Its ability to adsorb NAPL is relatively low. Therefore, the retention of low-permeability lens bodies is the most important cause of residual NAPL.

4.2. Effects of Pore Characteristics on NAPL Retention

To elucidate the relationship between various types of porosity and the residuals of NAPL, as well as to investigate the effects underlying the variations in S_r across different pore size ranges, an analysis of the forces acting on residual NAPL droplets within the pores was performed (Figure 13).

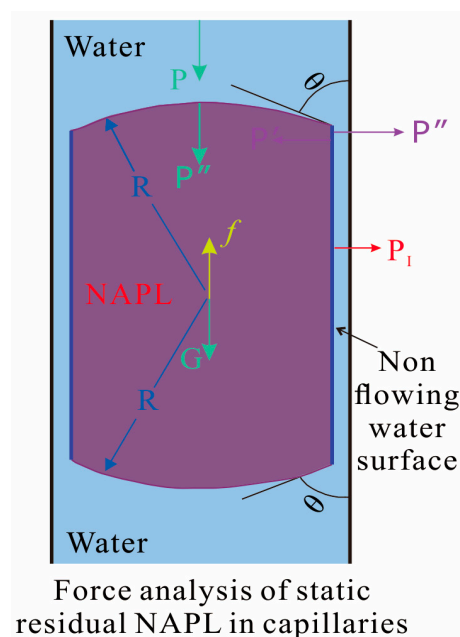


Figure 13. Force analysis of static residual NAPLs in capillaries.

As shown in Figure 13, the pores function as capillary tubes with a uniform diameter, while the residual NAPL is represented as a stationary spherical droplet. This droplet is subjected to several forces: the water flow pressure (p), its own gravitational force (G), buoyancy (f), the spherical capillary force exerted on the pore wall (P''), and the cylindrical capillary force acting at the center of the pore (P'). The resultant force (P_I), which is directed towards the pore wall, is the vector sum of P'' and P' . The calculations for P'' , P' , and P_I are derived based on the Laplace equation [45], where P'' and P' can be obtained as follows:

$$P'' = \frac{2\sigma \cos\theta}{r} \quad (4)$$

$$P' = \frac{\sigma}{r} \quad (5)$$

Therefore, P_I can be determined as follows:

$$P_I = \frac{2\sigma}{r} (\cos\theta - 0.5) \quad (6)$$

The function of P_I is to enhance the adhesion of an NAPL droplet to the pore wall. For the droplet to migrate, the additional frictional resistance along the pore wall induced by P_I must be surmounted. Given that the residual NAPL exists as a spherical droplet, θ remains constant, while the magnitude of P_I is contingent upon the pore radius (r). An increase in pore radius results in a reduction in resistance to NAPL migration, thereby decreasing S_r . Conversely, a decrease in pore radius leads to an increase in resistance to NAPL migration, resulting in a higher S_r .

Huang [37] and Thomasson [38] suggested that when the pore diameter exceeds 60 μm , the capillary forces within the pores become weak. In such instances, the driving force for the migration of NAPL surpasses the capillary force, resulting in reduced resistance to NAPL migration and a decreased likelihood of NAPL retention. Therefore, S_r demonstrates a negative correlation with n_{max} ; specifically, as n_{max} increases, S_r decreases (Figure 11a). Conversely, when the pore diameter ranges from 30 μm to 60 μm , the pores exhibit enhanced capillary action. In this scenario, the capillary force exceeds the driving force for NAPL migration, thereby increasing resistance to NAPL movement and enhancing the probability of NAPL residuals. Therefore, S_r is positively correlated with n_{mid} . As n_{mid} increases, S_r also increases (Figure 11b). In cases where the pore diameter is less than 30 μm , the pores exhibit very strong capillary forces and may contain certain extremely small capillary pores. In these situations, discontinuous NAPL droplets that enter these pores can become encapsulated by water and retained within the pores [46]. However, the storage capacity for residual NAPL within these pores is limited, which consequently restricts the amount of NAPL that can be retained. Although there is a positive correlation between S_r and n_{min} , this correlation diminishes when the porosity exceeds 7.8%, as the increase in S_r slows down (Figure 11c). Therefore, while small pores do contribute to NAPL residuals, their effect on S_r is less pronounced than mesopores.

4.3. Effects of K_{mn} on S_r

To examine the effect of K_{mn} on S_r , K_{mn} was designated as the independent variable. The proportions of various pore types in Table 8 were utilized as dependent variables. The resulting correlation variation curves are illustrated in Figure 14.

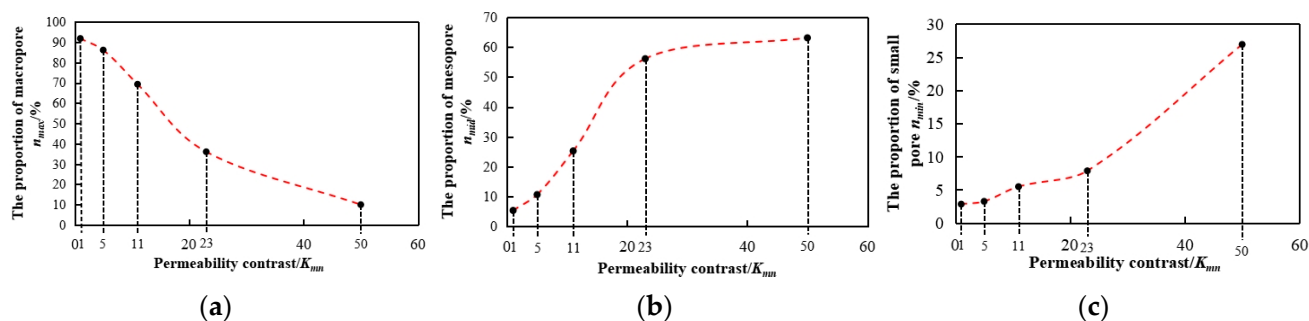


Figure 14. Correlation curve between the proportions of various pore volumes and the permeability contrast K_{mn} . NOTE: (a) is the variation curve of n_{max} with K_{mn} , (b) is the variation curve of n_{mid} with K_{mn} , and (c) is the variation curve of n_{min} with K_{mn} .

As shown in Figure 14, an increase in K_{mn} is associated with a decrease in n_{max} . Specifically, when K_{mn} is less than 23, the rate of change in the curve is relatively pronounced, suggesting that for K_{mn} values below 23, n_{max} diminishes rapidly as K_{mn} increases. In the range of K_{mn} between 23 and 50, the rate of decrease in n_{max} diminishes with further increases in K_{mn} (Figure 14a). Conversely, n_{mid} shows an increasing trend with rising K_{mn} . For K_{mn} values below 23, the rate of change is significant, indicating that n_{mid} increases rapidly as K_{mn} rises. However, within the interval of K_{mn} from 23 to 50, the rate of increase in n_{mid} begins to slow (Figure 14b). Similarly, n_{min} also increases with an increase in K_{mn} . Notably, when K_{mn} is less than 23, the rate of change is relatively modest, indicating that n_{min} increases gradually as K_{mn} rises. In contrast, for K_{mn} values within the range of 23 to 50, the increase in n_{min} accelerates (Figure 14c).

The integration of the experimental results in Section 3.1 with the effect of NAPL residuals discussed in Section 4.2 allows for the conclusion that the inflection point observed at $K_{mn} = 23$ in S_r versus K_{mn} curve (Figure 6) is attributable to specific changes in pore volume distribution. When K_{mn} is less than 23, there is a rapid decrease in n_{max} (diameter $> 60 \mu m$), accompanied by a rapid increase in n_{mid} (diameter $= 30\sim60 \mu m$), while n_{min} (diameter $< 30 \mu m$) increases at a slower rate. This dynamic results in a significant increase in the space available for NAPL residuals. Conversely, within the range of $K_{mn} \in (23, 50)$, the rate of increase in S_r diminishes primarily due to a slower increase in n_{mid} , contrasted with a rapid increase in n_{min} . This shift leads to a more gradual increase in the space available for NAPL residuals.

5. Conclusions and Outlook

5.1. Conclusions

1. Experimental Results from Soil Columns with Different K_{mn} : S_r generally increases with K_{mn} , as demonstrated by the experimental results. However, when K_{mn} exceeds 23, an inflection point is observed. Specifically, for K_{mn} less than 23, S_r increases rapidly with increasing K_{mn} . In the range $K_{mn} \in (23, 50)$, the increase in S_r slows down. This phenomenon can be attributed to the following: when $K_{mn} < 23$, n_{max} (diameter $> 60 \mu m$) decreases sharply, n_{mid} (diameter $= 30\sim60 \mu m$) increases significantly, and n_{min} (diameter $< 30 \mu m$) increases gradually. This leads to an enhanced availability of space for NAPL residuals. However, when $K_{mn} \in (23, 50)$, the rate of increase in S_r slows down primarily because n_{mid} increases at a reduced rate, while n_{min} increases rapidly, limiting the available space for NAPL residuals.
2. Contribution of Particle Adsorption and Retention to NAPL Residuals: The maximum contribution of NAPL adsorption by particles in low-permeability lenses to the total NAPL residual is only 0.45%, while retention accounts for over 99.5% of the total

- NAPL residual. This indicates that the primary factor affecting NAPL residuals in low-permeability lenses is retention. This result is explained by the fact that although both quartz sand and NAPL particles exhibit similar double-layer structures on their surfaces, enabling the formation of a common ion layer upon contact, the attraction between these particles is sufficient to cause NAPL to adhere to the surface of quartz sand particles. This interaction forms a stable structure that facilitates NAPL adsorption. However, due to the extremely low solubility of NAPL in water, and because the quartz sand used in this study is of high purity with a highly crystalline structure and few active adsorption sites, its capacity for NAPL adsorption is limited. Therefore, retention is the dominant factor controlling NAPL residuals in low-permeability lenses.
3. **Effect of Pore Size Distribution on NAPL Residuals:** The primary reason for the formation of NAPL residuals in low-permeability lenses is the differential distribution of pore sizes, specifically $n_{\max}$ (diameter $> 60 \mu\text{m}$), n_{mid} (diameter $= 30\sim60 \mu\text{m}$), and $n_{\min}$ (diameter $< 30 \mu\text{m}$). In macropores, the resistance to NAPL migration is minimal, meaning that the larger $n_{\max}$, the lower S_r . In contrast, mesopores exhibit the strongest capillary action, which hinders NAPL migration, thereby facilitating the formation of NAPL residuals. Therefore, a larger n_{mid} results in a higher S_r . Small pores, which contain bound water, exhibit strong capillary action but are limited in their ability to store NAPL due to the small volume of space available for liquid flow. Consequently, while small pores contribute to NAPL residuals, their effect on NAPL saturation is less significant than mesopores.

5.2. Outlook

This study takes diesel as an example to investigate the primary controlling factors of NAPL residuals in low-permeability lenses of aquifers and examines the effects underlying their persistence. However, diesel is an LNAPL, and its properties differ significantly from those of DNAPLs. Therefore, the conclusions of this study are applicable to LNAPL pollutants with properties similar to diesel, such as aviation kerosene and xylene. In addition, high-purity quartz sand was used for the low-permeability lenses in this study. But, in actual subsurface lenses, there are often a large number of clay minerals, which can increase the influence of adsorption on NAPL residues. Whether the conclusions of this study are applicable when clay minerals are present in low-permeability lenses remains unknown.

Consequently, in the next step, we will use trichloroethylene (TCE) as a representative of DNAPLs to continue the research on NAPL residues in low-permeability lenses of aquifers [47]. Different proportions of clay minerals will be added to the low-permeability lenses to explore whether DNAPL residues in low-permeability lenses of aquifers conform to this conclusion, and whether the presence of clay minerals in low-permeability lenses will change the NAPL residue mechanism. This will further reveal the influencing mechanism of NAPL residues in low-permeability lenses of aquifers.

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