

Article

Migration Behavior and Influencing Factors of Petroleum Hydrocarbon Phenanthrene in Soil around Typical Oilfields of China

Hao Chen ¹, Mengfan Lang ¹, Changjun Liao ^{2,*} and Xuetao Guo ^{1,3,*} ¹ Faculty of Natural Resources and Environment, Northwest A&F University, Xianyang 712100, China² Guangxi Bossco Environmental Protection Technology Co., Ltd., Nanning 530007, China³ Key Laboratory of Plant Nutrition and the Agri-Environment in Northwest China, Ministry of Agriculture, Xianyang 712100, China

* Correspondence: liaocj@bossco.cc (C.L.); guoxuetao2005@nwfafu.edu.cn (X.G.)

Abstract: Petroleum spills and land contamination are becoming increasingly common around the world. Polycyclic aromatic hydrocarbons (PAHs) and other pollutants found in petroleum are constantly migrating underground, making their migration in soil a hot research topic. Therefore, it is of great significance to evaluate the migratory process of petroleum hydrocarbons in petroleum-polluted soil to clarify its ecological and environmental risks. In this study, Phenanthrene (PHE) was used as a typical pollutant of PAHs. The soil was gathered from three typical oilfields in China, and a soil column apparatus was built to simulate the vertical migration of PHE in the soil. The migration law and penetration effect of PHE in various environmental conditions of soil were investigated by varying the ionic strength (IS), pH, particle size, and type of soil. According to the literature, pH has no discernible effect on the migration of PHE. The migration of PHE was adversely and positively linked with changes in IS and soil particle size, respectively. The influence of soil type was mainly manifested in the difference of organic matter and clay content. In the Yanchang Oilfield (YC) soil with the largest soil particle size and the least clay content, the mobility of PHE was the highest. This study may reveal the migration law of PAHs in soils around typical oilfields, establish a new foundation for PAH migration in the soil, and also provide new ideas for the management and control of petroleum pollution in the soil and groundwater.

Keywords: penetration curve; petroleum pollution; PHE; soil column; typical oilfields; vertical migration



Citation: Chen, H.; Lang, M.; Liao, C.; Guo, X. Migration Behavior and Influencing Factors of Petroleum Hydrocarbon Phenanthrene in Soil around Typical Oilfields of China. *Processes* **2022**, *10*, 1624. <https://doi.org/10.3390/pr10081624>

Academic Editors: Guining Lu, Zenghui Diao and Kaibo Huang

Received: 13 July 2022

Accepted: 11 August 2022

Published: 17 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Petroleum is a complex organic compound composed of various straight paraffins, naphthenes, monocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) [1]. Petroleum hydrocarbons in petroleum are composed of organic components with different molecular weights [2]. As a kind of non-renewable energy, petroleum is often the main goal of geological exploration. In today's world market, the demand and price of petroleum are rising constantly [3], and China's oil industry is also developing rapidly [4]. Therefore, the leakage of hydrocarbons is inevitable [5]. Oil spill on land can cause serious soil diffusion pollution [6], and the high content of toxic compounds in crude oil can also cause physical and biochemical poisoning to soil microbes [7]. Petroleum spills will cause the overflow of PAHs and benzene, ethylbenzene and other benzene series, which are collectively referred to as persistent organic pollutants, and they are extremely harmful to the environment [8,9].

PAHs are one of the typical pollutants of petroleum, formed by incomplete combustion or pyrolysis of organic matter [10], and they contain two or more benzene rings. They are characterized by high hydrophobicity, high toxicity, high lipophilicity, low volatility and high chemical stability [11–13]. The sources of PAHs include natural and human

activities, and the concentration of PAHs in urban soil is much higher than that in places far away from urban areas [14]. Petroleum spills are the most important source of PAHs in soil. As an important area for petroleum exploration, there is a large amount of oil pollution in the oil production site. In this region, large amounts of volatile oil carry a large number of organic pollutants such as PAHs. The transport of oil in the soil, in turn, can have environmental and human health impacts [15]. PAHs can cause carcinogenic [16], teratogenic, mutagenic and genotoxic effects on the environment [17]. The pollution of PAHs in soil to surface soil will be greater than that in deep soil [14], and PAHs in soil will be directly or indirectly exposed to human beings, endangering human health [15]. Studies have shown that the pathogenic factors of human lung cancer are closely related to the excessive inhalation of PAHs [18]. In addition, PAHs in the atmosphere will migrate and deposit on water, soil and plants, eventually threatening human health due to their accumulation in the food chain [19]. Therefore, it is necessary to study the environmental behaviors and characteristics of PAHs.

High hydrophobicity makes PAHs easily adsorbed on environmental media such as water and soil, and finally deposited in the matrix through migration and adsorption [13]. Therefore, the research on migration of PAHs has gradually become the focus of attention. At present, the research on the vertical distribution of PAHs in soil sediments shows that its concentration is inversely proportional to the soil depth [20–23]. However, PAHs have been capable of migrating deeper into the soil profile for a long time [24]. Sun et al. found that PAHs migrate from the soil surface to the ground through pore infiltration in the rainy season and surface dissolution in the dry season [25]. When studying the cotransport of PAHs and other substances, Fang et al. found that the nanoparticles (NPs) in soil with high organic matter are the most effective in transporting phenanthrene (PHE) through columns [26]. In addition, the presence of oxidized multi-walled carbon nanotubes (O-MWCNTs) in the influent significantly improved the mobility of PHE in the chromatographic column [26]. Due to the complex chemical nature of PAHs, its transport and diffusion processes in soil will be affected by adsorption-desorption, volatilization, leaching and bioaccumulation [27]. However, research on the migration of single PAHs in soil, especially in the soil of typical oilfields, has not been carried out systematically.

In order to make up for the deficiency of research on PAHs migration in the soil of typical oilfields, we selected the soil around the typical oilfields in northern China (Shengli Oilfield in Shandong, Nanyang Oilfield in Henan and Yanchang Oilfield in Shaanxi) as the medium. PHE, one of the PAHs, was chosen as the target pollutant. As an internationally recognized priority pollutant, PHE not only has two methods of co-metabolic oxidation and direct oxidation, but also has stable chemical properties. Therefore, it is widely used in the study of degradation, adsorption and migration of PAHs [28].

In order to explore the migration behavior and influencing factors of petroleum hydrocarbon component PHE in the soil around typical oilfields, we simulated the migration process of PHE in soil by building a soil column migration device in the laboratory. The experiments were conducted to explore the effects of different factors on the migration of PHE in soils around oilfields by varying the ionic strength (IS), pH, soil particle size and type, respectively. Our experimental process strictly followed the single-factor variable control principle. The mobility was reflected by measuring the concentration of PHE in the solution after migration. This study could further enhance our understanding of the migration behaviors of PAHs in soils around typical oilfields and the influence of soil environment on their migration effects. It may provide new ideas for the study of the migration of PAHs in soil, thus providing a basis for the pollution management of petroleum pollution in soils around typical oilfields.

2. Materials and Methods

2.1. Materials

PHE with a purity greater than 90% was purchased from Bailingwei Technology Co., Ltd. in Beijing, while other chemicals such as sodium chloride (NaCl, >99.5%), hydrogen

peroxide (30%) and calcium chloride (CaCl_2 , 96%) were purchased from Guanghua Co., Ltd., a company in Guangdong. Methanol (>99%) was purchased from AMPEL Laboratory Technology Co., Ltd., a company in Shanghai. After washing the quartz sand, it should be thoroughly cleaned with 0.1 M hydrochloric acid and 5% hydrogen peroxide. The two chemicals will remove any contaminants from the surface of the sand particles [29,30]. After a rinse with deionized water, the pH gradually becomes neutral and the sand is dried in a 35 °C oven.

2.2. Sampling and Pretreatment

We selected the uncontaminated soil around three typical oilfields in northern China (Shengli Oilfield, Nanyang Oilfield and Yanchang Oilfield). The Shengli Oilfield is located in the Yellow River delta area of Dongying City, Shandong Province, with geographical coordinates of 37°23' N and 118°31' E. The Nanyang Oilfield is located in Nanyang City, southwest of Henan Province, with geographic coordinates of 32°41' N and 112°34' E. The Yanchang Oilfield is located in Yan'an City, northern Shaanxi Province; the landforms are mainly the Loess Plateau and hilly areas, and the geographical coordinates are 36°40' N and 109°33' E. We measured the content of PHE in the sampled soil, and found no accumulation of PHE in these uncontaminated soils. The three soils were named SL, NY and YC, respectively. The geographical location of the three sampled oilfields is shown in Figure 1.



Figure 1. Geographical location of soil sampling in three typical oilfields.

Three types of soils were taken from the laboratory, dried and, firstly, impurities such as small stones, debris, plant and animal residues were picked up with forceps [31,32]. The soils were then placed in a mortar for grinding and sieved using a standard test sieve (Shangyu Dahengqiao laboratory instrument factory, Zhejiang, China). During the sampling process, we found that the main particle sizes of all soils were distributed around 1 mm. When exploring the influence of other variables, it is necessary to control the soil to be in the same particle size range. Moreover, if the particle size is too large or too small, it is not conducive to the penetration of the solution. Taking all into consideration, the soil

particle sizes of SL after sieving were 0.45~1 mm, 0.15~0.45 mm, 0~0.15 mm, and 0~1 mm, while the particle sizes of NY and YC were 0~1 mm.

2.3. Preparation of PHE and Electrolyte Solution

Based on the study of Liu et al. [32], we made appropriate improvements to the preparation of the solution. To make a 1 g/L PHE stock solution, place 0.5 g of PHE solid powder in a beaker, dissolve it in methanol and transfer it to a volumetric flask. PHE solutions of 1000 ppb, 800 ppb, 400 ppb, 200 ppb, 100 ppb and 50 ppb were prepared using the concentration gradient method. In a volumetric flask, CaCl_2 (0.555 g) was added, and the original solution of 50 mM CaCl_2 was obtained by constant volume with ultrapure water. CaCl_2 solutions of 1 mM, 0.5 mM and 0.1 mM were made by diluting the original solution. Similarly, 1 mM, 5 mM and 10 mM NaCl solutions were prepared. In addition, mixed solutions containing the above two electrolytes were prepared with a background concentration of 500 ppb PHE. All solutions are sealed and stored for subsequent column transport experiments.

2.4. Column Transport Experiments

According to existing research [29,31–35], the column transmission experiment was conducted. In order to prevent the sand core from being blocked by soil, quartz sand (1 cm) should be loaded into the bottom of the soil column. The dried treated soil was slowly filled into a clean and dry column and the column was shaken to prevent the formation of large pores. The length of the column used in the experiment was 10 cm and the inner diameter was 10 mm. The soil was filled to a height of 8 cm. A 1 cm layer of quartz sand was added to the top and bottom of the soil column to prevent water droplets from eroding the column.

The experiment made some adjustments to the leaching method and sequence used in the previous study [32]. A peristaltic pump was used to inject about 30 mL of ultrapure water into the column from top to bottom, followed by 30 mL of electrolyte solution to stabilize the chemical properties of the system. Then, 40 mL PHE-electrolyte solution (500 ppb PHE) was injected into the column from top to bottom by peristaltic pump at a flow rate of 0.5 mL/min (2 rpm). Finally, the column was rinsed with 30 mL electrolyte solution until the concentration of PHE solution was stable. The sample of solution collected from the outlet at the bottom of the soil column during injection and flushing was stored in a brown chromatograph bottle, and the eluent was collected every 5 mL during the experiment until the end of the experiment. Finally, the column was washed with ultrapure water [32,36]. The pH value of the leaching solution was adjusted with hydrochloric acid and sodium hydroxide, and the IS was adjusted with calcium chloride and sodium chloride solutions.

The soil column experiment's design procedure was as follows: First, six groups of IS migration experiments were conducted using three different concentrations of NaCl and CaCl_2 , a neutral pH solution, and soil with SL of 0~1 mm. Permeability was calculated from the concentration of PHE in the solution collected for this experiment. The IS with the best migration effect was selected as the constant condition of the subsequent experiments, and then the solution under three pH (4, 7 and 10) conditions and the soil under three particle sizes (<0.15 mm, 0.15~0.45 mm and 0.45~1 mm) was selected for migration experiments. The former controls the soil particle size to be 0~1 mm, and the latter controls the pH to be neutral. Finally, three different soil migration experiments of SL, YC and NY were carried out, and other solutions and soil conditions were kept the same. After each experiment, the soil column was washed with deionized water and ultrapure water and dried for reuse. The experimental design strictly followed the single-factor variable control principle. Through the comparison of the concentration of PHE in the solution collected under the influence of various factors, the longitudinal migration behavior of PHE in the soil around typical oilfields under different factors was comprehensively analyzed.

2.5. HPLC Determination Conditions of PHE

During High Performance Liquid Chromatography analysis, the analytical methods and parameter conditions used were adjusted and improved on the basis of the research of the previous study [32]. The concentration of PHE was determined using an Agilent High Performance Liquid Chromatography (HPLC, Agilent 1200) equipped with a fluorescence detector (FLD) and an ultraviolet detector (UVD). C18 reversed-phase column (Luna, 250 mm × 4.6 mm) was used as the chromatographic column. At a flow rate of 1 mL/min, the mobile phase was a combination of 90% acetonitrile and 10% aqueous solution. The fluorescence detector's excitation wavelength was 250 nm, and its emission wavelength was 364 nm. The UV detector's wavelength was set at 250 nm. The peak area was quantified using an external standard technique, and the retention duration was qualitative [31,36].

2.6. Statistical Analysis

Potassium dichromate was used as an oxidant to undergo a redox reaction with the organic matter in the soil, and the content of the organic matter in the soil was determined by a titration method. Soil total nitrogen was determined by the more conventional Kjeldahl method (national standard method: HJ 717-2014); total phosphorus was determined by the molybdenum-antimony resistance colorimetric method (NY/T 88-1988 Determination of soil total phosphorus). The specific operation steps of the two can be found in the national standard. Soil nitrate nitrogen (NO_3^- -N) and ammonium nitrogen (NH_4^+ -N) were measured using SmartChem automatic discontinuous chemical analyzer. When measuring, rinse the sample cup three times with the sample before adding the sample. Add the corresponding reagent to the corresponding reagent position. Pour the reagent into the reagent bottle slowly to prevent air bubbles from forming. The composition of soil particle size was sieved and counted by a step-by-step sieving method. According to the corresponding relationship between the permeability and time of PHE, the Origin 2018 software was used to make the penetration curve of PHE under each group of experiments.

3. Results

3.1. The Physical and Chemical Properties of Three Soils

We characterized and measured the physical and chemical properties of three soils. Table 1 shows the physical and chemical properties of the surrounding soil in SL [37], NY and YC.

Table 1. The physical and chemical properties of the three soils.

Soil	OM * (g/kg)	TN * (g/kg)	NO_3^- -N (mg/kg)	NH_4^+ -N (mg/kg)	TP * (g/kg)	Particle Size Composition (%)			
						<0.002 mm	0.002~0.02 mm	0.02~2 mm	>2 mm
SL	7.86	0.40	9.77	1.52	0.56	5.50	54.49	30.27	9.74
YC	11.14	0.70	24.44	1.48	0.76	1.43	22.46	63.16	12.95
NY	15.92	0.83	19.87	2.61	0.47	3.22	44.75	30.32	21.71

* OM—organic matter; TN—total nitrogen; TP—total phosphorus.

As can be seen from Table 1, different soils show different structural and compositional characteristics. The contents of inorganic nutrients such as N and P in the three soils differed somewhat, with YC soils having higher contents of NO_3^- -N and TP than the other two soils. Moreover, the highest contents of inorganic nutrients in NY soils were TN and NH_4^+ -N compared to YC and SL. Additionally, in terms of organic matter, NY soil also had the highest content of it. In contrast, SL had the lowest organic matter and N element content. In addition, through the investigation of soil particle size, we determined that the overall particle size of the three kinds of soil was YC > NY > SL. Among the three, YC had the biggest particle size, with 63.16% of the soil particle size in 0.02~2 mm. SL and NY had a more uniform particle size distribution (Table 1).

3.2. The Influence of Types of Soil

Under the condition of soil particle size of 0~1 mm, maintaining the same IS and pH, and using the soil types as a variable, the differences in the vertical migration of PHE in three soils of SL, YC and NY were explored. The penetration curve was shown in Figure 2. Permeability (C/C_0) is defined as the ratio of the concentration of PHE in the solution flowing from the bottom of the soil column to the concentration of PHE in the added PHE-electrolyte solution, i.e., the concentration ratio of contaminants after migration and before migration.

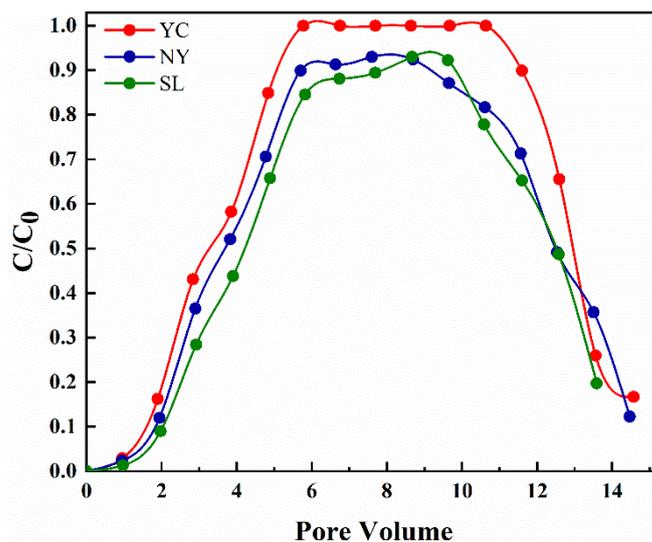


Figure 2. The influence of types of soil on vertical migration of phenanthrene (PHE).

As can be seen from Figure 2, the penetration curve of PHE (expressed as C/C_0) in different soil types showed a rapid upward trend at first, then entered a stable period when the pore volume was about 6, and finally decreased rapidly after the pore volume was 10. The initial growth rate of C/C_0 from fast to slow is YC, NY and SL, respectively. After the plateau period, the decline rate from fast to slow was also YC, NY and SL. It can be seen that the penetration effect of YC was the best, with the highest permeability of 1.00; that is, YC can completely penetrate the soil column. Followed by NY, the C/C_0 value of the stable period was 0.93. A little worse than NY was SL, whose permeability C/C_0 was basically around 0.9. It is speculated that this may be due to the differences of soil composition and physical and chemical properties in different areas. During the process of migration of pollutants such as PAHs, different physical and chemical conditions in soil will inevitably produce different migration results [38,39].

3.3. The Influence of IS

As an important factor in soil, IS will affect the physical and chemical properties of soil and the environmental behaviors of coexisting substances [35]. In this experiment, NaCl and CaCl₂ electrolyte solutions were used to simulate the effect of is on the vertical migration of PAHs in soil. The type of soil should be unchanged when exploring the effects of other factors on migration of PHE, so we used SL soils in our studies of IS, pH and soil particle size.

The penetration curves of PHE under different conditions of IS are shown in Figure 3. It can be seen that the migration and dissolution rate of PHE in the soil decreased with the increase of IS, which leads to the widening and delay of the penetration curve. This was consistent with the results of previous studies [32,40]. It could be that the increase in IS leads to the formation of more cations and anions in solution, which compresses the soil particles [41]. Therefore, electrostatic electric double layer particles reduce the repulsion of soil particles. Moreover, the increase of metal ions will adsorb and deposit a certain

amount of PHE, which will enhance its migration resistance. In the presence of the two selected electrolyte solutions, it can be clearly seen that the ability of NaCl to promote PHE migration was significantly stronger than that of CaCl₂. Different concentrations of NaCl (1 mM, 5 mM, 10 mM) had little effect on the migration of PHE, but the highest migration of PHE was observed under the electrolyte solution with 1 mM NaCl, up to 93%. However, under the action of CaCl₂, its promotion effect was weaker. It can be found that when the concentration of CaCl₂ was between 0 and 1 mM, the lower the electrolyte concentration, the higher the degree of PHE migration.

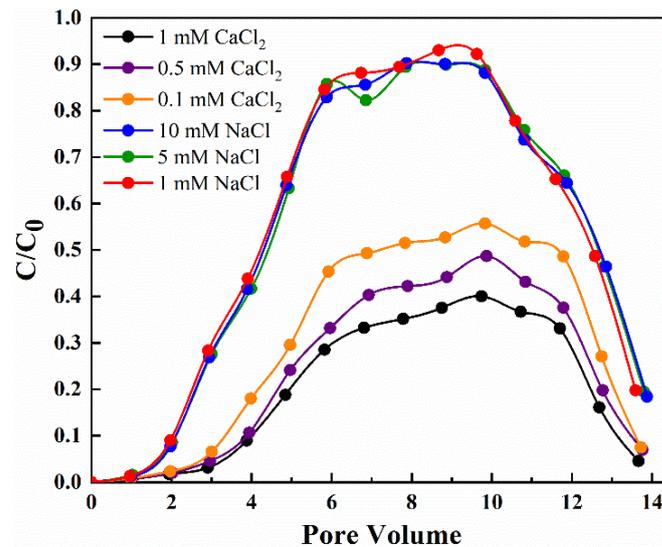


Figure 3. The influence of the ionic strength (IS) on the vertical migration of PHE in soil.

3.4. The Influence of pH

Figure 4 shows the influence of pH value on the vertical migration of PHE in soil. Under the experimental settings of pH 4, 7 and 10, the three penetration curves kept the same form. Under these three conditions, the fluidity reached the maximum when the pore volume was about 9.8. It can be seen from the penetration curve that change of pH value had no obvious effect on the vertical migration of PHE. It is inferred that the transport of PHE in soil has no significant correlation with the change of pH.

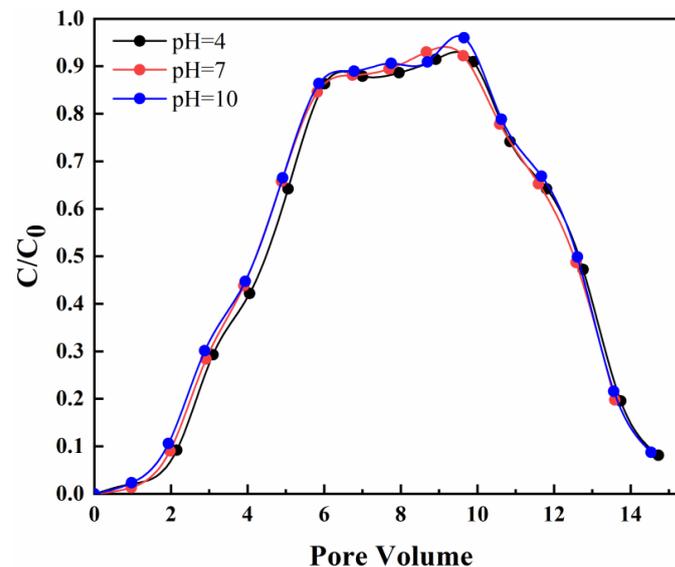


Figure 4. The influence of the pH value on the vertical migration of PHE in soil.

3.5. The Influence of Particle Size of Soil

The penetration curves of PHE in soils with different particle sizes are shown in Figure 5. Within the pore volume range of 1~15, there was a peak in the penetration curves of the three particle sizes, which indicated that PHE can completely (0.45~1 mm) or partially (0~0.15 mm and 0.15~0.45 mm) pass through the leaching process of soil column. Additionally, the penetration curve with a particle size of 0.45~1 mm appeared to have a stable peak value of 1.00.

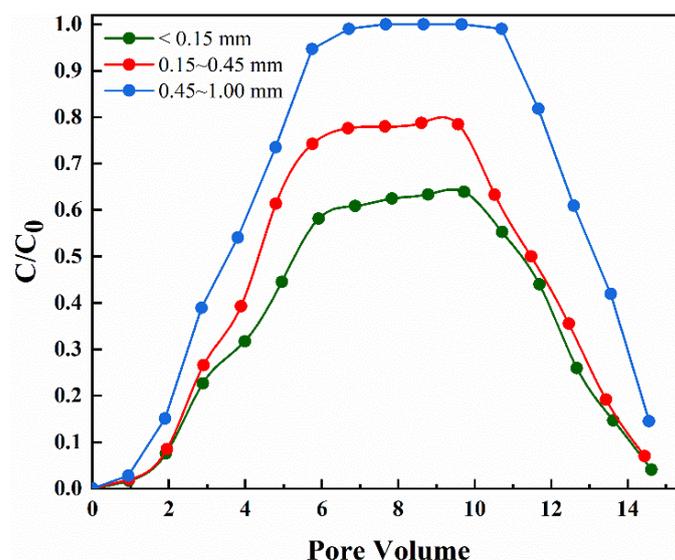


Figure 5. The influence of the particle size on the vertical migration of PHE in soil.

4. Discussion

4.1. The Influence of Types of Soil

The soil particle size showed that the particle size of NY and SL was dominated by silt (0.002~0.02 mm), accounting for 44.75% and 54.49%, respectively, while the particle size of YC was mainly 0.02~2 mm, accounting for 63.16% (Table 1). It can be inferred that the particle size composition of the soil significantly affects the migration of PHE, and the large particle size dominates. The larger the proportion of large particle size in the soil, the faster the migration rate of PHE (Figure 2). Therefore, the vertical migration of PHE in soil is positively correlated with soil particle size [34,35,42,43]. Study have shown that the mobility of PAHs in soil is positively correlated with gravel content (0.02~2 mm) and negatively correlated with clay content (<2 μm) [26]. The results of this experiment were consistent with them. In the literature, clay minerals are thought to be an important factor affecting the uptake of organic pollutants in soil [24,44], because the increase of fine-grained clay content will have a larger specific surface area and more adsorption sites, which will adsorb more PHE and reduce its mobility [38,39].

We can find that the soil of YC contained higher NO_3^- -N and TP than the other two soils (Figure 2). Rich inorganic nutrients are more conducive to carrying high hydrophobic pollutants such as PHE, and thus, they migrate to the underground [38,39]. In addition, previous studies have shown that the vertical migration of PAHs is negatively correlated with soil organic matter content [26,34,35,42,43]. However, through the analysis of Table 1, it was found that the contents of organic matter in the SL, NY and YC soils are 7.86, 15.92 and 11.14 g/kg, respectively, so the migration rates of PHE should decrease. It was not consistent with the results of YC, NY and SL in Figure 2. Furthermore, it may be inferred that in previous studies, large-scale soil columns were used for long-term migration experiments [26], and the organic matter in the soil had enough time and space to adsorb PAHs, which affected the migration of PAHs. However, in this experiment, a small soil column was used for short-term migration and leaching experiment, so the content of

organic matter in the soil did not play a leading role in the vertical migration of PHE. At the same time, compared with the penetration curve of YC, the penetration curve of NY was lower, which indicates that the positive correlation between soil organic matter content and soil adsorption capacity may be only one aspect of the effect of migration [24,32]. Because the overall soil particle size of NY was smaller than that of YC, its permeability was also lower than that of YC. We speculate that the combined effect of soil particle size and organic matter is the dominant factor affecting the migration of PHE in soil.

4.2. The Influence of IS

From the results in Figure 3 (Section 3.3), the high mobility of PHE at a low electrolyte concentration may be closely related to environmental factors in soil. This may be due to the increase of IS, which leads to the existence of a large number of cations and anions in the solution. Their existence compresses the soil particles, and the electrostatic electric double layer particles reduce the repulsion of soil particles [35,40]. In addition, the increase of metal ions also adsorbed and deposited some PHE, thus enhancing the resistance of PHE migration in soil [42,43]. This was consistent with previous research [32], showing that the decrease of IS leads to an increase in the thickness of the electric double layer and the change of surface charge of the quartz sand and pollutants, thus promoting the release of pollutants. Therefore, it can be speculated that the vertical migration of PHE in soil is negatively correlated with IS, and soil with lower metal ion concentration is more favorable for the migration of PAHs. However, the migration in the solution of monovalent metal ion has no obvious effect, which was consistent with the findings of other studies [29,31–35]. In addition, Liu and Wang found that the influence of divalent Ca^{2+} on the migration ability of pollutants is significantly higher than that of monovalent K^+ [32,36]. Combining these two conclusions, it can be inferred that divalent metal ions have an influence on the migration of PHE in soil. The inhibition of this ability is more obvious than that of univalent metal ions [32].

4.3. The Influence of pH

It is inferred that the transport of PHE in soil had no significant correlation with the change of pH (see in Figure 4). Liu measured the penetration curves of soil colloids under different pH values (5, 7 and 9) and 30 mM NaCl solution, and found that the penetration curves basically overlapped between pH values 7 and 9 [41]. According to present studies, PHE is a highly non-ionizable hydrophobic organic chemical that can maintain a high degree of hydrophobicity across all pH settings. As a result, changes in the pH value had no clear influence on the migration of PHE in saturated sand columns [28,32], so the speciation of PHE does not change with the decrease of pH value, and there was no obvious difference between the penetration curves of PHE. The chemical stability of PHE will not be affected by the difference of pH values. From this experiment, it can be concluded that the pH value has no significant influence on the vertical migration of PHE in soil. According to experimental results, the neutral conditions of PHE were used in the subsequent experiments to explore the influence of other soil conditions.

4.4. The Influence of the Particle Size of Soil

As the soil particle size increased, the pores between the soil particles increased, which was more conducive to the penetration and leaching of the solution, thus speeding up the downward migration of PHE [14,28]. Relevant research shows that as the particle size increases, the inorganic NPs in the soil will move downward at an accelerated rate, so the PHE carried on its surface will move downward completely [32]. Sun et al. confirmed that clay with finer particles has a larger specific surface area and more adsorption sites [38]. Moreover, the ability of fine and dense soil to block and adsorb pollutants is obviously larger than that of coarse-grained soil. As shown in Figure 5, in the fine-grained soil with 0~0.15 mm, the maximum permeability (C/C_0) of PHE can reach above 0.6. It is speculated that this is closely related to the related physical and chemical properties of the

soil surrounding the oilfield [45]. Therefore, it can be inferred that the vertical migration of PHE in soil is positively related to the soil particle size. This further corroborates the results of previous studies that the migration rate of PAHs is negatively related to the content of clay in soil [34,35,42,43].

5. Conclusions

To investigate the vertical migration of petroleum pollutants in soil, we chose PHE (one PAHs in petroleum) as the pollutant for soil column migration experiments to simulate this process. The findings revealed that the vertical migration of PHE in soil was inversely linked with IS, and that divalent metal ions have a stronger inhibitory effect than monovalent metal ions. Because pH has no effect on PHE's chemical characteristics, it had little impact on PHE's migration. Furthermore, the migration of PHE in soil was positively connected with soil particle size, because larger pores are more conducive to solution leaching and PHE infiltration. In descending order, the mobility of PHE in different soil types was YC, NY and SL. This is because the soil in YC was mostly made up of large particles, whereas the soil in NY and SL was mainly composed of smaller clay particles. The results reveal that the clay component had a negative impact on penetration rate. This experiment provides a new basis for researching the migration of petroleum pollutants in soil surrounding a real oilfield, as well as a point of reference for estimating the extent of petroleum pollution in deeper soil.

Author Contributions: Conceptualization, X.G.; Data curation, H.C.; Formal analysis, H.C. and C.L.; Funding acquisition, X.G.; Investigation, H.C. and M.L.; Methodology, H.C. and M.L.; Project administration, X.G.; Supervision, X.G.; Writing—original draft, H.C.; Writing—review and editing, M.L., C.L. and X.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (No. 2019YFC1804101).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data discussed in this work are presented in the form of Tables and Figures in the article, and no data are withheld. All the data can be accessed from the journal article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Toro, D.M.; McGrath, J.A.; Stubblefield, W.A. Predicting the toxicity of neat and weathered crude oil: Toxic potential and the toxicity of saturated mixtures. *Environ. Toxicol. Chem. Int. J.* **2007**, *26*, 24–36. [\[CrossRef\]](#)
2. Tang, J.; Wang, M.; Wang, F.; Sun, Q.; Zhou, Q. Eco-toxicity of petroleum hydrocarbon contaminated soil. *J. Environ. Sci.* **2011**, *23*, 845–851. [\[CrossRef\]](#)
3. Bachmann, R.T.; Johnson, A.C.; Edyvean, R.G. Biotechnology in the petroleum industry: An overview. *Int. Biodeterior. Biodegrad.* **2014**, *86*, 225–237. [\[CrossRef\]](#)
4. Yuan, H.; Li, T.; Ding, X.; Zhao, G.; Ye, S. Distribution, sources and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface soils of the Yellow River Delta, China. *Mar. Pollut. Bull.* **2014**, *83*, 258–264. [\[CrossRef\]](#)
5. Varjani, S.J.; Gnansounou, E.; Pandey, A. Comprehensive review on toxicity of persistent organic pollutants from petroleum refinery waste and their degradation by microorganisms. *Chemosphere* **2017**, *188*, 280–291. [\[CrossRef\]](#)
6. Qin, G.; Gong, D.; Fan, M.Y. Bioremediation of petroleum-contaminated soil by biostimulation amended with biochar. *Int. Biodeterior. Biodegrad.* **2013**, *85*, 150–155. [\[CrossRef\]](#)
7. Guo, H.; Yao, J.; Cai, M. Effects of petroleum contamination on soil microbial numbers, metabolic activity and urease activity. *Chemosphere* **2012**, *87*, 1273–1280. [\[CrossRef\]](#)
8. Boll, M.; Löffler, C.; Morris, B.E.; Kung, J.W. Anaerobic degradation of homocyclic aromatic compounds via arylcarboxyl-coenzyme A esters: Organisms, strategies and key enzymes. *Environ. Microbiol.* **2014**, *16*, 612–627. [\[CrossRef\]](#)
9. Hoffman, D.R.; Okon, J.L.; Sandrin, T.R. Medium composition affects the degree and pattern of cadmium inhibition of naphthalene biodegradation. *Chemosphere* **2005**, *59*, 919–927. [\[CrossRef\]](#)
10. Wang, C.H.; Wu, S.H.; Zhou, S.L.; Shi, Y.X.; Song, J. Characteristics and source identification of polycyclic aromatic hydrocarbons (PAHs) in urban soils: A review. *Pedosphere* **2017**, *27*, 17–26. [\[CrossRef\]](#)

11. Mazarji, M.; Minkina, T.; Sushkova, S. Effect of nanomaterials on remediation of polycyclic aromatic hydrocarbons-contaminated soils: A review. *J. Environ. Manag.* **2021**, *284*, 112023. [[CrossRef](#)] [[PubMed](#)]
12. Khadhar, S.; Higashi, T.; Hamdi, H.; Matsuyama, S.; Charef, A. Distribution of 16 EPA-priority polycyclic aromatic hydrocarbons (PAHs) in sludges collected from nine Tunisian wastewater treatment plants. *J. Hazard. Mater.* **2010**, *183*, 98–102. [[CrossRef](#)]
13. Basavaiah, N.; Mohite, R.D.; Singare, P.U. Vertical distribution, composition profiles, sources and toxicity assessment of PAH residues in the reclaimed mudflat sediments from the adjacent Thane Creek of Mumbai. *Mar. Pollut. Bull.* **2017**, *118*, 112–124. [[CrossRef](#)]
14. Ren, K.; Wei, Y.; Li, J. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated PAHs, azaarenes, and sulfur/oxygen-containing heterocyclic PAHs) in surface soils from a typical city, south China. *Chemosphere* **2021**, *283*, 131190. [[CrossRef](#)] [[PubMed](#)]
15. Yang, W.; Lang, Y.; Li, G. Cancer risk of polycyclic aromatic hydrocarbons (PAHs) in the soils from Jiaozhou Bay wetland. *Chemosphere* **2014**, *112*, 289–295. [[CrossRef](#)]
16. He, Y.; Yang, C.; He, W.; Xu, F. Nationwide health risk assessment of juvenile exposure to polycyclic aromatic hydrocarbons (PAHs) in the water body of Chinese lakes. *Sci. Total Environ.* **2020**, *723*, 138099. [[CrossRef](#)]
17. Deutsch-Wenzel, R.P.; Brune, H.; Grimmer, G.; Dettbarn, G.; Misfeld, J. Experimental studies in rat lungs on the carcinogenicity and dose-response relationships of eight frequently occurring environmental polycyclic aromatic hydrocarbons. *J. Natl. Cancer Inst.* **1983**, *71*, 539–544.
18. Xia, Z.; Duan, X.; Tao, S. Pollution level, inhalation exposure and lung cancer risk of ambient atmospheric polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Environ. Pollut.* **2013**, *173*, 150–156. [[CrossRef](#)]
19. Ghosal, D.; Ghosh, S.; Dutta, T.K.; Ahn, Y. Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): A review. *Front. Microbiol.* **2016**, *7*, 1369. [[CrossRef](#)]
20. Ke, L.; Yu, K.S.H.; Wong, Y.S.; Tam, N.F.Y. Spatial and vertical distribution of polycyclic aromatic hydrocarbons in mangrove sediments. *Sci. Total Environ.* **2005**, *340*, 177–187. [[CrossRef](#)]
21. Li, C.H.; Zhou, H.W.; Wong, Y.S.; Tam, N.F.Y. Vertical distribution and anaerobic biodegradation of polycyclic aromatic hydrocarbons in mangrove sediments in Hong Kong, South China. *Sci. Total Environ.* **2009**, *7*, 5772–5779. [[CrossRef](#)]
22. Ohura, T.; Sakakibara, H.; Watanabe, I. Spatial and vertical distributions of sedimentary halogenated polycyclic aromatic hydrocarbons in moderately polluted areas of Asia. *Environ. Pollut.* **2015**, *196*, 331–340. [[CrossRef](#)]
23. Yan, W.; Chi, J.; Wang, Z.; Huang, W.; Zhang, G. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environ. Pollut.* **2009**, *157*, 1823–1830. [[CrossRef](#)]
24. Cai, T.; Ding, Y.; Zhang, Z. Effects of total organic carbon content and leaching water volume on migration behavior of polycyclic aromatic hydrocarbons in soils by column leaching tests. *Environ. Pollut.* **2019**, *254*, 112981. [[CrossRef](#)]
25. Sun, Y.; Xie, Z.; Wu, K. Speciation, distribution and migration pathways of polycyclic aromatic hydrocarbons in a typical underground river system in Southwest China. *J. Hydrol.* **2021**, *596*, 125690. [[CrossRef](#)]
26. Fang, J.; Wang, M.; Shen, B.; Zhang, L.; Lin, D. Distinguishable co-transport mechanisms of phenanthrene and oxytetracycline with oxidized-multiwalled carbon nanotubes through saturated soil and sediment columns: Vehicle and competition effects. *Water Res.* **2017**, *108*, 271–279. [[CrossRef](#)]
27. Kumar, M.; Bolan, N.S.; Hoang, S.A. Remediation of soils and sediments polluted with polycyclic aromatic hydrocarbons: To immobilize, mobilize, or degrade? *J. Hazard. Mater.* **2021**, *420*, 126534. [[CrossRef](#)]
28. Waigi, M.G.; Kang, F.; Goikavi, C.; Ling, W.; Gao, Y. Phenanthrene biodegradation by sphingomonads and its application in the contaminated soils and sediments: A review. *Int. Biodeterior. Biodegrad.* **2015**, *104*, 333–349. [[CrossRef](#)]
29. Xia, T.J.; Lin, Y.; Guo, X.T. Co-transport of graphene oxide and titanium dioxide nanoparticles in saturated quartz sand: Influences of solution pH and metal ions. *Environ. Pollut.* **2019**, *251*, 723–730. [[CrossRef](#)]
30. Mattison, N.T.; O'Carroll, D.M.; Kerry Rowe, R.; Petersen, E.J. Impact of porous media grain size on the transport of multi-walled carbon nanotubes. *Environ. Sci. Technol.* **2011**, *45*, 9765–9775. [[CrossRef](#)]
31. Wang, D.; Bradford, S.A.; Harvey, R.W.; Hao, X.; Zhou, D. Transport of ARS-labeled hydroxyapatite nanoparticles in saturated granular media is influenced by surface charge variability even in the presence of humic acid. *J. Hazard. Mater.* **2012**, *229*, 170–176. [[CrossRef](#)]
32. Liu, F.; Xu, B.; He, Y.; Brookes, P.C.; Xu, J. Co-transport of phenanthrene and pentachlorophenol by natural soil nanoparticles through saturated sand columns. *Environ. Pollut.* **2019**, *249*, 406–413. [[CrossRef](#)]
33. Schwarz, K.; Gocht, T.; Grathwohl, P. Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. *Environ. Pollut.* **2011**, *159*, 133–139. [[CrossRef](#)]
34. Lu, Y.; Yang, K.; Lin, D. Transport of surfactant-facilitated multiwalled carbon nanotube suspensions in columns packed with sized soil particles. *Environ. Pollut.* **2014**, *192*, 36–43. [[CrossRef](#)]
35. Li, M.; Zhang, X.; Yi, K. Transport and deposition of microplastic particles in saturated porous media: Co-effects of clay particles and natural organic matter. *Environ. Pollut.* **2021**, *287*, 117585. [[CrossRef](#)]
36. Wang, D.; Jin, Y.; Jaisi, D.P. Cotransport of hydroxyapatite nanoparticles and hematite colloids in saturated porous media: Mechanistic insights from mathematical modeling and phosphate oxygen isotope fractionation. *J. Contam. Hydrol.* **2015**, *182*, 194–209. [[CrossRef](#)]

37. Uddin, M.N.; Islam, A.S.; Bala, S.K. Mapping of climate vulnerability of the coastal region of Bangladesh using principal component analysis. *Appl. Geogr.* **2019**, *102*, 47–57. [[CrossRef](#)]
38. Sun, Y.; Zhang, S.; Lan, J. Vertical migration from surface soils to groundwater and source appointment of polycyclic aromatic hydrocarbons in epikarst spring systems, southwest China. *Chemosphere* **2019**, *230*, 616–627. [[CrossRef](#)]
39. Biel-Maeso, M.; Burke, V.; Greskowiak, J. Mobility of contaminants of emerging concern in soil column experiments. *Sci. Total Environ.* **2021**, *762*, 144102. [[CrossRef](#)]
40. Alimi, O.S.; Farnier, J.M.; Tufenkji, N. Exposure of nanoplastics to freeze-thaw leads to aggregation and reduced transport in model groundwater environments. *Water Res.* **2021**, *189*, 116533. [[CrossRef](#)]
41. Liu, F.; Xu, B.; He, Y. Differences in transport behavior of natural soil colloids of contrasting sizes from nanometer to micron and the environmental implications. *Sci. Total Environ.* **2018**, *634*, 802–810. [[CrossRef](#)] [[PubMed](#)]
42. Li, M.; He, L.; Zhang, X.; Rong, H.; Tong, M. Different surface charged plastic particles have different cotransport behaviors with kaolinite* particles in porous media. *Environ. Pollut.* **2020**, *267*, 115534. [[CrossRef](#)]
43. Sun, Y.; Pan, D.; Wei, X. Insight into the stability and correlated transport of kaolinite colloid: Effect of pH, electrolytes and humic substances. *Environ. Pollut.* **2020**, *266*, 115189. [[CrossRef](#)] [[PubMed](#)]
44. Banach-Szott, M.; Debska, B.; Wisniewska, A.; Pakula, J. Changes in the contents of selected polycyclic aromatic hydrocarbons in soils of various types. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5059–5069. [[CrossRef](#)] [[PubMed](#)]
45. Hong, W.J.; Li, Y.F.; Li, W.L. Soil concentrations and soil-air exchange of polycyclic aromatic hydrocarbons in five Asian countries. *Sci. Total Environ.* **2020**, *711*, 135223. [[CrossRef](#)]