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Infiltration characteristics of non-aqueous phase liquids in undisturbed loessal soil cores

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Abstract

The widespread contamination of soils and aquifers by non-aqueous phase liquids (NAPL), such as crude oil, poses serious environmental and health hazards globally. Understanding the infiltration characteristics of NAPL in soil is crucial in mitigating or remediating soil contamination. The infiltration characteristics of crude and diesel oils into undisturbed loessal soil cores, collected in polymethyl methacrylate cylindrical columns, were investigated under a constant fluid head (3 cm) of either crude oil or diesel oil. The infiltration rate of both crude and diesel oils decreased exponentially as wetting depth increased with time. Soil core size and bulk density both had significant effects on NAPL infiltration through the undisturbed soil cores; a smaller core size or a greater bulk density could reduce oil penetration to depth. Compacting soil in areas susceptible to oil spills may be an effective stratage to reduce contamination. The infiltration of NAPL into soil cores was spatially anisotropic and heterogeneous, thus recording the data at four points on the soil core is a good stratage to improve the accuracy of experimental results. Our results revealed that crude and diesel oils, rather than their components, have a practical value for remediation of contaminated loessal soils.

Key words: crude oil; diesel oil; soil compaction; soil core sample size; the Loess Plateau of China

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Introduction

The crude oil industry has been developed to the point where more than 65 million barrels per day is extracted world-wide to meet the greater part of the world's energy requirements. However, the industry inevitably risks accidental discharges into soils, surface water or groundwater during transportation, whether by land or by sea, or during the oil drilling process, or due to leakages from storage tanks, etc. (Nicolotti and Egli, 1998; Schirmer and Butler, 2004; Zaidel *et al*., 1996). When these accidental discharges occur, severe and persistent contamination can be caused in both the local area and those further a field, damaging the health of ecosystems. For example, when a recent spill of about 100 tons of diesel, a main constituent of crude oil, occurred in Ningqiang County in Shaanxi Province on July 27, 2008, a 10-km stretch of river was polluted. Due to their toxicity and bio-accumulative properties, contamination of the environment by oil pollutants, which are non-aqueous phase liquids (NAPL), is an issue of major concern. Therefore, it is crucial to remediate and reclaim oil contaminated sites (Khamehchiyan *et al*., 2007; Zalidis *et al*., 1998; Zhang *et al*., 2006).

Many researchers have stated that understanding the migration, fate and distribution of NAPLs is one of the preconditions for devising effective measures to remediate contaminated soils (Fine *et al*., 1997; Oostrom *et al*., 2006; Schirmer and Butler, 2004; Soga *et al*., 2004). Factors which affect the infiltration of NAPL into the soil, and then result in a deep contamination that possibly affects the groundwater, have received much attention (e.g., Hofstee *et al*., 1998a; Lee, 2008). Hofstee *et al*. (1998b) conducted perchloroethylene (PCE) infiltration experiments in nominally 1- and 2-dimensional, stratified porous media. Kechavarzi *et al*. (2005) used a quantitative two-dimensional laboratory experiment to investigate the immiscible flow of a light NAPL in the vadose zone combined with an image analysis technique. However, little has been reported on the effect of sample size and soil compaction on NAPL infiltration, which are factors that may help us to improve the accuracy of data collection and the efficacy by means of model prediction of soil remediation practices.

Measures to remediate the contaminated soils can generally be divided into two categories: (1) field remediation technologies that are site specific, and (2) laboratory experiments that provide data for mathematical and numerical simulations which are intended to provide an important means by predicting the movement and fate of NAPLs (Jia *et al*., 1999). A number of studies have used two-phase

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models (Hofstee *et al*., 1998b; Huyakorn and Pinder, 1978; Kechavarzi *et al*., 2005; Lee, 2008) or three-phase models (Falta *et al*., 1992; Fenwick and Blunt, 1998; Goldstein *et al*., 2007; Kuiper and Illangasekare, 1998; Yoon *et al*., 2007) to assess the infiltration and redistribution in heterogeneous disturbed porous media of either light non-aqueous phase liquids (LNAPL), e.g., hexane, isooctane, diesel and decane (Lee, 2008; Waduge *et al*., 2007; Zhou and Blunt, 1997), or dense non-aqueous phase liquids (DNAPL), e.g., perchloroethylene, 1,2,4-trichlorobenzene, and trichloroethene (Hofstee *et al*., 1998b; Panday *et al*., 1997; Yoon *et al*., 2007). However, owing to the complex chemical components of crude oil, the majority of the related studies have been confined to laboratory tests that have focused on only a few of chemical compounds that make up crude oil. The studies cannot, therefore, represent the actual process of whole crude oil movement in natural, undisturbed soils. Moreover, most related studies use disturbed soils as the porous medium, which cannot truly represent field soils. Thus, an alternative approach is to monitor the infiltration and migration process of the crude oil, itself, into undisturbed soils, which may give a better understanding of the processes involved.

The Loess Plateau of China is a region of deep loess deposits, unique landscapes and intensive soil erosion. It is rich in petroleum resources which play an important role in the Chinese national economy. However, the fragile ecosystem is at risk from accidental surface discharges and from improper disposal of crude and diesel oils. Few studies have dealt with the basic physical process of the infiltration and distribution of these oils (Huang and Ren, 2000; Huang *et al*., 2001), and much needs to be done in the area of simulation of crude oil migration and its fate in loessal soils.

Therefore, in this article, our intention was using laboratory experiments to quantitatively describe the transport of crude and diesel oils within undisturbed soil cores, taken from the Loess Plateau. Specifically, the objectives of this study were to: (1) investigate the infiltration characteristics of a local crude oil and diesel oil; (2) investigate the effect of soil compaction and the size of soil core samples on the infiltration process of crude oil; (3) provide data for the breakthrough process of diesel oil.

1 Materials and methods

1.1 Non-aqueous phase liquid

The non-aqueous liquids used in the experiments were crude oil and diesel oil, which were obtained from Ansai County in Shaanxi Province, China. The crude oil was a LNAPL (density (0.844–0.854) × 10^6 kg/m^3). Some basic properties of the crude oil are given in Table 1 (Guo *et al*., 2006). The diesel oil, refined from the crude oil, had a kinematic viscosity of 4.3 ×10^{-6} m^2/s.

1.2 Materials

A typical loessal soil (Calcaric Regosol, FAO/Unesco, 1988) (Gong, 2003) from the center of the Loess Plateau under permanent grassland was used. Undisturbed soil cores were collected using polymethyl methacrylate tubes. To explore the effect of sample size on the infiltration characteristics of NAPL, we used tubes of two sizes: (1) 30 cm long and 5 cm diameter (for samples referred to hereafter as small cores); (2) 45 cm long and 10 cm diameter (for samples referred to hereafter as large cores). For each size, three undisturbed soil cores were collected.

Additional soil cores and disturbed soil samples were collected from the same location and soil depth to measure physical and chemical properties of soil. Three small soil cores were also taken from a nearby earthen trail where soil compaction had occurred (bulk density, 1.53 g/cm^3; soil porosity, 42%). Soil porosity was determined from following equation:

$$f = 1 - \frac{\rho_b}{\rho_s}$$

where, ρ_b is the bulk density of the soil determined from its over-dried mass and the known volume within the tube, and ρ_s is the soil particle density, taken to be 2.65 g/cm^3.

The disturbed soil samples were air-dried, crushed, and passed through a 0.25-mm mesh for the determination of soil organic carbon (SOC) content using the dichromate oxidation method, with external heat applied in two replications (Nelson and Sommers, 1982). Soil particle size composition of air-dried samples was measured by a laser diffraction technique using the Master Sizer2000 (Malvern Instruments, Malvern, England) (Liu *et al*., 2005) after sample was crushed to pass through a 1-mm sieve and dispersed using ultrasound. Soil hydraulic conductivity

Table 1 Properties of the crude oil and the soil used in this study*

Crude oil		Undisturbed soil	
Saturated hydrocarbon (%)	76.22	Saturated water content (%)	35.85
Aromatics (%)	16.38	Initial water content (%)	2.07
Non-hydrocarbon (%)	5.48	Bulk density (g/cm^3)	1.32
Asphaltene (%)	1.93	Hydraulic conductivity (water) (cm/s)	0.02
Saturated hydrocarbon/Aromatics	4.66	Sand (%)	22.62
Non-hydrocarbon/Asphaltene	3.25	Loam (%)	60.91
Sulphur content (%)	0.11	Clay (%)	16.47
Kinematic viscosity at 50°C (× 10^{-6} m^2/s)	5.9–10.3	Apparent porosity (%)	50.20
Freezing point (°C)	11–21	Soil organic carbon (g/kg)	10.20

* The properties of crude oil are cited from GUO *et al*., 2006.

was determined using deionized water and the constant head method (Klute and Dirksen, 1986). Some physical and chemical properties of the soil are presented in Table 1.

1.3 Experiment

We used one or two sizes of soil cores to perform four sets of column infiltration experiments to examine factors affecting the hydraulic properties of a crude oil and/or a diesel oil in the loessal soil (Table 2). To simulate a continuous spill, a constant pressure head (3 cm) of NAPL was maintained in all the experiments using a Mariotte bottle (Fig. 1). The column outlet for the diesel oil breakthrough experiment directed into a graduated container thereby permitted the measurement of the effluent volume for time intervals, from which the cumulative volume and the flow velocity of the effluent were determined.

Prior to the infiltration experiments, the soil cores were air-dried to reduce the moisture content to a low initial level (Table 1). The flow of the NAPL was initiated rapidly at the top of the air-dry soil columns to establish the hydraulic head. The wetting front of the NAPL was monitored at four points on the sides of the soil core, separated by 90°, to account for the heterogeneity of the undisturbed soil (Fig. 1). The average wetting depth in each core at any given time was then determined from these four measurements.

1.4 Data analysis

Primary statistical analyses, i.e., means, standard deviations, and coefficients of variation, and the curve fitting of the infiltration process were carried out using Sigma Plot 10.0 and Excel 2003.

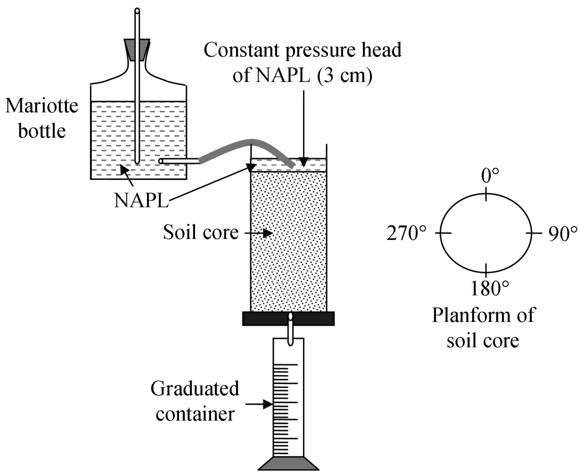

Fig. 1 Schematic of non-aqueous phase liquid (NAPL) infiltration experiments.

Table 2 Infiltration experiments on NAPL

Experimental purpose	NAPL	Size of soil core in length, i.d. (cm × cm)
Infiltration of NAPL	Crude oil, diesel oil	30 × 5[a]; 45 × 10[b]
Effects of sample size	Crude oil	30 × 5; 45 × 10
Effects of soil compaction	Crude oil	30 × 5
Break through of NAPL	Diesel oil	45 × 10

[a] Small cores; [b] large cores.

2 Results and discussion

2.1 Infiltration of crude oil into soil core

The infiltration process of crude oil is shown in Fig. 2. Infiltration commenced immediately when the crude oil contacting the soil surface. Initially infiltration into the soil core proceeded relatively quickly while the wetting front advanced at the maximum observed rate. With time, and as the wetting front depth increasing, the wetting front advancing rate decreased and kept lastly stable. The NAPL was introduced into the soil column under the pressure of a crude oil head of 3 cm and, while the wetting front was advancing, gravity and the matric potential that existed between the wet and air-dry soil played important roles in the infiltration process. While the crude oil head and matric potential remained constant, the force required to move the NAPL through an increasing depth of soil became greater so that the rate of the advance of the wetting front decreased. This force had to overcome the resistance of the oil due to its viscosity and it is also possible that pores could be reduced in size if the oil was adsorbed onto the soil aggregate surfaces. This infiltration characteristic of crude oil is similar to those reported in other NAPL studies (Huang and Ren, 2000; Wang *et al*., 1998, 2000). The infiltration data occurring in both the small and large cores in present study were fitted with an exponential curve ($R^2 > 0.96$) (Fig. 2).

2.2 Effects of the soil core sample size on the infiltration of crude oil

Generally, the size of the undisturbed soil core sample is very important because of the heterogeneity of the soil and the effect of the sides of the tube on the soil core, i.e., the edge or boundary effect. In Figs. 2a–2d, we can see the effect of the core size on the infiltration of the crude oil into the small and large soil cores. For the small cores, the infiltration of the crude oil within the first 50 min was relatively rapid, then the infiltration rate was reduced to a slow and almost steady rate as observed by the slow advancement rate of the wetting front (0.08 cm/min); this value can be considered as the steady state of the wetting front advance under the 3 cm hydraulic head. Thus, after 160 min, the crude oil had infiltrated to a depth of about 14 cm in the small cores (Figs. 2a and 2b). In contrast, in the large cores (Figs. 2e and 2f), the time taken until the wetting front advancement rate had reached a relatively steady state of 0.097 cm/min was 600 min, and the infiltration depth was 43 cm at that time. This shows that there was a highly significant effect of the sample core size on the infiltration behavior of the crude oil. To further highlight this effect, the infiltration curve for the large cores was plotted for the same infiltration time as for the small cores for comparison (Figs. 2a and 2b to Figs. 2c and 2d). From Fig. 2, sample core size did not change the exponential form of the infiltration model relating the

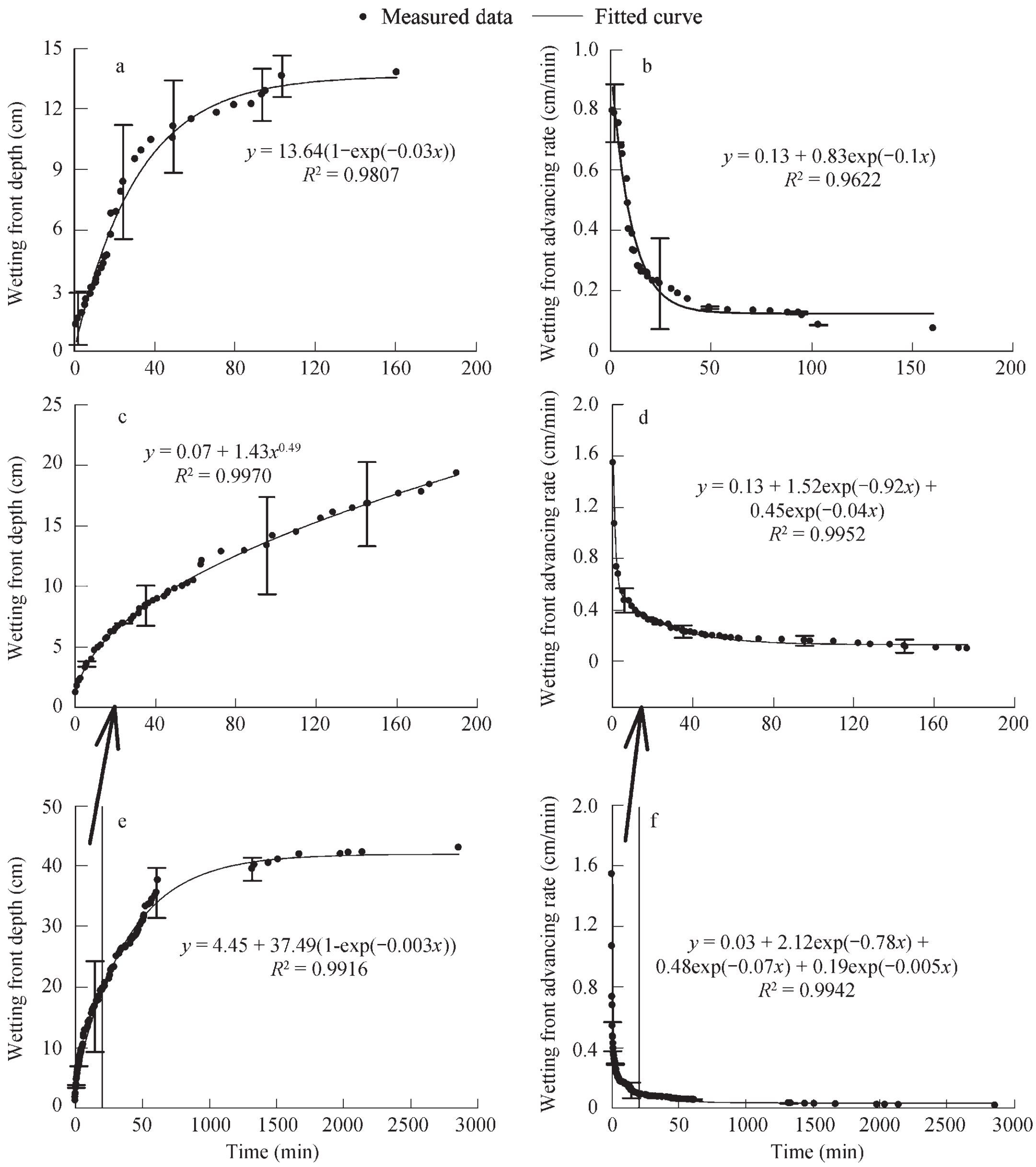

Fig. 2 Infiltration, over time, of crude oil into undisturbed cylindrical loessal soil cores. (a) and (b) small core size (30 cm long × 5 cm diameter); (c) and (d) large core size (45 cm long × 10 cm diameter) over the same time period as (a) and (b); (e) and (f) large core size over the entire infiltration process. Error bars represent standard deviation.

rate of wetting front advancement to infiltration time, but greatly affected the parameters of that model.

Explanations for the notable effect of sample core size on the infiltration behavior of the crude oil include soil heterogeneity and the boundary effect of the soil cores. First, soil properties such as porosity can demonstrate high variability within a short distance, readily measured at the centimeter scale. Thus, the probability that a sample may include larger macropores was formed, for example, by soil cracking, the roots of plants, or the activities of burrowing soil animals, etc., increase with sample core size. Likewise the probability that such macropore systems would be also continuous increased with sample core size. Both factors would facilitate the crude oil infiltration process along preferential flow pathways in larger samples. Furthermore, a larger soil core size will probably contain more of the features present in the soil *in situ* and thus will represent it more accurately. When polymethyl methacrylate tubes were inserted into the soil, the destruction of soil structure close to the sides of the tube was unavoidable. Shear forces would damage the pore system not only at the immediate interface between the tube and the soil but for some distance from the tube walls into the soil that would be dependent upon the soil properties, prevailing conditions such as moisture content, and the way for tube inserting into the soil. As implied above, the side of the tube represents an interruption of the soil pore system. In smaller cores, a proportionally greater volume of soil is affected by the boundary conditions. Therefore, in general, a larger soil core will be more similar to the field soil and will yield more accurate information in laboratory experiments about the actual infiltration of crude oil into the field soil. However, in practice there are limitations to the size of a soil core that may be obtained and used in the laboratory.

2.3 Effects of soil compaction on the infiltration of crude oil

We compared the infiltration process of crude oil into similar soils sampled in the small cores that differed mainly in the value of their bulk densities and associated porosities. Infiltration data for crude oil into the cores containing undisturbed and compacted soil (bulk density, 1.53 g/cm^3; soil porosity, 42%) (Fig. 3) can be compared with those for the undisturbed soil cores (bulk density, 1.32 g/cm^3; soil porosity, 50.2%), as shown in Figs. 2a and 2b. The effects of increased soil bulk density and reduced porosity on the infiltration of crude oil into the soil cores are significantly different. Initially, the crude oil penetrates the compacted soil at a faster rate than in the case of the uncompacted soil. This can probably be ascribed to the present of greater matric potential due to the finer pore system that is likely present in the compacted soil compared with that found in the uncompacted soil. However, because of the finer pore system, the force needed to maintain flow through the compacted soil is greater than that required to do so through the uncompacted soil. Thus, the crude oil was unable to penetrate to the same depth in the compacted soil as it in uncompacted soil, and the maximum observed depth was 9 cm in 10000 min for the former (Fig. 3) and 14 cm in 160 min for the latter (Fig. 2a). Similarly, because of these larger required forces, the infiltration rate was more sharply reduced for compacted soil than that for uncompacted soil. These differences due to compaction are reflected in the fitted models of the infiltration process for both soils (Figs. 2a, 2b, and 3). Thus, we can conclude that soil compaction has a significant impact on the infiltration of the crude oil.

Reducing the depth of penetration, and thus the contamination of the soil at depth, and increasing the migration time of crude oil into the soil by intentionally inducing soil compaction may effectively reduce the damage caused by pollution contamination at depth within the soil. Furthermore, increasing migration time of petroleum pollutants may permit clean up operations of spills to commence in time to reduce damage. Compaction of soils in areas at risk of oil spills, e.g., beneath oil pipelines, around oil storage facilities, etc., could be an effective management practice. However, the possibility which the area might increase over the pollution occur should also be considered. A similar management strategy has been also proposed by other researchers (Zhao *et al*., 2004; Zhang *et al*., 2005) who have suggested that soil compaction can be beneficial for soil water conservation, especially in semi-arid areas, since it results in more water being held in the rooting zone and reduces water losses due to the percolation to deeper layers.

2.4 Infiltration and breakthrough of diesel through undisturbed soil cores

The infiltration process of diesel oil into large undisturbed soil cores is presented in Fig. 4 and shows that the rate of its wetting front advancement is greater than that of the crude oil into soil cores of the same size (Figs. 2c–2f). Whereas crude oil took 1300 min to infiltrate to a depth of 40 cm (Fig. 2e), diesel took 65 min (Fig. 4). This can be explained by the composition of the NAPLs being different when considering crude and diesel oils, especially with regard to their different viscosities (5.9×10^{-6}–10.3×10^{-6} m^2/s compared to 4.3×10^{-6} m^2/s), but possibly also due to other physical and chemical properties. During the period of infiltration, the maximum observed infiltration depths of both the diesel and crude oils were about 40 cm, and further infiltration would have proceeded at a slow rate. This may account for the findings of Geng and Lu (2003) who pointed out that petroleum pollutants are typically concentrated in the upper 80 cm of soil in the northwest region of China.

Diesel oil was able to penetrate to the base of the 45 cm deep soil core after about 65 min from the initiation of infiltration (Fig. 5). Once the diesel had begun to flow from the bottom of the soil core, we monitored its breakthrough process by collecting it in graduated containers. As shown in Fig. 5, the effluent velocity was slow at beginning (point a), and increased to a maximum within 13 min (point b), which remained constant until the inflow of oil into the soil core was stopped (point c), when the flow gradually ceased (point d). This breakthrough process is similar to that of solute transport (Shi *et al*., 2003; Yang and Ye, 1994).

It was also noted that the color of the effluent became

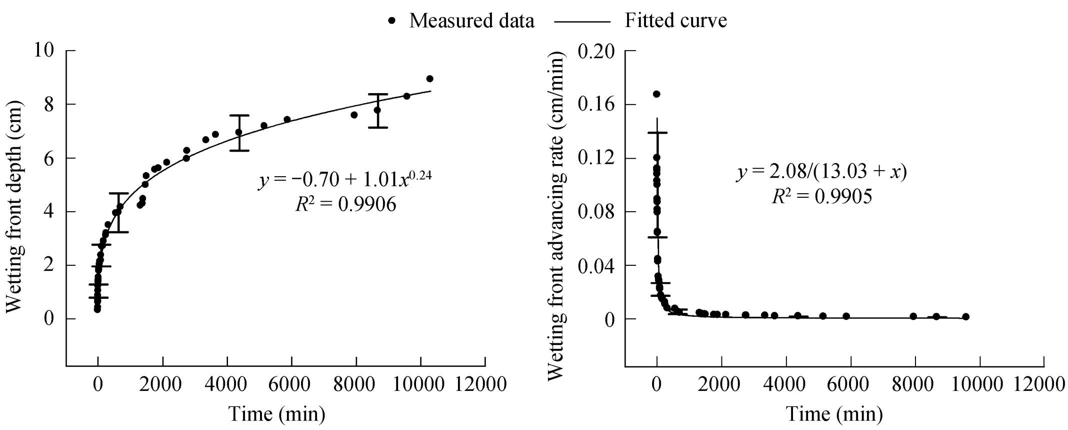

Fig. 3 Infiltration process of crude oil into undisturbed compacted loessal soil cores. Error bars represent standard deviation.

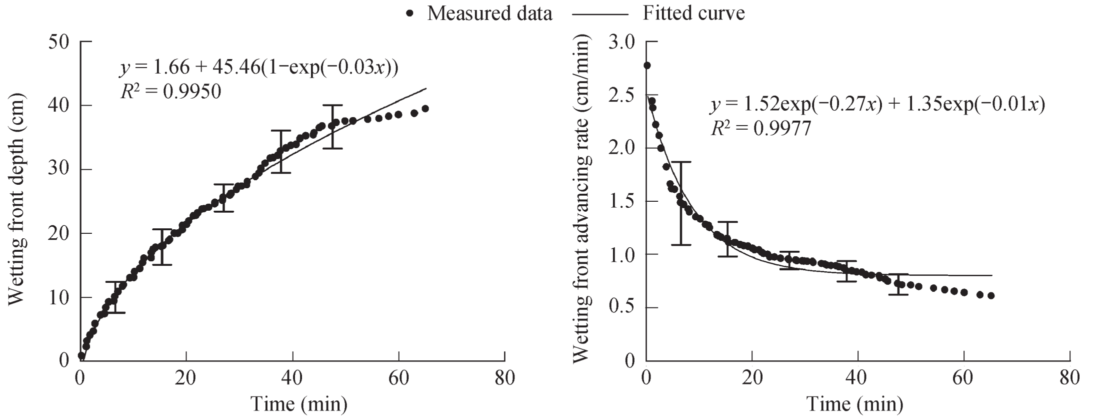

Fig. 4 Infiltration process of diesel oil into undisturbed loessal soil cores. Error bars represent standard deviation.

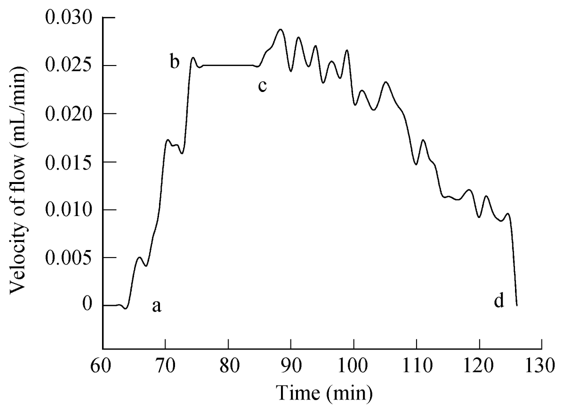

Fig. 5 Diesel effluent breakthrough (a) progress from the base of the large soil cores, to maximum flow rate (b), termination of inflow (c) and decrease to flow cessation (d).

darker with time suggesting that some changes in the composition of the diesel oil occurred during the infiltration process. However, investigating the exact nature of any such possible changes was beyond the scope of this study.

2.5 Variability of wetting front advancement for diesel and crude oils

Typically wetting front advancement within a column is reported as if it was measured only at one point without considering the variability of the advancement as a factor that may reflect the heterogeneity of the soil within columns and in turn did not considering how this heterogeneity may affect the flow of liquids. In this article, we have analyzed the variability of the wetting front advancement rate of crude and diesel oils at four points around the soil core in all the infiltration experiments (Fig. 1). Figure 6a illustrates the variability in the raw data obtained for one column during the diesel oil infiltration. The variability is due to the heterogeneity of the soil pore system that is particularly affected by the presence or the absence of macropores formed by plant roots, soil fauna, etc., whether such pores are continuous.

We examined the coefficient of variation for the wetting front depth at the four points as a function of time (Fig. 6b). As the wetting front advanced to lower depths with time, the coefficient of variation decreased. This occurs because the differences in wetting front depths that occur initially are proportionally large when compared to the magnitude of the depth. As the wetting front depth becomes greater, the differences between the depth values at the four points may remain approximately the same but are relatively small in comparison to the total depth of diesel oil penetration. This implies that soil heterogeneity, and thus the variability of the wetting front advancement, is a factor that is most significant in the early stages of infiltration.

We also looked at the variability of the wetting front advancement in the case of the infiltration of crude oil for both soil core sizes (Fig. 6c). Here it can be seen that the variability of wetting front advancement in large soil cores was generally greater than that in small soil cores, which can be attributed to the greater degree of soil heterogeneity within these cores due to the reasons discussed above.

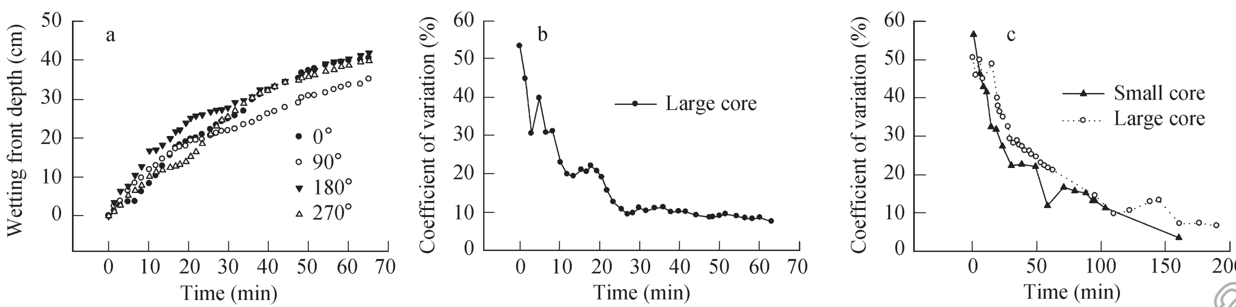

Fig. 6 Infiltration process curves of diesel (a, b) at large cores, and crude oils both in large and small cores (c).

3 Conclusions

The infiltration behavior of both crude and diesel oils, under a constant fluid head, into various undisturbed loessal soil cores was studied. Infiltration rates and wetting front advancement of the oils declined exponentially. Soil core size significantly affected the rate of crude oil wetting front advancement and the depth to which crude oil penetrated. Therefore, soil core size is a very important factor when monitoring the infiltration and movement of NAPLs. Larger soil cores are recommended for laboratory studies because they better represent the heterogeneity of the field soil pore system.

Soil compaction, with an associated higher bulk density, generally impeded the infiltration of crude oil to depth, although initial infiltration rates were higher. Compaction of the soil in areas susceptible to the risk of oil pollution may reduce the contamination of lower soil layers while providing time for clean up measures to be implemented. However, the risk of increasing the area over which the oil might spread should also be considered. As a major component of the crude oil that has a lower viscosity, the diesel oil wetting front advancement rate was higher than that of the crude oil, and its breakthrough process was similar to that associated with solute transport.

The variability of wetting front depth is that greater care should be exercised during the initial stages of infiltration than at the end of the process in obtaining a representative mean value by increasing the number of measuring locations. Generally, the variability of wetting front depth in large soil cores was greater than that in small soil cores.

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