

## Implication of hydraulic properties of bioremediated diesel-contaminated soil

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### Abstract

The hydraulic properties, such as hydraulic conductivity and water retention, of aged diesel-contaminated and bioremediated soils were examined and implications of the hydraulic properties for assessing bioremediation performance of soils were proposed. Bioremediation of diesel-contaminated soil was performed over 80 d using three treatments; (I) no nutrient added, column-packed soil, (II) nutrient added, column-packed soil, and (III) nutrient added, loosen soil. Diesel reduction in treatment I soil (control soil) was negligible while treatment III showed the greatest extent of diesel biodegradation. All treatments showed greatest rates of diesel biodegradation during the first 20 d, followed by a much retarded biodegradation rate in the remaining incubation period. Reduction of the degradation rate due to entrained diesel within inaccessible soil pores was hypothesized and tested by measuring the hydraulic properties of two column-packed soils (treatments I and II). The hydraulic conductivity of treatment II soil (nutrient added) was consistently above that of treatment I soil (no nutrient added) at pressure heads between 0 and 15 cm. In addition, the water retention of treatment II soil was greater at pressure heads <100 cm (equivalent to pore size of >30 μm), suggesting that biodegradative removal of hydrocarbons results in enhanced wettability of larger soil pores. However, water retention was not significantly different for control and biodegraded soils at pressure heads >100 cm, where smaller size soil pores were responsible for the water retention, indicating that diesel remained in smaller soil pores (e.g., <30 μm). Both incubation kinetics and hydraulic measurements suggest that hydrocarbons located in small pores with limited microbe accessibility may be recalcitrant to bioremediation.

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### 1. Introduction

Knowledge of the structure of soil pores is a key factor for refining our understanding of water flow/retention and the leaching potential of dissolved solutes in soil–water system. Water movement through soil is determined by complex interfacial reactions, i.e., attractive forces between bulk water and soil surfaces within soil matrices. Drainage occurs when the hydraulic energy (e.g., head) of a water

molecule exceeds the attractive forces exerted by soil matrices. Therefore, any factors affecting water affinity to the soil matrix can lead to a change in soil water retention. The literature is replete with descriptions of water retention and/or transport with varied soil conditions, such as compactness, degree of aggregates and particle/pore size distribution. However, little attempt have been performed to elucidate the effect of hydrocarbon contamination on the alternation of soil hydraulic nature so far. Few exceptions are Roy et al. (2003) and Cofield et al. (2007) who reported change of water repellency associated with petroleum contamination.

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Diesel fuel is a complex chemical mixture of crude oil intermediate distillates, composed of approximately 40% *n*-alkanes, 40% *iso*- and cycloalkanes, 20% aromatic hydrocarbons, and a few percent isoprenoids and sulfur, nitrogen and oxygenated compounds (Mackay et al., 1985). When spilled on soil, diesel compounds can migrate by diffusion and capillary forces, via either saturated or unsaturated flow, and to a less extent, by the dissolution to soil pore water (Cole, 1994; US EPA, 1995). Recent studies have shown that prolonged exposure to anthropogenic organic chemicals such as crude oil, petroleum or polycyclic aromatic hydrocarbon will lead to reduced affinity of soil surfaces toward water molecules (Li et al., 1997; Heyse et al., 2002; Quyum et al., 2002; Roy et al., 2003; Bachmann et al., 2007; Cofield et al., 2007).

The presence of diesel in soil can directly affect its water retention properties because of its water-repellent properties and indirectly due to its effect on the soil structure. Potential mechanisms contributing to the changes in the wettability of soil include: (1) surface coating of the solid–air interface, and (2) the clogging of soil macro and micro channels, which destroy soil aggregates (Heyse et al., 2002; Quyum et al., 2002). Several investigations (Dekker and Ritsema, 1994; Sawatsky and Li, 1997; Bachmann et al., 2007) have reported the negative effect of hydrocarbon contamination on the hydraulic characteristics of soil, and indicated that changes to the water retention characteristic of contaminated soil are only apparent at low soil wetness (e.g., matric suction greater than 1500 cm).

The efficacy of bioremediation for the removal petroleum hydrocarbon from contaminated soils is well documented (e.g., Cerniglia, 1992; Alexander, 1994; Hwang and Cutright, 2002). Increases in contaminant bioavailability (Lee et al., 2001; Okuda et al., 2007) and microbial metabolic activity (Namkoong et al., 2002; Saponaro et al., 2002; Riffaldi et al., 2006; Pena et al., 2007) have been reported by optimizing environmental conditions such as oxygen level, moisture, nutrients, and temperature in soil–hydrocarbon systems. However, most previous bioremediation studies were performed in either a slurry/disturbed soil system (Saponaro et al., 2002; Okuda et al., 2007) or artificially contaminated soils (Namkoong et al., 2002; Sarkar et al., 2005; Riffaldi et al., 2006; Serrano et al., 2006; Pena et al., 2007), where contact between the microorganisms and contaminated soils was unrealistically maximized. In contrast, actual subsurface soil systems contaminated with petroleum, such as due to fuel tank leakage, are likely to be rather compressed and thus reducing bioremediation performance. The bioavailability of hydrocarbon will also be influenced by the aging process, where the hydrocarbon may diffuse into soil micropores, making it unavailable for biodegradation (Hatzinger and Alexander, 1997).

Information on the impact of soil structure on the performance of bioremediation is currently scarce, and there has been no comparison between bioremediation effectiveness in column-packed versus loosened soils. The objective

of this study, therefore, was to characterize and compare the efficacy of bioremediation of column-packed and loosened diesel-contaminated soils. Following an 80 d incubation of diesel-contaminated soil, facilitated by the addition of nutrient, water flow and water retention properties of the bioremediated soil were measured using tension disc infiltrometer and pressure chamber methods, respectively. The hydraulic measurement data were inferred for apportioning residual diesel components after bioremediation.

## 2. Materials and methods

### 2.1. Aged diesel-contaminated soil

#### 2.1.1. Soil sample

Subsurface soil was collected at depths between 1.5 and 2.0 m from a former diesel fuel storage facility. Leakage from aboveground diesel and mineral oil storage tanks installed over forty years (late 1960s–early 2000s) were suspected as the cause of the contamination of the subsurface soils in this area. Bulk density of on-site subsurface soil, measured by a metal cylinder core (100 mm diameter and 0.5 m thick) was 1.23 g cm<sup>-3</sup>. The diesel concentration in the soil sample determined upon arrival at the laboratory was 4620 ± 210 mg kg<sup>-1</sup>. Selected physical and chemical properties were characterized for air-dried soil samples, and summarized in Table 1. The pH of a 1:5 (g ml<sup>-1</sup>) soil–solution ratio was 6.5. The soil texture measured after the removal of the organic constituents using the pipette method (Gee and Bauder, 1996) was sandy loam, composed of 53% sand, 18% silt and 29% clay. The total organic carbon was 1.3%, as determined using the Tyurin method (Nelson and Sommers, 1996). The available NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N (Mulvaney, 1996) were 1.19 and 0.85 mmol kg<sup>-1</sup>, respectively. The extractable-PO<sub>4</sub> was 0.22 mmol kg<sup>-1</sup>, as determined using the Bray method (Kuo, 1996).

#### 2.1.2. Determination of diesel concentration

The diesel concentration in the soils, initially and during predetermined incubation sampling times was determined

Table 1  
Selected properties of the diesel-contaminated soil used in this study

Property	Value
Sand (%)	52.5 (8) <sup>b</sup>
Silt (%)	18.2 (4)
Clay (%)	29.3 (4)
Particle density (g cm <sup>-3</sup> )	2.65
Bulk density (g cm <sup>-3</sup> )	1.23
NH <sub>4</sub> <sup>+</sup> - N (mmol kg <sup>-1</sup> )	0.85 (0.13)
NO <sub>3</sub> <sup>-</sup> -N (mmol kg <sup>-1</sup> )	1.19 (0.10)
PO <sub>4</sub> -P (mmol kg <sup>-1</sup> )	0.22 (0.02)
TOC <sup>a</sup> (%)	1.3 (0.1)
Diesel (mg kg <sup>-1</sup> )	4620 (210)

<sup>a</sup> Total organic carbon.

<sup>b</sup> Numbers in parenthesis are standard error for replicates.

by measuring a range of extractable diesel hydrocarbon compounds. Eight *n*-alkane compounds (even carbon-numbered from 10 to 24) were selected as representative of diesel hydrocarbons as a whole. Changes in the diesel concentrations were then estimated as the change in the total mass of these eight diesel hydrocarbons per unit of soil mass.

Extraction of residual diesel was carried out on about 5 g of soil mixed with 25 ml of dichloromethane. The mixtures were ultra-sonicated in a 1 s on/off pulse mode for 45 s (US EPA, 1990). The extract was then dehydrated by passing it through an anhydrous sodium sulfate packed glass column. A 10 ml aliquot was then transferred to a vial containing 0.4 g of silica gel and shaken vigorously to remove the impurities.

The concentration of diesel compounds in the purified extract was determined using a Shimadzu 17A gas chromatography system, equipped with flame ionization detection and a capillary column (30 cm × 0.53 mm, ID, 1.5 μm). N<sub>2</sub> gas was used as the carrier gas and 1 μl injections were split at a ratio of 1:20. The peak intensity was calibrated using external standards (Fluka Chemical Corp., Milwaukee, WI).

## 2.2. Bioremediation incubations

### 2.2.1. Bioremediation condition and incubation

Based on the assumptions of 233 g mol<sup>-1</sup> for the average molecular weight of diesel (Lee et al., 1992) and an equal number of even and odd carbon-numbered compounds, the initial C:N:P ratio of the diesel-contaminated soil was calculated as 2530:10:1 (w/w). Thus, 58.3 mmol NH<sub>4</sub>NO<sub>3</sub> and 11.65 mmol of KH<sub>2</sub>PO<sub>4</sub> was mixed well and homogenized before column packing with 1 kg of diesel-contaminated soil to produce a molar C:N:P ratio of 200:10:1 (w/w), which is suggested as theoretical balanced nutrient ratio for complete biodegradation of hydrocarbon from contaminated soils (Alexander, 1994).

Diesel-contaminated soil with and without adding nutrients was packed into 500 cm<sup>3</sup> stainless steel columns (8 cm height and 10 cm diameter) so that the bulk density of the soil was similar to that of *in situ* conditions. A glass frit was placed at the bottom of the column while the top of the column was open to the air. As a reference to observe the effect of column packing, 200 g of nutrient added loosened soil was transferred into and spread out inside a 1 l open-top glass bottle. The water content of the soil sample was maintained at approximately 50–60% of the water holding capacity by the addition of deionized water, as needed during incubation. Each treatment, (I) column-packed soil with no added nutrients, (II) column-packed soil with added nutrients and (III) unpacked (e.g., loosened) soil with added nutrients, was conducted in triplicate.

The incubations were conducted in the dark at 22 ± 3 °C. At the end of 5, 10, 20, 30, 50 and 80 d, 10 g of soil was collected from each column or the bottle for residual diesel analysis. After 80 d of incubation, soil cores

were taken from two columns for measurement of the hydraulic properties. All losses in diesel mass (i.e., initial mass–final mass) were attributed to microbial degradation.

## 2.3. Measurement of hydraulic properties of column soils

### 2.3.1. Hydraulic conductivity

Upon finishing an 80-d incubation experiment, the hydraulic conductivities of the soil of treatments I and II were measured using a tension disc infiltrometer (Soil Measurement Systems, Tucson, AZ). Six successive pressure heads (*h*) of 0, 1.0, 3.0, 5.0, 7.0, 9.0 and 15 cm were applied, and the steady-state water infiltration rates were measured. Due to the geometry of the instrument, the measurable pressure range was restricted to about 20 cm (lower than the reported air-entry value of the disc membrane). A 1.5 cm long thin-walled PVC ring (radius = 4.5 cm), with a sharp cutting edge at the base, was inserted straight onto the soil surface. To reduce irregularities and ensure hydraulic contact between the disc and underlying soil, a 1 cm-thick layer of coarse sand (mesh size of 20) was lightly compressed inside the PVC ring between the disc and soil surface. The measurements were triplicates. The steady-state infiltration data were interpreted using Wooding's analytical solution (Reynolds and Elrick, 1991), and the saturated hydraulic conductivity (*K<sub>s</sub>*) is estimated by fitting the measured *K(h)* data to Gardner's model (Gardner, 1958);

$$K(h) = K_s \exp(\alpha_G h) \quad (1)$$

where the fitting factor,  $\alpha_G$ , represents the slope of the *K(h)* function.

### 2.3.2. Water retention characteristics

Following measurement of the steady-state infiltration rate, soil cores were taken from the soil beneath the disc to determine the water retention properties using a pressure chamber. Soil cores (50 mm height and 72 mm diameter) were laid on a ceramic plate, with a bubbling pressure of 10 m water (≈100 kPa). The pressure chamber (Soil Measurement System, Tucson, AZ) was modified to obtain precise reading of the supply pressure head by adapting a 230 cm-water column. The soil cores were water-saturated from the base, and allowed to reach equilibrium. Stepwise pressure heads (*h*) of 7, 15, 20, 35, 50, 70, 100, 150, 333, 1000 and 1500 cm were applied. At each pressure potential, the pressure chamber was allowed to achieve pressure equilibration, and then the soil water content was determined gravitationally. The volume wetness ( $\theta(h)$ ) of the soil sample was calculated by multiplying the gravimetric water content by the soil bulk density. The fraction of the total pores occupied by water at a given pressure, therefore, was determined by dividing the volume wetness by the porosity.

A widely used water retention model, which performs well for most soils, is given by the van Genuchten model (1980):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha_V \cdot h)^n]^{1-1/n}} \quad (2)$$

where  $\theta(h)$  is the volume wetness of a soil ( $\text{cm}^3 \text{cm}^{-3}$ ) for a given pressure head,  $h$  (cm), and  $\theta_s$  and  $\theta_r$  correspond to the saturated and residual volume wetness, respectively. Two model parameters,  $\alpha_V$  and  $n$ , were estimated by fitting the soil water retention data collected for each equilibrium pressure to the model. The model is known to perform better for soils with S-shaped retention curve. Further details regarding the experimental settings of the infiltrometer and pressure chamber, as well as the parameter optimization procedure are reported elsewhere (Yoon et al., 2007).

### 3. Results and discussion

#### 3.1. Bioremediation of diesel-contaminated soil

The changes in the residual diesel concentration in the differently treated soils as a function of the incubation period are presented in Fig. 1. Generally, the loss of diesel mass in treatment III (nutrient added unpacked soil) was the greatest for each incubation period. After 80 d of incubation, 70% of the initial total diesel was removed from treatment III soil (nutrient added unpacked soil), while approximately 10% and 40% of the initial masses were removed from treatments II (nutrient added packed soil) and I (untreated packed soil), respectively. For treatments II and III, results were similar to those of a number of previous bioremediation studies performed with diesel-contaminated soils (De Jonge et al., 1997; Namkoong et al., 2002; Sarkar et al., 2005; Riffaldi et al., 2006; Okuda et al., 2007); that is, degradation rate was greatest during the first 20–30 d of incubation, followed by much retarded degradation rate over the following 50–60 d. This decrease in petroleum degradation rate has been frequently attributed to (1) decreased microbial metabolic activity as growth condition became less favorable due to nutrient or oxygen depletion or build up of toxic metabolic products, etc. or (2) the preferential degradation of more labile petroleum components early, leaving only a more refrac-

tory fraction remaining. In both treatments I and II (packed soil with and without additional nutrients), the degradation of diesel after 20 d was non-significant.

For many petroleum-contaminated subsurface soils, the bioavailability of residual petroleum components could be further reduced when (1) the rate of diesel release from the soil surface is slower or (2) the microorganism-hydrocarbon interfacial contact area is limited (Heyse et al., 2002; Okuda et al., 2007). Since petroleum is not a wetting fluid, most diesel would be found only in larger pore spaces, and the chances of diesel entering the soil micropores is generally quite low. Only in the case of aged diesel-contaminated soils can diesel occupy soil micropores due to diffusive movement displacing the resident water molecules during repeated dry-wet cycles (US EPA, 1995; Heyse et al., 2002). The diesel fraction entrained in the micropores will be less susceptible to microbial attack due to the limited microbial exoenzyme accessibility (Zimmerman et al., 2004).

It is commonly accepted that the degradation rate of individual  $n$ -alkane components in the aqueous/slurry phase decreases with increasing molecular weight (Cerniglia, 1992; Alexander, 1994; De Jonge et al., 1997; Prince et al., 2007). In this study, even after a period of apparent retarded biodegradation (e.g., 30–80 d), a significant fraction of low molecular weight  $n$ -alkane compounds (e.g., C10–C18) were still detected for treatment II soil, whereas these same light  $n$ -alkanes were found in negligible quantities from treatment III soil. The retarded disappearance of more easily biodegradable  $n$ -alkanes in column-packed soil (treatment II) relative to loosened soil (treatment III) suggests that the retarded biodegradation observed for treatment II was due to the soil compaction and compound inaccessibility rather than compound inertness. Rate of gas exchange through soil compacted soil (treatment II) will be much slower compared to loosened soils (treatment III). Therefore, in pore air of column packed soils, the amount of oxygen consumed and carbon dioxide produced by microbial respiration may not be sufficiently refurnished by gas exchange rate, which will be acting as a limiting factor for aerobic microbial degradation. In addition, enhanced chance to contact with atmospheric air in unpacked soils (treatment III) would likely facilitate the lower molecular weight  $n$ -alkanes loss by volatilization process.

#### 3.2. Hydraulic conductivity of diesel-contaminated and bioremediated soil

The hydraulic conductivity function,  $K(h)$ , determined for the two column-packed soils (treatments I and II) at pressure heads ( $h$ ) of 0.5, 2.0, 4.0, 6.0, 8.0 and 12 cm are presented in Fig. 2. The Gardner's exponential model fits for each soil are also shown in Fig. 2 and the values of  $K_s$  and  $\alpha_G$  are reported in Table 2. The goodness of the model fitting ( $r^2$ ) is 0.861 and 0.887, for control and bioremediated soil, respectively. Since little diesel degradation

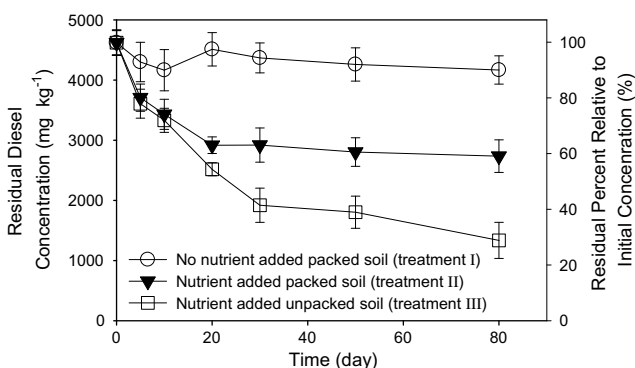


Fig. 1. Residual diesel concentration in soils for each treatment over the 80-d incubation.

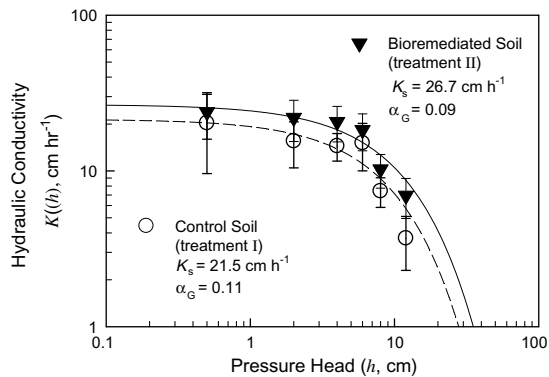


Fig. 2. The unsaturated hydraulic conductivities ( $K(h)$ ) of control (treatment I) and bioremediated (treatment II) soils. Data points are the average of triplicate experiments, with the standard error between measurements shown by the error bar. The solid and dashed lines are the Gardner's exponential model fit ( $r^2 > 0.90$ ) for bioremediated and control soils, respectively.

occurred without the addition of nutrients whereas bioremediation apparently occurred in treatment II over 80 d, the soils retrieved from treatments I and II will hereafter be referred to as control and bioremediated soil, respectively.

Under the given operating pressure head range, the  $K(h)$  of the bioremediated soil was consistently above that of control soil, with the  $K(h)$  function shape factors ( $\alpha_G$ ) being similar for the two soils. The  $K_s$  determined for bioremediated soil was 23% greater, suggesting the importance of diesel contamination in lowering the  $K(h)$  of soil. Other researchers have also shown that soil water transport/retention become less efficient in the presence of hydrocarbon compounds (Sawatsky and Li, 1997; Bachmann et al., 2007; Cofield et al., 2007). In general, water flow through a soil system depends on the wetting properties of different sized soil pores (Hillel, 1998; Bachmann et al., 2007). As noted earlier, during bioremediation in the packed soil of treatments II, the diesel fraction in larger pores was expected to be preferentially depleted by microorganism. Thus, the larger pores would become progressively more water-conductive during 80 d of incubation. In addition, within the pressure head range of <12 cm, the water flow in soils preferentially occurs through macro pores and the

flow-through contribution of micro pores would be minor. The enhanced hydraulic conductivity observed for soil bioremediated over 80 d is, therefore, likely due to the improved wetting properties of the macro pore spaces (Li et al., 1997) from which 40% of the initial diesel mass was lost during incubation.

### 3.3. Soil water characteristic curve

The soil water retention data measured for the control and bioremediated soils are presented in Fig. 3, along with their van Genuchten model (Eq. (2)) fits. The water retention parameters,  $\alpha_V$  and  $n$  (Table 2), were estimated by setting the  $\theta_s$  equal to the porosity, and the  $\theta_r$  to the average volume wetness measured at pressure heads of 1000 and 1500 cm. The goodness of model fitting ( $r^2$ ) is 0.966 and 0.995 for control and bioremediated soil, respectively. Also shown in Fig. 3, as a second  $x$ -axis, are the corresponding largest soil pore sizes that begin to drain under given pressure heads, as calculated using the capillary equation:

$$r(h) = \frac{2\gamma}{\rho_w g h} \quad (3)$$

where  $\gamma$  is the surface tension ( $\text{kg s}^{-2}$ ) of water,  $\rho_w$  the density of water ( $\text{kg m}^{-3}$ ) and  $g$  the gravitational acceleration ( $9.81 \text{ m s}^{-2}$ ).

Within the pressure head range from 7 to 100 cm, the amount of water retained by bioremediated soil was greater than that of the control soil. With increasing pressure head >100 cm, the difference in water retention of the two soils becomes negligible. These data suggest that the bioremediation process increased water retention within larger soil pores (>30  $\mu\text{m}$ ), likely by preferentially removing diesel from these locations. The fitting parameter,  $\alpha_V$  ( $\text{l}^{-1}$ ), was assumed to be related to the inverse of the air-entry value (van Genuchten, 1980). A smaller  $\alpha_V$  value for the bioremediated soil was indicative of a broader air-entry range. Another dimensionless parameter,  $n$ , the slope of water retention curve, is a measure of the width of the pore-size distribution (Carsel and Parrish, 1988). The larger  $n$  value for the fitted bioremediated soil data indicates the broader

Table 2  
Hydraulic parameters of control and bioremediated soils

Soils <sup>a</sup>	Hydraulic conductivity		Water retention			
	$K_s^b$ ( $\text{cm h}^{-1}$ )	$\alpha_G^c$ ( $\text{cm}^{-1}$ )	$\theta_s^d$ ( $\text{cm}^3 \text{ cm}^{-3}$ )	$\theta_r^e$ ( $\text{cm}^3 \text{ cm}^{-3}$ )	$\alpha_V^f$ ( $\text{cm}^{-1}$ )	$n^g$
Control soil	$21.5 \pm 2.3$	$0.11 \pm 0.03$	0.502	0.170	0.49	1.81
Bioremediated soil	$26.7 \pm 2.3$	$0.09 \pm 0.02$	0.515	0.184	0.22	2.86

<sup>a</sup> Control soil and bioremediated soil are retrieved from treatments I and II, respectively.

<sup>b</sup> Saturated hydraulic conductivity.

<sup>c</sup> Gardner's model (Eq. (1)) fitting parameter; the slope of  $K(h)$  function.

<sup>d</sup> Saturated volume wetness.

<sup>e</sup> Residual volume wetness which was estimated as the average value of data measured at pressure heads of 1000 and 1500 cm.

<sup>f</sup> van Genuchten model (Eq. (2)) fitting parameters; the slope of  $\theta(h)$  function which is related to pore size distribution index.

<sup>g</sup> Dimensionless parameter.

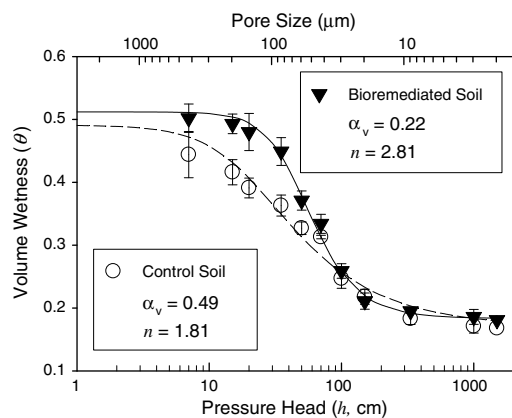


Fig. 3. Soil moisture characteristics curves of control (treatment I) and bioremediated (treatment II) soils. Measured data were fitted using Eq. (2), and are shown as solid and dashed lines for treatments I and II, respectively.

range of soil pore sizes that had become water-conductive following bioremediation.

The shape of the water retention curve depends on the capillarity of the soil pores and the specific area of the soil surface. The former is more important with lower suction, and the contribution of the latter increases significantly with increasing suction (Hillel, 1998). Note that the equilibrium soil wetness ( $\theta(h)$ ) function in Fig. 3 was obtained using a desorption method; that is, stepwise suctions were applied to an initially saturated soil to gradually drain the wet soils. Therefore, the initial water drainage from saturated soil takes place from water-filled macropores that cannot retain water against the suction applied. In the control soil (open circle in Fig. 3), hydrophobic diesel components occupying the larger soil pores will greatly reduce the affinity (e.g., capillarity) of water molecules for the surfaces of soil pores (Roy et al., 2003); thus, lowering the amount of water retention for a given range of similar pressure heads. Similar inferences were made by Cofield et al. (2007), who measured soil hydrophobicity changes during phytoremediation.

With increasing pressure head, the water retention will be less influenced by the macro-sized soil pores and more by the specific area of micropores. The slower degradation rate after 20 d of incubation for (Fig. 1; treatment II) was ascribed to (1) the likelihood of a recalcitrant diesel fraction entrained within soil micropores or (2) lack of oxygen as gas exchange between pore air and atmospheric air is limited in column packed soil. In Fig. 3, the reduction in the difference in the  $K(h)$  values between the two soils with pressure heads  $>100$  cm indicates that flow through the smaller pores  $<30$   $\mu\text{m}$  is both low and was unaffected by biodegradation possibly providing evidence for the presence of micro pores filled with diesel components for both the bioremediated and control soils.

The slope of the soil water retention curve, ( $C(h) = d\theta/dh$ ), known as the specific water capacity, is shown in Fig. 4 for pressure heads ranging between 0 and 200 cm.

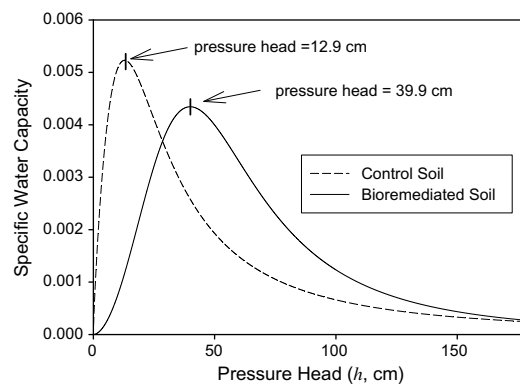


Fig. 4. Specific water capacities of control and bioremediated soils (treatments I and II, respectively).

The difference between the two curves for pressure heads  $>180$  cm is within 10% of each other and is not shown here. The relative maximum  $C(h)$  values, the inflection point of the  $K(h)$  function, are 12.9 and 39.9 cm, for control and bioremediated soils, respectively, and the two curves meet at a pressure head of 28.6 cm. Both soils manifested no definite range of pressure heads where  $C(h)$  remained zero near water saturation; that is, there was no clear air entry range. However, as an estimation, it can be presumed that the air entry point would be greater for a soil exhibiting a greater peak  $C(h)$  value, indicating that the removal of diesel would cause a greater number of air entry points within bioremediated soil.

#### 4. Summary and conclusions

The comparison of the hydraulic properties of aged diesel-contaminated and bioremediated soils has provided insight toward understanding the distribution of residual diesel components and their effect on water retention/flow characteristics of soil. In this study, bioremediation was facilitated by adjusting nutrients (e.g., adding N and P) for column packed soil and the effect of fertilization-induced bioremediation on soil hydraulic properties was investigated. The direct effect of fertilization on soil hydraulic properties was assumed negligible and was not considered to interpret experimental result. The wettability of bioremediated soil was increased as a result of the removal of diesel, which was proved by enhanced hydraulic properties. After 40% of diesel components were removed, hydraulic conductivity was enhanced by approximately  $50 \pm 20\%$  under the pressure heads investigated (e.g.,  $<12$  cm). However, the impact of diesel on the water retention characteristics varied with pressure heads. In the pressure head range between 7 and 100 cm, the bioremediated soil held more water, suggesting increased affinity of water molecules for the soil matrices following bioremediation. Based on capillary equation, the soil water is retained mostly in the soil macropores within the pressure head range stated above; thus, the corresponding size of soil

pores (e.g., >30  $\mu\text{m}$ ) are expected to play the greatest role in improving the water retention properties. The difference in the water retention properties with pressure heads >100 cm was not discernible. At the greater pressure head range, smaller pores (e.g., <30  $\mu\text{m}$ ) are responsible for the water flow. Thus, bioremediation process under given experimental conditions did not improve the water wettability of these smaller soil pores.

Direct experimental measurement revealing the location of the diesel components (e.g., *n*-alkanes) within soil pores was not attempted in the present study. However, two distinct rates of biodegradation for the packed soil and loosened soil, as well as the observed change in hydraulic properties of the soils following biodegradation suffice to presume that the preferred initial diesel degradation is driven by labile diesel present in bio-accessible pores and diesel fraction entrained in the micro soil pores are less labile. In addition, lack of oxygen and limited gas exchange, both of which are characteristics of compacted soils, would be another possible explanation responsible for slower bioremediation for column packed soils. The performance and rate of *in situ* bioremediation of diesel-contaminated subsurface soil may, therefore, be enhanced by increasing the chance of microbial access and facilitating oxygen supply to diesel components entrained in non-accessible pore spaces.

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### References

- Alexander, M., 1994. Biodegradation and Bioremediation. Academic Press, New York, NY.
- Bachmann, J., Deurer, M., Arye, G., 2007. Modeling water movement in heterogeneous water-repellent soil: I. Development of a contact angle-dependent water-retention model. *Vadose Zone J.* 6, 436–445.
- Carsel, R.F., Parrish, R.S., 1988. Developing joint probability distribution of soil water retention characteristics. *Water Resour. Res.* 24, 755–769.
- Cerniglia, C.E., 1992. Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation* 3, 351–368.
- Cofield, N., Banks, M.K., Schwab, A.P., 2007. Evaluation of hydrophobicity in PAH-contaminated soils during phytoremediation. *Environ. Pollut.* 145, 60–67.
- Cole, G.M., 1994. Assessment and Remediation of Petroleum Contaminated Sites. CRC Press, Inc., Boca Raton, FL.
- De Jonge, H., Freijer, J.L., Verstraten, J.M., Westerveld, J., van der Wielen, F.W.M., 1997. Relation between bioavailability and fuel oil hydrocarbon composition in contaminated soils. *Environ. Sci. Technol.* 31, 771–775.
- Dekker, L.W., Ritsema, C.J., 1994. How water moves in a water repellent sandy soil. I. Potential and actual water repellency. *Water Resour. Res.* 30, 2507–2517.
- Gardner, W.R., 1958. Some steady-state solutions of the unsaturated moisture flow equation with application to evaporation from a water table. *Soil Sci.* 85, 228–232.
- Gee, G.W., Bauder, J.W., 1996. Particle-size analysis. In: Klute, A. (Ed.), *Method of Soil Analysis: Part I-Physical and Mineralogical Methods*. Amer. Soc. Agron., Madison, WI, USA, pp. 384–411.
- Hatzinger, A.W., Alexander, M., 1997. Biodegradation of organic compounds sequestered in organic solid or in nanopores within silica particles. *Environ. Toxicol. Chem.* 16, 2215–2221.
- Heyse, E., Augustijn, D., Rao, P.S.C., Delfino, J.J., 2002. Non-aqueous phase liquid dissolution and soil organic matter sorption in porous media: Review of system similarities. *Crit. Rev. Environ. Sci. Technol.* 32, 337–397.
- Hillel, D., 1998. *Environmental Soil Physics*. Academic Press, New York, NY.
- Hwang, S., Cutright, T.J., 2002. Biodegradability of aged pyrene and phenanthrene in a natural soil. *Chemosphere* 47, 891–899.
- Kuo, S., 1996. Phosphorus. In: Sparks, D.L. (Ed.), *Method of Soil Analysis: Part III-Chemical Methods*. Amer. Soc. Agron., Madison, WI, USA, pp. 869–919.
- Lee, L.S., Hagwall, M., Delfino, J.J., Rao, P.S.C., 1992. Partitioning of polycyclic aromatic hydrocarbons from diesel fuel into water. *Environ. Sci. Technol.* 26, 2104–2110.
- Lee, P.-H., Ong, S.K., Golchin, J., Lelson, G.L., 2001. Use of solvents to enhance PAH biodegradation of coal tar-contaminated soils. *Water Res.* 35, 3941–3949.
- Li, X., Feng, Y., Sawatsky, N., 1997. Importance of soil–water relations in assessing the endpoint of bioremediated soils. *Plant Soil* 192, 219–226.
- Mackay, D., Shiu, W.Y., Chau, A., Southwood, J., Johnson, C.I., 1985. Environmental fate of diesel fuel spills on land. Reported for Association of American Railroads. Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada.
- Mulvaney, R.L., 1996. Nitrogen-inorganic forms. In: Sparks, D.L. (Ed.), *Method of Soil Analysis: Part III-Chemical Methods*. Amer. Soc. Agron., Madison, WI, USA, pp. 1123–1184.
- Namkoong, W., Hwang, E.-W., Park, J.-S., Choi, J.-W., 2002. Bioremediation of diesel-contaminated soil with composting. *Environ. Pollut.* 119, 23–31.
- Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Sparks, D.L. (Ed.), *Method of Soil Analysis: Part III-Chemical Methods*. Amer. Soc. Agron., Madison, WI, USA, pp. 961–1010.
- Okuda, T., Alcantara-Carduno, M.E., Suzuki, M., Matsui, C., Kose, T., Nishijima, W., Okada, M., 2007. Enhancement of biodegradation of oil adsorbed on fine soils in a bioslurry reactor. *Chemosphere* 68, 281–286.
- Pena, W., Trasar-Cepeda, C., Gil-Sotres, F., Leiros, M.C., 2007. Modification of the degradative capacity of a soil artificially contaminated with diesel. *Chemosphere* 67, 1057–1063.
- Prince, R.C., Parkerton, T.F., Lee, C., 2007. The primary aerobic biodegradation of gasoline hydrocarbons. *Environ. Sci. Technol.* 41, 3316–3321.
- Quyum, A., Achari, G., Goodman, R.H., 2002. Effect of wetting and drying and dilution on moisture migration through oil contaminated hydrophobic soils. *Sci. Total Environ.* 296, 77–87.
- Reynolds, W.D., Elrick, D.E., 1991. Determination of hydraulic conductivity using a tension infiltrometer. *Soil Sci. Soc. Am. J.* 55, 633–639.
- Riffaldi, R., Levi-Minzi, R., Cardelli, R., Palumbo, S., Saviozzi, A., 2006. Soil biological activity in monitoring bioremediation of diesel oil-contaminated soil. *Water Air Soil Pollut.* 170, 3–15.
- Roy, J.L., McGill, W.B., Lowen, H.A., Johnson, R.L., 2003. Relationship between water repellency and native and petroleum-derived organic carbon in soils. *J. Environ. Qual.* 32, 583–590.
- Saponaro, S., Bonomo, L., Petruzzelli, G., Romele, L., Barbaferi, M., 2002. Polycyclic aromatic hydrocarbons slurry phase bioremediation of a manufactured gas plant site aged soil. *Water Air Soil Pollut.* 135, 219–236.
- Sarkar, D., Ferguson, M., Datta, R., Birnbaum, S., 2005. Bioremediation of petroleum hydrocarbons in contaminated soils: comparison of

- biosolids addition, carbon supplementation, and monitored natural attenuation. *Environ. Pollut.* 136, 195–198.
- Sawatsky, N., Li, X., 1997. Importance of soil–water relations in assessing the endpoint of bioremediated soils. *Plant Soil* 192, 227–236.
- Serrano, A., Gallego, M., Gonzalez, J.L., 2006. Assessment of natural attenuation of volatile aromatic hydrocarbons in agricultural soil contaminated with diesel fuel. *Environ. Pollut.* 144, 203–209.
- US EPA, 1990. Method 3550A, Ultrasonic Extraction. US Environmental Protection Agency, Washington, DC.
- US EPA, 1995. Light non-aqueous phase liquids, Ground Water Issue, EPA/540/S-95/500, Office of Solid Waste and Emergency Response, Office of Research and Development, US Environmental Protection Agency, Washington, DC.
- van Genuchten, M.Th., 1980. A closed form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.
- Yoon, Y., Kim, J.-G., Hyun, S., 2007. Estimating soil water retention in a selected range of soil pores using tension disc infiltrometer data. *Soil Till. Res.* 97, 107–116.
- Zimmerman, A.R., Chorover, J., Goyne, K.W., Brantley, S.L., 2004. Protection of mesopore-adsorbed organic matter from enzymatic degradation. *Environ. Sci. Technol.* 38, 4542–4548.