

## **Significance of Residual Hydrocarbon in Sandy Soils with and without Hysteresis Effects**

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*Abstract.* Soil and groundwater contamination due to accidental spills of hydrocarbons represents a serious environmental problem that threatens groundwater. The presence of such product as a non-aqueous phase liquid near the water table, or as a trapped residual in the porous media, creates a continuous contamination source that keeps contributing to groundwater contamination for a very long time. This paper gives a quick estimation of the residual hydrocarbon in porous media based on simple to collect data, including free product thickness in monitoring wells and fluid and porous media properties, along with the influence of hysteresis on this estimation. Such procedure can be used to come up with a quick quantitative estimation of the components of the spill which is valuable information that can be used in the early stages of remediation planning of contaminated aquifers.

Theoretical estimates of the volume of the spill were made using the hydraulic properties of the soil and assuming a quasi-hydrostatic equilibrium distribution for the hydrocarbon and the water. The hydrocarbon spill volume is divided into two portions: a. recoverable hydrocarbon which is the part of the hydrocarbon under positive pressure that will flow into a monitoring well and b. residual hydrocarbon, which is the portion of the hydrocarbon in the soil and is under negative pressure. Calculations were carried out to determine the relative amounts of the residual hydrocarbon in sandy soils. The effects of hysteresis on the estimated residual hydrocarbon were also evaluated and found to be significant. Similar to published experimental results on well graded and uniform sandy soils, the model predicted that a significant portion of the spill will exist as a residual phase. This portion could reach 100% of the original spill for small spills, decreasing continuously as the total spill volume increases.

*Keywords:* Groundwater contamination; LNAPLS; Spill; Remediation.

## 1. Introduction

Groundwater is one of the most important natural resources on earth, if not the most important, since in many regions around the globe people rely on it as their main source of potable water. Therefore, special measures and plans must be implemented in order to preserve its quality. A prominent source of groundwater contamination is that resulting from sources designed to store, transport, and dispose hazardous substances. Such sources include pipelines, above ground storage tanks (AGSTs) and under ground storage tanks (UGSTs). UGSTs are often used to store light non-aqueous phase liquids (LNAPLs) like common fuels and other organic products. Such chemicals are frequently stored at farms, industrial facilities and mostly at gas stations. Each gas station has at least one large UGST. An UGST may leak- through holes in the tank itself or through the associated piping. Such tanks are usually made from steel rendering them susceptible to corrosion. Once a leak starts, the LNAPL will percolate through the unsaturated zone of the soil and, depending on the amount of the spill, it may be held by capillary forces at minimum saturation values as an immobile phase. If the spilled amount is high the LNAPL will continue to percolate downward until it reaches the water table where it will spread laterally forming what can be described as an LNAPL pool above the water table. A small part of the LNAPL will dissolve in water and a dissolved contaminant plume will be created which will spread in the general direction of the regional groundwater flow degrading the groundwater quality. Since these processes take place underground, it is rare that such problem is discovered early.

Precise estimation of the volume spilled is very important to evaluate the severity of the contamination problem at hand and to properly plan for groundwater and aquifer remediation. A leak or spill may be indicated by the presence of a free hydrocarbon product in a monitoring well. The thickness of the free product in the well is the easiest parameter to measure and use to estimate the amount spilled<sup>[1]</sup>. The absence of a free product in monitoring wells may indicate that almost the entire amount of hydrocarbon is in the residual phase. Although this phase is essentially immobile, it represents a continuous threat to groundwater quality because it acts as a continuous source of pollution by dissolving part of its original mass in recharge water leading to a continuous supply of dissolved contaminant into the underlying aquifer.

In this study the two components of a hydrocarbon spill volume, the residual phase and the mobile phase are estimated using relatively easy to collect data like soil hydraulic characteristics, which are used to obtain the hydrocarbon saturation along the soil profile, and the free product thickness in monitoring wells. This allows the examination of the significance of the residual phase of a spill. The influence of hysteresis on the relation between the

free product thickness and the computed hydrocarbon spill components is also examined.

## 2. Hydrocarbon Distribution Profile in Soils

An accidental spill of a light hydrocarbon will lead to the creation of a zone in the soil void space that will generally contain three “fluids”: water, oil and air. The distribution of these fluids within the void space depends on factors related to the soil as well as factors related to the fluids. The most important properties of the fluids include surface tension and relative density, while the soil hydraulic parameters of importance include size and distribution of soil grains. More details on how these factors affect the fluids distribution are given by Corey <sup>[2]</sup>. Two well known equations, namely the Brooks-Corey <sup>[3]</sup> and the van Genuchten equation <sup>[4]</sup> are frequently used to describe the distribution of two heterogeneous fluids (air and water) in a porous medium.

The Brooks-Corey equation in terms of the wetting fluid content is<sup>[2]</sup>:

$$\theta = \theta_r + (\Phi - \theta_r) (h / h_d)^{-\lambda} \quad (1)$$

Where:

- $\theta$  Wetting fluid (water) content,
- $\theta_r$  Residual water content,
- $\Phi$  Porosity,
- w Subscript referring to wetting fluid,
- nw Subscript referring to non-wetting fluid,
- h Capillary head =  $P_c / (\rho_w - \rho_{nw}) g$
- $P_c$  Capillary pressure =  $P_{nw} - P_w$
- $P_{nw}$  Pressure of non-wetting fluid,
- $P_w$  Pressure of wetting fluid,
- g acceleration due to gravity,
- $h_d$  Displacement pressure head =  $P_d / (\rho_w - \rho_{nw}) g$
- $P_d$  Minimum capillary pressure needed for both wetting and non-wetting fluids to coexist in the porous media,
- $\Lambda$  Pore size distribution index (Brooks-Corey fitting parameter).

The van Genuchten equation is written as<sup>[4]</sup> :

$$\theta = \theta_r + (\Phi - \theta_r) (1 + (\alpha h_c)^n)^{-m} \quad (2)$$

Where:

- $\alpha, n$  van Genuchten fitting parameters
- $m = 1 - 1/n$

Parker *et al.* [5] suggested extending the two fluid parameters  $h_d$  and  $\alpha$ , for say air water system, by a scaling process to come up with the proper parameters that govern the more complex three-phase system using:

$$h_d / \sigma = h_d^{ao} / \sigma_{ao} = h_d^{ow} / \sigma_{ow} \quad (3)$$

$$\alpha \sigma = \alpha_{ao} \sigma_{ao} = \alpha_{ow} \sigma_{ow} \quad (4)$$

Where:

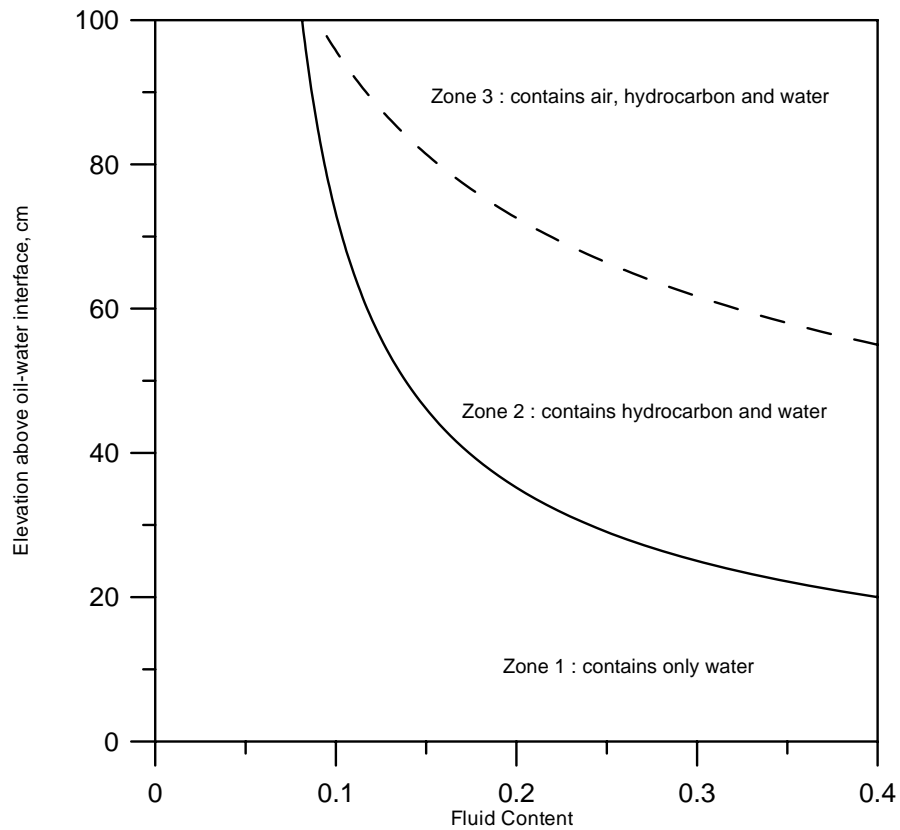
- $\Sigma$  Interfacial tension
- ao Refers to the parameters for air/oil system, and
- ow Refers to the parameters for oil/water system.

A typical distribution of a three-phase system in a porous medium is shown in Fig. 1. This figure gives the content of each fluid as a function of the elevation above the bottom of the oil-water interface in a monitoring well under static equilibrium.

It can be concluded by examining the fluids distribution in this figure that there are at least three different zones. Starting from the bottom of the oil-water interface in a monitoring well and moving up, in the first zone the void space is occupied by water only, the second zone contains both oil and water and the third zone contains all the three fluids. The figure also indicates that the water content decreases as we move up while the hydrocarbon content starts at zero then increases to reach a maximum value then starts to decrease.

Employing the assumptions of hydrostatic or quasi-hydrostatic conditions and using the scaled three-phase parameters Farr *et al.* [6] and Lenhard and Parker [7] developed an analytical model to estimate the volume of spilled hydrocarbon per unit area in homogeneous soils by integrating the hydrocarbon content over the depth of the contaminated medium.

Bashir [8], Al-Suwaiyan and Bashir [9] and Al-Suwaiyan *et al.* [10] extended this model to layered soils by calculating the individual spill volume for each layer using its own hydraulic properties then adding the contribution from each layer to come up with the total estimated spill volume for the layered system. They also presented experimental results quantifying the amount of recoverable hydrocarbon for two types of sandy soils. The hydraulic properties for the soils considered in their study were generated using the soil size distribution data and employing the procedure given by Mishra *et al.* [11].



**Fig. 1. Fluids distribution in a vertical soil profile.**

Mariner *et al.* <sup>[12]</sup> presented an algorithm that can quantify hydrocarbon saturation and composition in soil sample using typical soil chemical analysis. Such algorithm can be used to obtain the hydrocarbon content at various locations which in turn can be integrated to come up with an estimate for the total hydrocarbon volume. However, this model requires extensive data, given that chemical analysis of the soil at various locations to be accurate.

### **3. Recoverable Versus Residual Hydrocarbon**

The value of the gage pressure of the hydrocarbon will determine whether it will flow into a screened well and therefore is mobile (recoverable) or will not flow into the well and remains as residual. Examining the fluids distribution in a fully screened well will allow us to determine a horizontal plane of zero hydrocarbon gage pressure. Above this plane the zone of residual hydrocarbon is encountered where the hydrocarbon will be under negative pressure. This portion of the hydrocarbon will remain in the soil as a residual

phase and cannot be pumped out due to its negative pressure. It will act as a continuous source of contamination since a small part of it will be continuously dissolved in any recharge water. The zone of mobile hydrocarbon will exist below the plane of zero hydrocarbon gage pressure. It is expected that the zone of residual hydrocarbon would dominate for small spills or for large spills distributed over large areas.

A simple computer algorithm, which utilizes the above concepts, was developed to compute the relative importance of the residual versus mobile hydrocarbon phases. The first task is to locate the plane that separates the mobile and the residual hydrocarbon (level at which the hydrocarbon gage pressure is zero). This should coincide with the free product level in a fully screened monitoring well. The next task is to locate the lowest level in the soil which contains hydrocarbon. Since the displacement pressure head is defined as the minimum value of capillary head at which both water and oil coexist in the porous media, it may be concluded that the capillary head between the hydrocarbon and water at this location must be equal to the displacement pressure head for these two fluids in that particular soil.

Once these critical positions are determined, the hydrocarbon content in a vertical profile can be obtained by taking the difference between the total liquid content and the water content which results in a distribution similar to the one shown in Fig. 2. This figure shows that the hydrocarbon content, which starts at zero at the lower end, increases as we move up continuing to increase as we leave the mobile zone and enter residual zone taking a maximum value at a level above the zero gage pressure level by a distance equal to the displacement pressure head for air into the hydrocarbon in the particular soil. The hydrocarbon content starts to drop rapidly reaching a negligible value quickly. The amounts of residual and mobile hydrocarbon are determined by integrating the obtained distribution curve.

This algorithm was used to quantify the relative residual hydrocarbon for a gasoline spill in two types of soils. The soils used in the modeling study were uniform sand, and well graded sand. The relevant hydraulic parameters for the soil types are given in Table 1. It is believed that most of natural sandy soils will exhibit similar relation between the relative residual phase and the amount of spill as the relations that govern these variables in the soils considered in this study. Experimental quantification for crude oil spills in soil 1 (uniform sand) and soil 2 (well graded sand) is available from a previous study<sup>[8]</sup>. The model predictions of the relative amount of residual hydrocarbon for various amounts of spills, which is reflected by the free product thickness in monitoring wells, are shown in Fig. 3. This figure shows clearly that most of the spill will be in the residual phase for small spills in both soil types. As the quantity of the spill volume

increases, the relative residual decreases with a decreasing rate and yet it remains significant. The relative residual is higher in uniform sand than in well

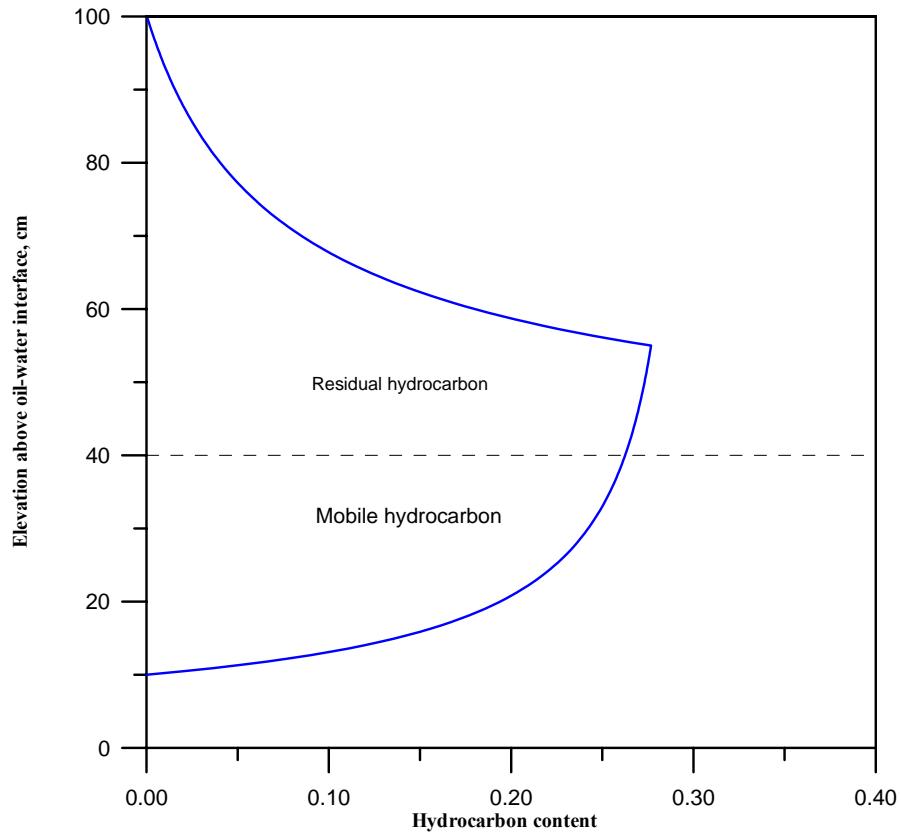


Fig. 2 . Hydrocarbon content in a vertical soil profile.

Table 1. Hydraulic properties of soils.

Soil type	Porosity ( $\Phi$ )	Residual water content ( $\theta_r$ )	Displacement pressure head (cm H <sub>2</sub> O) ( $h_d$ )	Pore size distribution index ( $\lambda$ )
uniform sand	0.32	0.06	12.6	2.0
well graded sand	0.26	0.09	6.66	1.27

graded sand which is a reflection of the significance of the capillary forces for media with smaller pores. Bashir <sup>[8]</sup> experiments indicated that the relative residuals were 60 % for a free product thickness of 50 cm and 52 % for a free product of 70 cm for soil 1 and soil 2 respectively. The corresponding model predictions for these soils at the given free product thickness are 40 % for soil 1 and 25 % for soil 2, indicating that the model underestimates the amount of the residual phase hydrocarbon. This can be attributed to the fact that the flow of the free product into a collection well declines quickly as a result of the high reduction in the non-wetting fluid conductivity when the saturation of the non-wetting fluid becomes small.

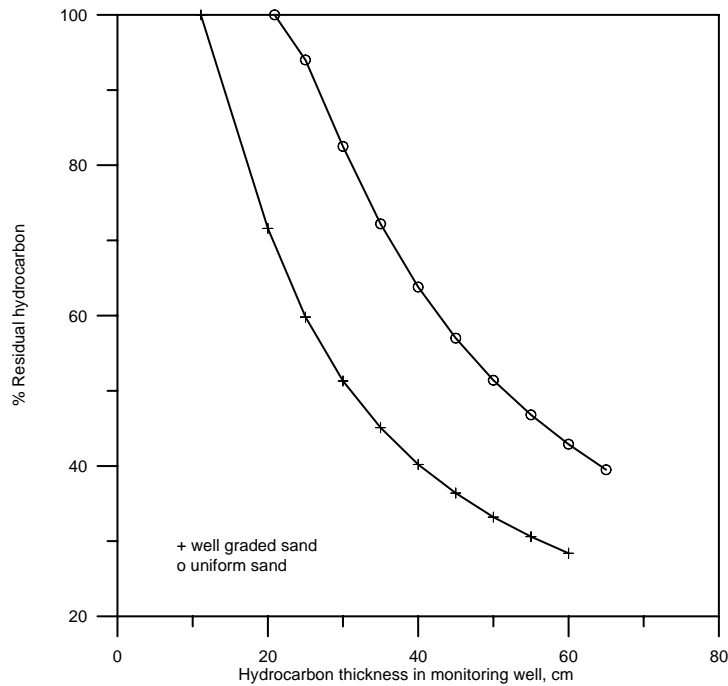


Fig. 3 . Residual hydrocarbon as percent of total spill for different product.

#### 4. Hysteresis Effects

Most soils exhibit a non-unique relation between the capillary pressure and the fluid content, which is called hysteresis. A typical relation between the two is shown in Fig. 4 which shows the main hysteresis loops. The wetting and drying curves represent an envelope for scanning curves. The curve of Fig. 4 ignores entrapment which results in full saturation at zero capillary pressure.

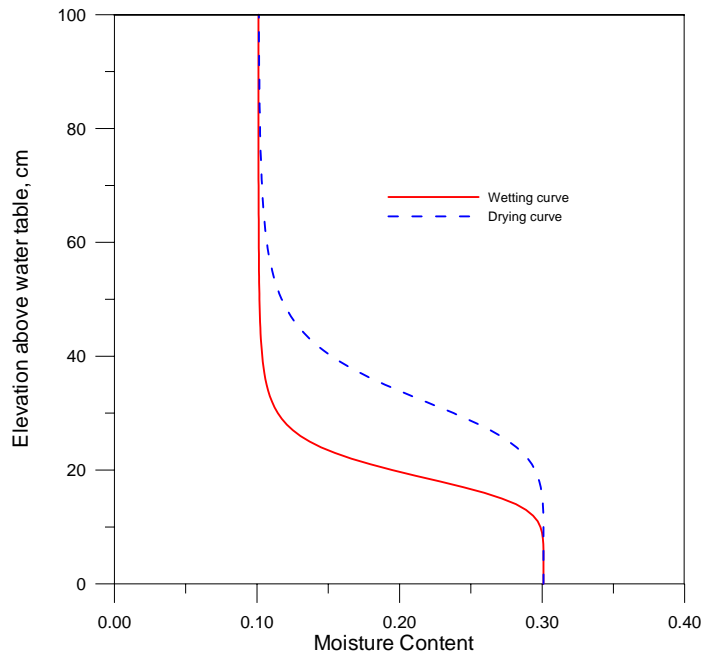


To study the influence of hysteresis on the estimation of the residual hydrocarbon in porous media, simulations for the fluids distribution and calculations for the residual hydrocarbon were carried out using the hydraulic properties for two types of sand: Dune Sand and Sand II whose hydraulic properties were reported by Kool and Parker <sup>[13]</sup>. In their paper, they reported the constrained parameters, which were generated by fitting experimental data to the van Genuchten model for the main wetting and main drying cycles. The data relevant to this study are given in Table 2. The main hysteresis curves in a two phase system for the two soils are given in Fig. 4 and 5. These curves were scaled up to generate the three phase system (air/oil/water), then the distributions of the fluids in soil columns were generated under both wetting and drying cycles.

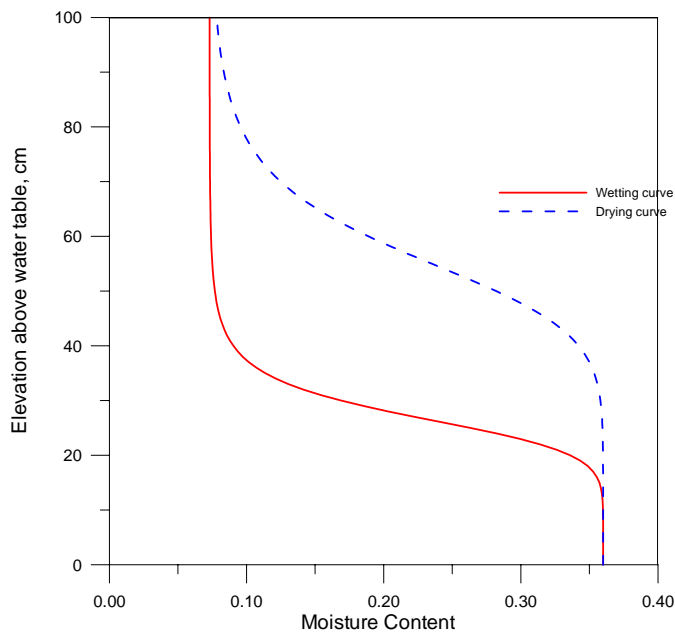
**Table 2 . Hydraulic properties for Kool and Parker soils.**

Soil type	$\Phi$	$\theta_r$	$\alpha$ drying	$\alpha$ wetting	n
Dune Sand	0.301	0.101	0.0306	0.0527	6.779
Sand II	0.360	0.073	0.0180	0.0375	7.826

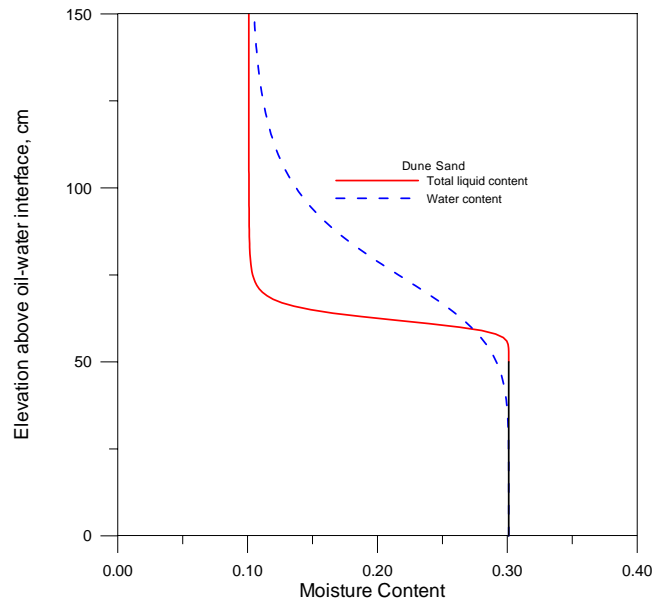
The drying cycle best describes conditions where the water table is dropping while wetting applies for situations in which a rising water table is met. The fluids distributions for the two soils for both cycles are presented in Fig. 6 to 9. Examination of these figures shows that the fluids distribution is highly influenced by hysteresis. The effect of hysteresis on the relative hydrocarbon residual is shown in Fig. 10 for Dune Sand in Fig. 11 for Sand II. From both figures, it can be concluded that hysteresis has a significant influence especially at low to high spills. Examination of these figures also indicates that predictions based on the main wetting curve gives conservative estimate for the relative hydrocarbon residual compared to predictions using the main drying cycles.



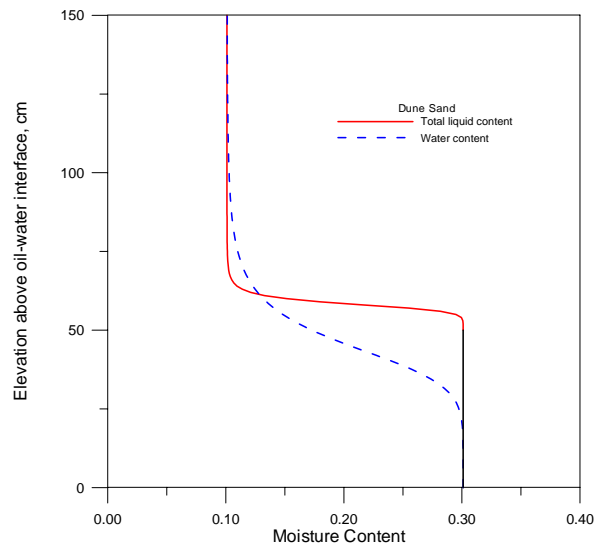
**Fig. 4. Main hysteresis loops for Dune Sand.**



**Fig. 5 . Main hysteresis loops for Sand II.**



**Fig. 6 . Fluids distribution along the vertical in Dune Sand column (drying cycle).**



**Fig. 7 . Fluids distribution along the vertical in Dune Sand column (wetting cycle).**

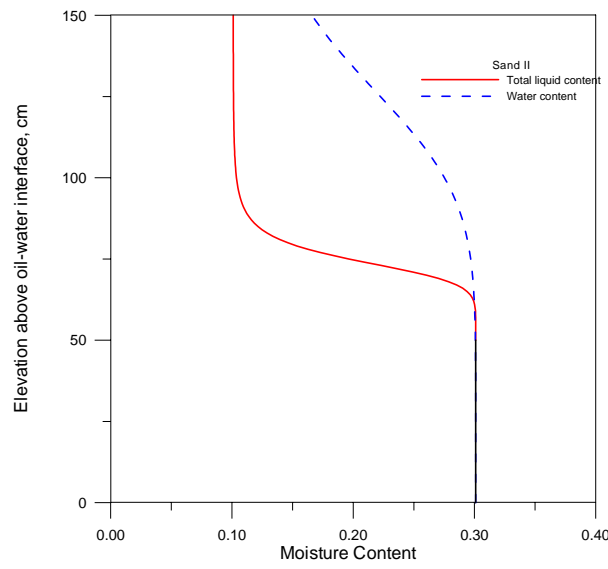


Fig. 8 . Fluids distribution along the vertical in Sand II column (drying cycle).

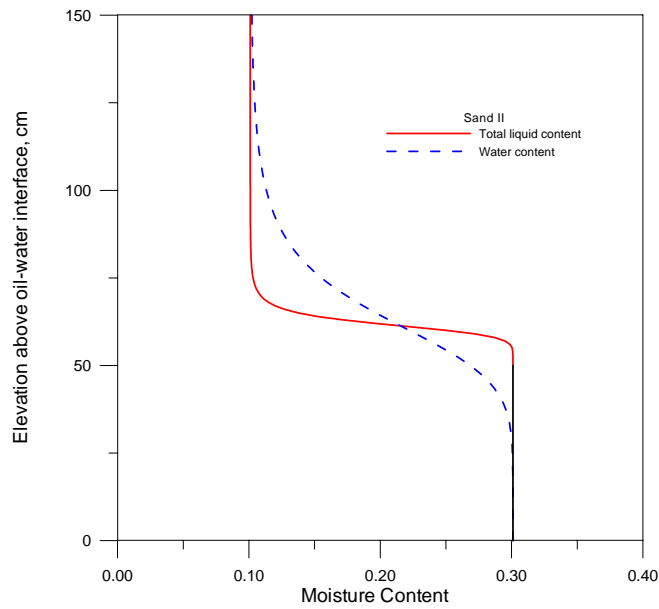
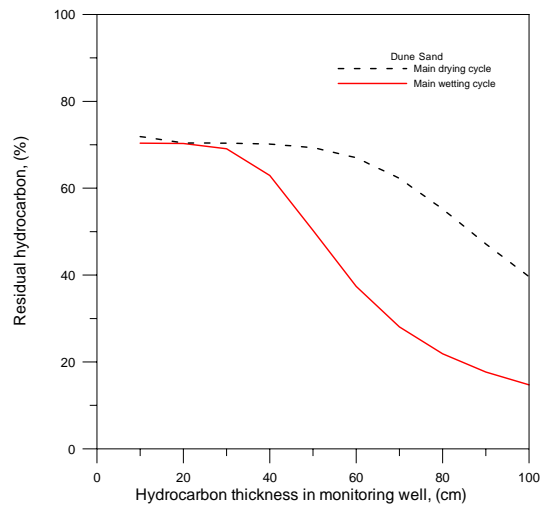
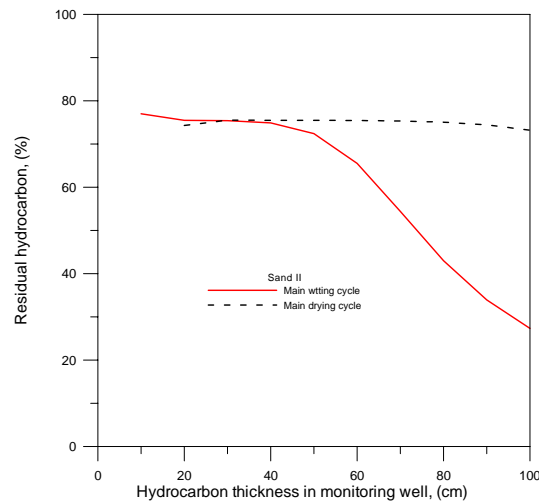


Fig. 9. Fluids distribution along the vertical in Sand II column (wetting cycle).



**Fig. 10. Hysteretic effects on residual hydrocarbon in Dune Sand.**



**Fig. 11. Hysteretic effects on residual hydrocarbon in Sand II.**

## 5. Conclusions

The relative amount of the residual hydrocarbon remaining in homogeneous soils after a spill and having the potential of being a contamination source for a long time was estimated using relatively easy to collect data such as free product thickness in a monitoring well, porous media hydraulic properties, and interfacial tensions values for the fluids involved. Such procedure could allow one to come up with a quick estimation of such

potential which can be used in the early stages of remediation planning of contaminated aquifers. The influence of hysteresis on estimating the residual hydrocarbon was also evaluated. The following conclusions can be drawn based on this study:

1) A high portion of the hydrocarbon content in the vertical profile exists in the residual zone which indicates that a large portion of the total hydrocarbon spill is not recoverable.

2) Hysteresis has a strong influence on residual phase volume estimate suggesting that prior knowledge about the nature of the water table conditions, *i.e.*, falling or rising is a key factor leading to significant improvements in model estimates.

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## أهمية التلوث الهيدروكربوني المتبقي في التربة الرملية مع و بدون التأثيرات التخلفية

قسم الهندسة المدنية، جامعة الملك فهد للبترول والمعادن-  
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