

## **Adsorption and degradation of aromatic and aliphatic hydrocarbons in the subsurface environment**

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### **Abstract**

Large volumes of petroleum hydrocarbons spilled on land during production, transportation and utilisation, have become one of the most prevalent contaminants in the subsurface environment. In this paper, an attempt has been made to study the subsurface contamination by hydrocarbons using solute transport model. The physical and reaction (adsorption, degradation) processes that control the hydrocarbon transport are described in this model. The result of the findings based on bulk oil flow and the concentration of different aromatic and aliphatic hydrocarbons present in oil, show that the spillage of oil have negative impact on the physical, chemical and biological properties of the soil.

**Keywords:** hydrocarbon transport, concentration, porous media.

**2010 Mathematics Subject Classification:** 76D05, 76S05.

## **I. Introduction**

Petroleum as the contaminant of interest, here, is a complex mixture of naturally occurring hydrocarbons in the solid (Asphalt, pitchblende, tar), liquid (crude oil) and gaseous state (natural gas). It is a mixture of hundreds of hydrocarbons consisting of both light and heavy components which have different compositions, whose individual physical and chemical properties vary widely. Hydrocarbons can be basically divided into two types: (i) Aromatics, including benzene, toluene, ethylbenzene and xylene (BTEX) and polyaromatic hydrocarbons. (ii) Aliphatics (saturated hydrocarbons (alkanes) and unsaturated hydrocarbons (alkenes and alkynes)). The proportions of these fractions vary from site to site. Of these, lighter aromatics

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(Eg. BTEX) and the short chain alkanes are readily biodegradable. Predicting the fate of these chemicals in the subsurface is a challenging problem that needs to be addressed at many sites, before an effective remediation result can be achieved.

Adsorption is the ability of a compound to "attach" itself to the soil, depending on the properties of soil and the compound (Miller and Hogan, 1996). Differences in solubility and reaction with organic materials help to make up a wide range of adsorption strengths. Sabbah et al. (2004) studied the transport of polycyclic aromatic hydrocarbons in porous medium in the presence of dissolved organic matter and predicted the sorption constants of polycyclic aromatic hydrocarbons to soil and their binding constants to dissolved organic matter using break through curves.

Degradation or decay plays an important role in the fate of oil spill. It is the biological decomposition or chemical alteration of dissolved compounds (Awobajo, 1981). Biodegradation, makes it possible to consider the effect of microorganisms upon reduction of hydrocarbon concentrations, especially oil fractions. Miller and Hogan (1996) stated that decay does not affect how fast or how far pollutants will travel. Biological or chemical processes will reduce the amount of compounds traveling through the system but the effects of advection will stay the same. These biological transformation may remove contaminants from the systems by biological degradation, or transform contaminants to other toxic compounds that are subject to mass transfer by the other processes such as precipitation and dissolution, oxidation and reduction. These processes tend to retard the rate of contaminant migration and act as mechanism to reduce concentrations (Mercer and Spalding, 1989).

A diffusive model of hydrocarbon migration in the soil has been taken into account in this paper. Incorporation of diffusion into the equation of mass transport including adsorption and biodegradation enables the description of hydrocarbon transport deep into the soil profile. In particular, the topsoil, which is the upper, outermost layer of soil consisting highest concentration of organic matter and microorganisms, and where earth's most biological soil activity occurs is taken under consideration for present study.

In the flow system, we apply the two-stage modeling approach as suggested by Eastcott et al. (1989). The first stage is considered with transport of the bulk oil phase and the second phase is applied to assess the fate of the individual compounds that separate from the bulk

phase. Models of this type are often called solute transport models. The use of this two-stage approach is justified because when bulk oil flow occur, it results in little or no component separation and the transport rate is usually fast relative to that of the dissolution rate.

The movement of oil flow and the characteristics of hydrocarbon components in the subsurface topsoil are examined in this model. The governing non-linear equations are solved by a linearization technique wherein the flow is assumed to be in two parts i.e., a base state and a perturbed part. The exact solutions are obtained for the base state. The perturbed part is solved numerically and the results are represented graphically.

## **II. Problem Formulation**

Assuming the spilled oil cover the flat surface as a positive pit of rectangular type, we use a rectangular coordinate system,  $(x, y)$  to model this flow, where,  $x$  and  $y$  denote the horizontal and vertical coordinates, respectively. The geometry under consideration consists of the topsoil region in the subsurface to be a fluid saturated homogeneous porous medium initially filled with water(Figure 1). Both water and oil are considered to be incompressible and the flow is transient. The flow of oil is modeled by Navier-Stokes equation coupled to a advective-diffusion equation for the concentration of hydrocarbon components. The hydrocarbon adsorption is described with a linear isotherm and the hydrocarbon degradation is assumed to be of the first order. We assume that the oil motion will be more in the longitudinal than in the vertical direction. This is due to the reason, as the oil have impacted the void spaces in the subsurface, they will tend to move longitudinally along the pathway.

By appropriate scaling, the dimensionless governing equations are rendered as follows :

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}$$

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{\partial p}{\partial x} + \frac{1}{Re} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) - \frac{\sigma^2}{Re} u \tag{2}$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{\partial p}{\partial y} + \frac{1}{Re} \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - \frac{\sigma^2}{Re} v \tag{3}$$

$$R \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \frac{1}{ReSc} \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) - \mu c \tag{4}$$

where,  $u$  and  $v$  are the velocities of oil in the topsoil along the  $x$  and  $y$  directions, respectively,

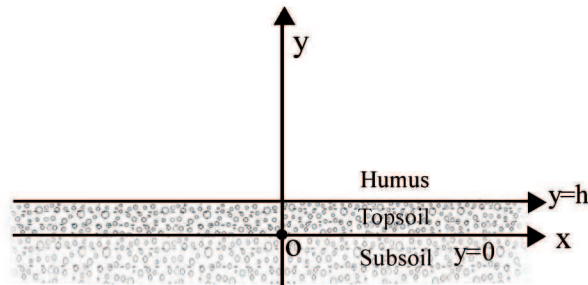


Figure 1: Physical configuration

$t$  is the time,  $c$  is the concentration of hydrocarbon components,  $p$  is the pressure and  $Re = \frac{v_0 h}{\nu}$  represents the Reynolds number,  $R = 1 + \frac{\rho_b k_d}{\beta_w}$  is the retardation factor, where,  $\rho_b$  is the soil bulk density,  $k_d$  is the adsorption coefficient,  $\beta_w$  is the volumetric water content of soil,  $Sc = \frac{\nu}{D}$  is the Schmidt number, where,  $\nu$  is the kinematic viscosity,  $D$  is the mass diffusivity and  $\sigma = \frac{h}{\sqrt{k_p}}$  is the porous parameter, where,  $h$  is the characteristic height,  $k_p$  is the permeability of the medium and  $\mu$  is the rate of degradation. Here, the density and viscosity are assumed to be constants.

Besides the reaction processes, the transport behavior of hydrocarbons in soil are strongly affected by the boundary conditions. The result is the linear relation of the natural logarithm of hydrocarbon concentration as a function of time i.e.  $\Delta \ln C = -\mu \Delta t$  (Zygadlo and Gawdzik, 2010). The velocity boundary are modeled using slip condition which states that the relative velocity of the fluid with respect to the wall (slip velocity) is proportional to the shear rate at the wall (Denn, 2001). This concept of slip which has been commonly used in many investigations, is applied at the soil-oil interface ( $y = 1$ ). At the lower boundary, the velocity and concentration gradients are assumed to be zero. Under these assumptions, the non-dimensional initial and boundary conditions for the velocity and concentration fields are:

$$u = v = 0, \quad c = c_0, \quad \text{at } t = 0, \quad 0 \leq y \leq 1 \quad (5)$$

$$\frac{\partial u}{\partial y} = 0, \quad v = 0, \quad \frac{\partial c}{\partial y} = 0 \quad \text{at } y = 0 \quad (6)$$

$$\frac{\partial u}{\partial y} = \alpha_p \sigma u, \quad v = 0, \quad c = c_0 e^{-\mu t} (1 + \epsilon e^{i(\alpha x + \omega t)}) \quad \text{at } y = 1 \quad (7)$$

where,  $\alpha_p$  is the slip parameter,  $c_0$  is the initial concentration of hydrocarbon components,  $\alpha$  is the stream-wise wave number,  $\omega$  is the frequency parameter and  $\epsilon$  is the perturbation parameter.

### III. Method of Solution

We decompose the velocity and the concentration variables as the sum of base state and two-dimensional linear perturbation part, as

$$(u, v, p, c) = (U_B(y), 0, P_B(x), C_B(y)) + (\hat{u}, \hat{v}, \hat{p}, \hat{c})(y) \epsilon e^{i(\alpha x + \omega t)} + o(\epsilon^2) \quad (8)$$

Substituting (8) in equations (1) to (4) and neglecting the higher order of ( $\epsilon^2$ ), equating the zeroth and first order terms yield the following set of ordinary differential equations for base state and perturbed part.

#### Base State

By assuming a steady, parallel, fully developed flow, the base state equations obtained are:

$$\frac{d^2 U_B}{dy^2} - \sigma^2 U_B = g_1 \quad (9)$$

$$\frac{d^2 C_B}{dy^2} - g_2^2 C_B = 0 \quad (10)$$

where,  $g_1 = Re \frac{dP_B}{dx}$  and  $g_2^2 = Re Sc \mu$

subject to the following boundary conditions

$$\frac{du_B}{dy} = 0, \quad \frac{dC_B}{dy} = 0 \quad \text{at } y = 0 \quad (11)$$

$$\frac{du_B}{dy} = \alpha_p \sigma u_B, \quad C_B = c_0 e^{-\mu t} \quad \text{at } y = 1. \quad (12)$$

The solution of the equations (9) and (10) satisfying the boundary conditions (11) and (12), results in the base state velocity and concentration as given below:

$$U_B = \frac{g_1 [\alpha_p (\cosh \sigma y - \cosh \sigma) + \sinh \sigma]}{\sigma^2 (\alpha_p \cosh \sigma - \sinh \sigma)} \quad (13)$$

$$C_B = \frac{c_0 e^{-\mu t} \cosh g_2 y}{\cosh g_2} \quad (14)$$

The dimensionless pressure gradient is determined from the condition  $\int_0^1 U_B dy = 1$ .

### **Perturbed Part**

Considering the real parts of the solution for the perturbed quantities, re-expressing them in terms of the stream-function  $(\hat{u}, \hat{v}) = (\hat{\phi}_y, -\hat{\phi}_x)$  and eliminating the pressure perturbations yields the following set of equations(after suppressing hat (^) symbols):

$$\begin{aligned} \phi'' + [Re \tan(\alpha x + \omega t) [\omega + \alpha U_B] + \alpha^2 \tan^2(\alpha x + \omega t) - \alpha^2 - \sigma^2] \phi'' \\ + [Re \alpha^2 \tan^3(\alpha x + \omega t) [\omega + \alpha U_B] \\ - Re \alpha \tan(\alpha x + \omega t) U_B'' - \alpha^2 \tan^2(\alpha x + \omega t) [\alpha^2 + \sigma^2]] \phi = 0 \end{aligned} \quad (15)$$

$$c'' + [(Re Sc \tan(\alpha x + \omega t) [\omega R + \alpha U_B] - K) - \alpha^2] c = Re Sc \alpha \tan(\alpha x + \omega t) c_B' \phi \quad (16)$$

where, the prime ( ' ) denotes differentiation with respect to y.

Equations (15) and (16) are solved numerically subject to the boundary conditions outlined below.

$$\phi'' = 0, \phi = 0, c'' = 0 \text{ at } y = 0 \quad (17)$$

$$\phi'' = \alpha_p \sigma \phi', \phi = 0, c = c_0 e^{-\mu t} \text{ at } y = 1 \quad (18)$$

When predicting the transport of oil derivatives in porous soils, hydrocarbon distribution are estimated as the transport of some key components present in oil. In this paper, we have considered three aromatic and three aliphatic hydrocarbons to examine the migration of petroleum contaminants. The hydrocarbons of interest in this study are

- (i) Aromatics(benzene, toluene, and m-xylene)
- (ii) Aliphatics(n-hexane, n-heptane, isooctane).

These components are selected due to their high toxicity and good water solubility. Table 1 provides their related physical properties.

## **IV. Results and Discussion**

Numerical evaluation of the velocity of oil and concentration of hydrocarbon components are analyzed and discussed graphically to study the effect of adsorption and degradation on hydrocarbon transport in the topsoil subsurface.

**Table 1: The physical properties of selected hydrocarbon components**

Molecule	Retardation factor <sup>(a)</sup> R (dimensionless)	Diffusivity <sup>(b)</sup> D (*10 <sup>-7</sup> m <sup>2</sup> s <sup>-1</sup> )	Degradation rate <sup>(b)</sup> $\mu$ (*10 <sup>-3</sup> d <sup>-1</sup> )	Kinematic viscosity <sup>(c)</sup> $\nu$ (*10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup> at30 deg C)
Benzene	2.4	3.5	4.9	0.65
Toluene	2.7	3.5	4.0	0.61
m-Xylene	6.2	8.5	2.5	0.83
n-Hexane	14.7	11	5.0	0.45
n-Heptane	32.0	10	5.9	0.55
Isooctane	60.0	24.0	6.0	0.72

Note:(a) Lyman, W.J, Reidy, P.J. and Levy, B. Mobility and degradation of organic contaminants in subsurface environments, CRC Press, 1992.(b) Zygadlo, M. and Gawdzik, J. Modeling the transport of petroleum products by soil filter method, Polish J. of Environ. Stud., 19(4), pp.841-847, 2010. (c) Fluid characteristics chart table.

The axial velocity profile for different porous parameter values are exhibited in figure 2. Here, we observe that the velocity increases with increasing porous parameter in the upper topsoil surface and decreases for increasing porous parameter as the oil goes deeper into the surface indicating the fact that the effect of porosity retards the flow. This is due to the frictional drag resistance against the flow that decelerates the fluid flow in the porous region. Generally the velocity of oil decreases with depth. Block of oil in soil pores, restricts the air supply to deeper soil strata. The movement of oil hinders the supply of water to plant roots, to a great extent. Additionally, they glue the surfaces of leaves thus obstructing the passage of light, air and water. Consequently, plants die, which leads to a drop in vegetal productivity. Chemical properties of hydrocarbons, on the other hand, are responsible for their toxicity to higher organisms including humans.

The concentration distributions for the selected hydrocarbons referred in table 1 are discussed in figure 3. Effect of retardation factor and degradation rate constant of these hydrocarbons on spatial and temporal concentration profiles at various fixed time and distances have been evaluated and presented graphically from figures 4 to 6. The surface plots for the concentration are pictured in figures 7 and 8.

Concentration decreases as it moves away from the point or line source of pollution due to dispersion and other attenuation effects, such as biological decomposition of organic hydrocar-

bons and precipitation of dissolved chemicals. Figure 3 shows that the aromatic fraction of concentration increases with depth and the concentration of aliphatic components decreases with the depth of soil.

Chemicals that are highly water-soluble biodegrade rapidly, whereas, the insoluble chemicals adsorb in soil, move with soil particles and perhaps very slowly biodegrade. Many components of petroleum are readily degraded by subsurface micro-organisms (Hult and Grabbe, 1985). Some petroleum constituents show a certain degree of water-solubility, and is considerably high for aromatic hydrocarbons, including benzene, toluene and xylene whereas shorter chain aliphatic compounds are rather more toxic and moderately soluble in water.

Figure 4 representing the concentration of selected hydrocarbons at various time indicates that higher values of retardation factor reduce the hydrocarbon concentration with increase in time. Biodegradation reduces both the aromatic and aliphatic hydrocarbon concentrations for increase in time. Concentration of selected hydrocarbons at various depth height and axial length are depicted in figures 5 and 6 respectively. Figure 5 shows that higher the degradation rate, lesser is the total amount of contaminant that will appear. The hydrocarbons move slowly towards the bottom of the soil column. From figure 6 we see that as the axial distance increases, concentration reduction is enhanced by both the reaction processes.

The spatiotemporal evolution of concentration surface plots are depicted in figures 7 and 8 for aromatic and aliphatic hydrocarbons respectively. A surface plot is used to explore the potential relationship between the predictor variables(x and t) and the response variable(c). Based on the regression model, the surface plot provides a clear concept of the response surface. From both these figures, we see that the concentration increases upto some axial distance and then decreases suddenly which continues in this manner. This is due to the nature of the trigonometric forms present in the solution. We also observe that as time increases concentration decreases initially. On further increase in time, the periodic concentration rises faster at the increasing limb of the curve and the tail becomes longer. In general, we conclude that at any fixed point and time,  $c_{m-Xylene} < c_{Toluene} < c_{Benzene}$  for aromatic components and  $c_{Isooctane} < c_{n-Heptane} < c_{n-Hexane}$  for aliphatic components due to the increase in the number of hydrogen and carbon molecules in these components.

The analysis of the concentration distribution of hydrocarbons by means of the described



diffusive model allows us to estimate the contamination risk . The health risk of volatile organic compounds like BTX(benzene, toluene, xylene) even at low concentration is well established and some of them have been identified as proven or probable carcinogens(Hallenbeck and Flowers, 1992). Aliphatic hydrocarbons exert a paralyzing effect on the central nervous system and have a narcotizing action.

## V. Conclusion

Petroleum products spilt on ground surface makes a way deep into the soil, affecting the soil in diverse ways. It is known that some oil components that are toxic can directly affect the soil organisms and other soil properties. It also make soil acidic, in other words, reduces the pH of the soil which in turn affects the availability of nutrients of soil. This affects the soil and its productivity in terms of growth of plants.

The analysis of the obtained results show that the reaction processes decreases the hydrocarbon concentration monotonously with increasing depth, axial distance and time. It is therefore necessary to raise the awareness of how harmful these hydrocarbon components are and try to prevent contamination with oil-derived products which has the potential to pose very long-term threats for the mechanism of resurfacing, to vegetation. The purpose of this model is not just to describe the science of chemical fate in soil, but to contribute an improved ability to describe, respond, and migrate the fate and effects of hydrocarbon spills in real spill situations.

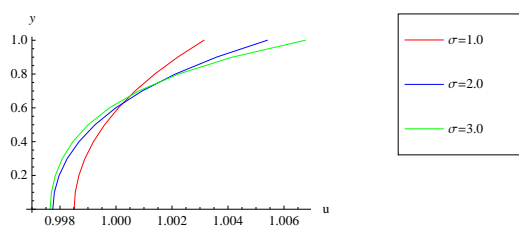


Figure 2: **Effect of porous parameter on axial velocity**

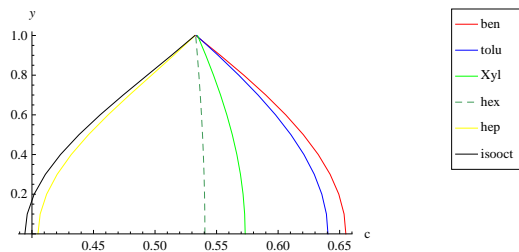


Figure 3: Concentration distribution for selected hydrocarbons

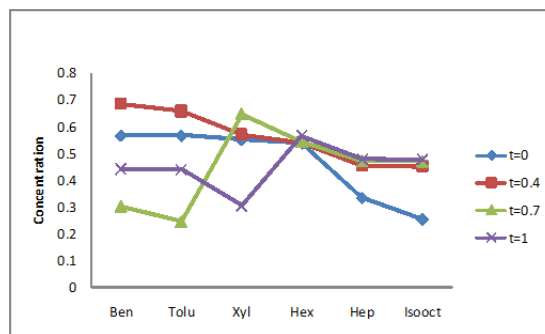


Figure 4: Temporal evolution for the concentration of selected hydrocarbons

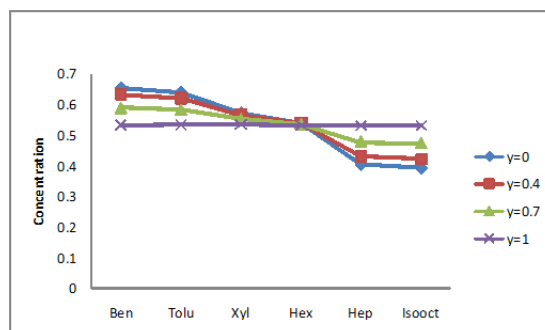


Figure 5: Concentration of selected hydrocarbons along various depth heights

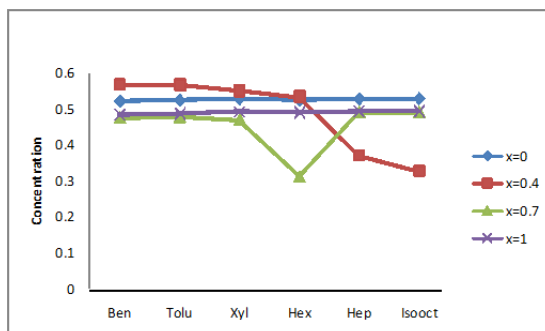


Figure 6: Concentration of selected hydrocarbons along various axial distance

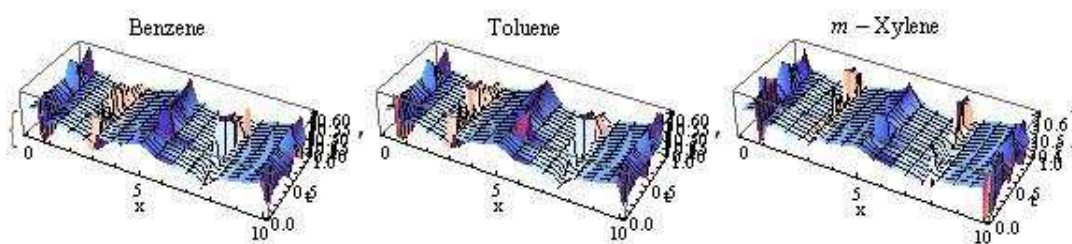


Figure 7: Spatiotemporal(x,t) evolution for concentration surface plot for aromatic hydrocarbons

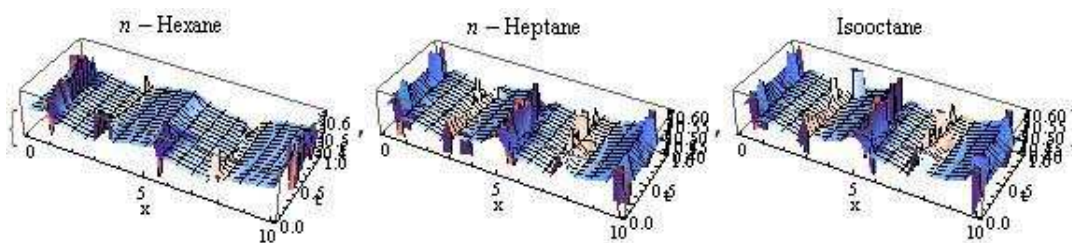


Figure 8: Spatiotemporal(x,t) evolution for concentration surface plot for aliphatic hydrocarbons

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