

Estimation of transport and degradation parameters for naphthalene and anthracene: Influence of mass transfer on kinetics

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Abstract

The method of temporal moment solutions (MOM) for one-dimensional convective-dispersive solute transport involving linear equilibrium sorption and first order degradation for time pulse sources has been applied to analyze experimental data from a soil microcosm reactor. Estimation of the pore-water velocity V for a non-reactive solute was aided by the use of only the first normalized moment while the dispersion coefficient D , first-order degradation rate constant λ and the retardation factor R were estimated using both first and second normalized moments. These transport and degradation parameters were compared to those obtained by a transport model using a nonlinear least square curve-fitting program CXTFIT (version 2.0). Results obtained showed that the MOM fits the breakthrough curve with tailing better than the CXTFIT. The initial estimates of these parameters aided the reduction of the dimensionality of the search process of the non-steady state model. A residual concentration of naphthalene 1.12E-5mg/l, 1.48mg/l, and anthracene 7.67E-4mg/l, 1.61mg/l in the axial and radial directions respectively suggests the preference of naphthalene during the biodegradation process. The surface concentration as depicted using three-dimensional plots, showed that there is occlusion of the aromatics (naphthalene and anthracene) within the soil micropores thereby limiting their bioavailability and in the long run increasing their toxicity.

Keywords

Normalized moments, surface concentration, breakthrough curves, biodegradation, and bioavailability

Nomenclature

V : pore water velocity (m/day)
 V_A : molar volume of pure solute as liquid at its normal boiling point (m^3/gmole)
 D : dispersion Coefficient (m^2/day)
 k_f : mass transfer coefficient for external film diffusion (cm/h)
 D_{pi} : pore diffusivity (m^2/day)
 D_f : diffusivity of the fluid phase (m^2/day)
 C_0 : initial concentration at time = 0 (mg/l)
 C_i : concentration of contaminant in the external pellet surface i.e. opening of the Pores (mg/l)

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C_{sl} : concentration of contaminant in the solid phase (mg/l)
 C_{pl} : concentration of contaminant in the fluid phase within the pore of soil particle (mg/l)
 ε_b : porosity of soil
 ε_p : internal porosity of soil particle
 R : distance from the centre of the particle (cm)
 R : radius of soil particle (cm)
 Z : axial distance (cm)
 t : exposure (contact) time between chemical and soil sediment (days)
 t_o : time of instantaneous injection of sorbing solutes (sec)
 x : distance in the direction of concentration distribution (cm)
 λ : first order degradation rate (per min)
 R : retardation factor
 $\mathcal{E}$: coefficient of deviation
 dp : average soil particle diameter (cm)
 H_L : height of liquid in the reactor (cm)
 $\bar{r}$: average pore radius (cm)
 μ : viscosity of the solution (cp)
 ψ_B : “association parameter” for the solvent
 M_B : molecular weight of pure solute
 θ_A : absolute temperature (K)
 R : molar gas constant
 T : absolute temperature (K)
 $\bar{T}$: tortuosity (usually between 2 and 6)
 D_T : reactor diameter (cm)
 D_S : impeller diameter (cm)
 RRE : relative error

Dimensionless parameters

$\tau = t/T$: dimensionless time
 $\bar{C} = C_i / C_{oi}$ or C_{si} / C_{oi} : dimensionless concentration
 α, β, γ : constants defined by equation (23)
 ψ, η, ϕ : constants defined by equation (24)
 $Z = Z_T/Z$: dimensionless depth
 μ_1 and μ_2 : first and second temporal moments
 μ_n : n th normalized moment of a distribution
 M_n : n th temporal moment of a concentration distribution
 M_0 : theoretical zeroth temporal moment of a concentration distribution
 Re_{dp} : Reynold's number of component

1.0 Introduction

Most of the interest in the biodegradation of polycyclic aromatic hydrocarbons (PAHs) in the field has been in the removal of the parent compounds, while most research on the pure cultures of PAH-degrading bacteria has focused on their ability to grow on or mineralize specific PAH substrates [6]; [17]. Consequently, the bioremediation of PAH contamination with naturally occurring microorganisms has been attempted at a number of sites [3], [5] and [14]. PAHs represent an important group of contaminants due to their carcinogenic effect. They are not particularly volatile, generally have poor water solubility and have a distinct tendency to bind to organic substances. Although interactions among chemical components of a mixture undergoing biodegradation play an important role in determining the overall effectiveness of the process, interactions amongst microbial species in a mixed culture may also be significant [7] and [8].

The interplay between degradation and sorption has become significant as issues such as availability of subsurface contaminants for microbial degradation are explored. Mathematical

models of mixed homologous substrates consumption and microbial growth around [4], [13] and [18].

This work has focused on the biodegradation of naphthalene and anthracene (a 2 and 3-ring PAHs). The work is aimed at characterizing the biodegradation process by considering the mass transfer limitations. Analytical solutions using the temporal moment solutions (MOM) described by [3] and a nonlinear least square curve-fitting program, CXTFIT (version 2.0) as described by [16] will be used to analyze and compare concentration breakthrough curves in the transport studies using experimental data from a soil microcosm reactor. The comparative analysis carried out in this study is an improvement on previous researches as it accounts for the effects of both film resistance, pore and aqueous phase diffusion which are critical parameters in sorption and remediation studies. This study will serve as a benchmark for providing viable solution/management strategy to maintaining the integrity of our environment in the light of limitations arising from experimental measurements over relatively long spatial and temporal scales.

2.0 Experimental

1kg of unimpacted surface and subsurface soils contained in the microcosm reactor shown in Figure 2.1 was spiked with a mixture of naphthalene and anthracene dispersed in 2 litres of water already containing 0.02% surfactant (sodium hexametaphosphate) and organization for economic cooperation and development (OECD) nutrients [15]. A separate experiment was set up and conducted without the contaminant solutes. This served as the control. Opening the valve at a constant flow rate ensured oxygen flow into the reactor.

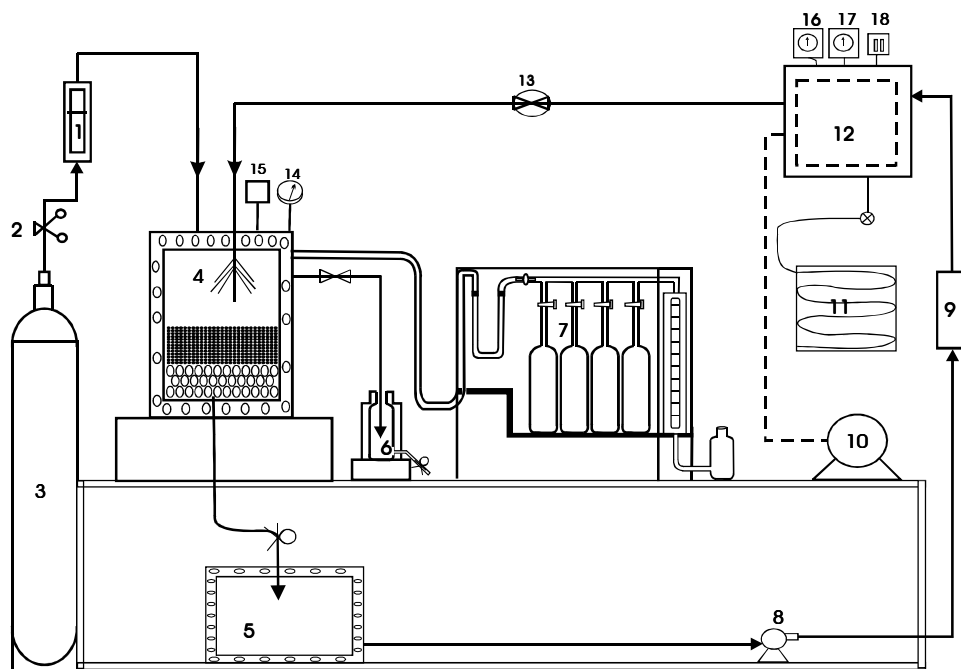


Figure 2.1: Schematic representation of experimental setup

Key:

1: rotameter,
2: regulator,
3: oxygen bottle,

7: orsat gas analyzer,
8: pump,

13: solenoid valve,

14: pressure gauge,

15: digital multimeter,

16: delay timer,

17: programmable timer and

18: electrical switch.

4 : microcosm reactor,
 5 : leachate holding tank,
 6 : oxygen absorption bottle,

The temperature and pressure of the microcosm reactor was monitored throughout the experiment by means of a digital multimeter and a pressure gauge. Standard solvent extraction using n-hexane and dichloromethane (HPLC grade) and gas chromatography methods were used to determine the aqueous phase concentration of the contaminants on a weekly basis.

The gas chromatography is equipped with flame ionization detector (FID) and nitrogen was used as a carrier gas at a pressure of 60-65psi. The injector and detector temperatures were 250°C and 320°C respectively. The column temperature was 40-300°C programmed at 10°C/min with computer interphase and a chem. Station software.

3.0 Unsteady state model

Naphthalene and anthracene transport through a saturated and homogeneous porous media in one-dimensional uniform flow considering convection, dispersion, linear equilibrium sorption and first order degradation has been described in our earlier paper [7]. The unsteady state models characterizing the reactions in both macro and microporous systems are intended to predict the concentration in the axial (z) and radial (r) directions using the experimental data from a soil microcosm reactor. The summary of the equations is given below.

3.1 Macroporous System

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial z^2} - \frac{V}{\varepsilon_b} \frac{\partial C_i}{\partial z} - \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \left(\frac{3}{R} \right) k_f C_i \quad (3.1)$$

The initial and boundary conditions are:

- (i) $C_i = C_{oi}$ at $t \leq 0, z_T \geq z \geq 0$
- (ii) Inlet condition ($z = 0, t \leq 0$): $C_{oi} + D \frac{\partial C_i}{\partial z} = C_i$
- (iii). Outlet condition ($z = z_T, t > 0$): $\frac{\partial C_i}{\partial z} \Big|_{z=z_T} = 0$

3.2 Microporous System

$$\frac{\varepsilon_p}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{pi} \frac{\partial C_{si}}{\partial r} \right) + k_f (C_{pi} - C_{si}) + R = \frac{\partial C_{si}}{\partial t} \quad (3.2)$$

The initial and boundary conditions are:

- (i) $C_{si}(r, t) = C_{si}(r)$
- (ii) $t \leq 0, 0 \leq r \leq R$
- (iii) $\frac{\partial C_{si}}{\partial r} \Big|_{r=R} = 0, 0 \leq r \leq R, t \geq 0$

The modeling equations contain the constant transport parameters V, D, D_j, k_j and D_{pi} required for the simulation of the biodegradation process. These parameters are estimated independently in order to reduce the dimensionality of the search process. The V and D for the non-reactive solute (surfactant) were obtained using the temporal moment solutions of Das and [3] and the curve-fitting program CXTFIT described by [16]

The pore water velocity (V) and dispersion coefficient (D) are estimated in order to calculate the retardation factor R and first-order degradation rate constant λ .

$$V = \frac{x}{\mu_1 - 0.5t_0} \quad (3.3)$$

and

$$D = \frac{V^3}{2x} \left(\mu_2 - \mu_1^2 - \frac{t_0^2}{12} \right) \quad (3.4)$$

The film mass transfer coefficient k_f was determined from the experimental data on adsorption/desorption, using the relationship of Parvatiyar 1992 cited by [15].

$$k_f = 0.32 \frac{D_{pi}^{2/3}}{D_T} V^{1/3} \text{Re}_{dp}^{3/4} \left[\frac{D_s^{1/2} d_p^{-3/4}}{D_T^{1/2} H_L^{1/4}} \right] \quad (3.5)$$

The pore diffusivities may also be estimated from the expression given by [12].

$$D_{pi} = \frac{\varepsilon_p}{\bar{T}} \left[\frac{3}{4\bar{r}} \left(\frac{\pi M}{2R\theta_A} \right)^{1/2} + \frac{1}{D_f} \right]^{-1} \quad (3.6)$$

where the fluid phase diffusivity D_f may be obtained from the correlation of Wilke and Chang, reported by [1]:

$$D_f = 7.4 \times 10^{-8} \frac{\sqrt{\psi_B M_B T}}{\mu V_A^{0.6}} \quad (3.7)$$

The solutions of the degradation rate constant (λ) and retardation factor (R) were obtained using the expressions of [11]

$$R = \frac{(\mu_1 - 0.5t_0) \sqrt{V^2 + 4D\lambda}}{x} \quad (3.8)$$

$$\lambda = \frac{V^2}{4D} \left[\left(1 - \frac{2D}{xV} \ln \frac{M_o}{C_o t_0} \right)^2 - 1 \right] \quad (3.9)$$

The n th temporal moment of a concentration distribution at a location x was defined by Kucera, and Valocchi, and cited by [11].

$$M_n = \int_0^\infty t^n C(x, t) dt \quad (3.10)$$

the n th normalized moment of the distribution was defined as

$$\mu_n = \frac{M_n}{M_o} = \frac{\int_0^\infty t^n C(x, t) dt}{\int_0^\infty C(x, t) dt} \quad (3.11)$$

Equations (3.10) and (3.11) may be used to obtain experimental temporal moments from concentration breakthrough curves.

4.0 Method of solution

The backward finite difference scheme was employed in the resolution of the second-order partial differential equations for the macro and microporous systems. Both

term on the right hand side (RHS) and left hand side (LHS) have the unit of concentration. The scheme involves the discretization of both depth (Z) and time (t) simultaneously into mesh or grid points with constant intervals. The z - t plane is subdivided into equal time steps $\Delta\tau = k$ and depth step $\Delta z = h$. The representative mesh point p is $z = ih$ and $\tau = jk$ where $i, j = 0, 1, 2, 3, \dots, N$. Thus

$$C_p = C(ih, jk) = C_{i,j}$$

The backward finite difference scheme is valid and converges for all values of k/h^2 i.e. $k/h^2 \geq 0$. This is known as the stability criterion. To allow for more flexibility of the result to the equations, some dimensionless variables given by equations (4.1) to (4.9) are defined

$$z = \frac{Z_T}{L} \Rightarrow \frac{\partial z}{\partial Z_T} = \frac{1}{L} \quad (4.1)$$

$$\tau = \frac{t}{T} \quad (4.2)$$

$$\bar{C} = \frac{C}{C_o} \quad (4.3)$$

$$C_o = 100$$

$$\frac{\partial \bar{C}}{\partial C} = \frac{1}{C_o} \quad (4.4)$$

also,

$$\frac{\partial^2 \bar{C}}{\partial^2 C} = \frac{1}{C_o} \quad (4.5)$$

$$C_o \frac{\partial \bar{C}}{\partial \tau} = C_o \frac{\partial^2 \bar{C}}{\partial z^2} \quad (4.6)$$

$$\frac{\partial \bar{C}}{\partial \tau} = \frac{\partial^2 \bar{C}}{\partial z^2} \quad (4.7)$$

$$C_o \frac{\partial \bar{C}}{\partial \tau} = C_o \frac{\partial^2 \bar{C}}{\partial r^2} \quad (4.8)$$

$$\frac{\partial \bar{C}}{\partial \tau} = \frac{\partial^2 \bar{C}}{\partial r^2} \quad (4.9)$$

Non-dimensionalizing equations 1 and 2, we have

$$\frac{\partial \bar{C}}{\partial \tau} = \alpha \frac{\partial^2 \bar{C}}{\partial z^2} - \beta \frac{\partial \bar{C}}{\partial z} - \gamma(\bar{C}_i) = 1 \quad (4.10)$$

$$\psi \frac{\partial \bar{C}}{\partial \tau} = \frac{\partial^2 \bar{C}}{\partial r^2} + \frac{\partial \bar{C}}{\partial r} - \eta \bar{C} + \phi = 1 \quad (4.11)$$

where

$$\alpha = D, \beta = \frac{V}{\epsilon_b}, \gamma = \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \frac{3}{R} k_f \quad (4.12)$$

$$\eta = \frac{k}{\alpha}, \psi = \frac{1}{\alpha}, \phi = \frac{R + kC_p}{\alpha} \quad (4.13)$$

$$\text{subject to } \bar{C} = \bar{C}_{0i} \quad 1 > z > 0, \tau = 0 \quad (4.14)$$

$$\bar{C}(z, 0) = 1, \tau = 0 \quad (4.15)$$

$$\bar{C} = \bar{C}_{0i} \quad 1 > r > 0, \tau = 0 \quad (4.16)$$

$$\bar{C}(r, 0) = 1, \tau = 0 \quad (4.17)$$

$$\text{Discretizing equation 1, we get } C = C_{i,j} \quad (4.18)$$

$$\frac{\partial C}{\partial z} = \frac{C_{i+1,j} - C_{i,j}}{h} \quad (4.19)$$

$$\frac{\partial^2 C}{\partial z^2} = \frac{C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1}}{h^2} \quad (4.20)$$

$$\frac{\partial C}{\partial t} = \frac{C_{i,j+1} - C_{i,j}}{k} \quad (4.21)$$

with $h = 0.015$, $k = 7$. Substituting equations (4.18) to (4.21) and values of α , β , γ , $\bar{C}$ into equation (4.10) we have

$$C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1} = -2.49E - 3C_{i,j} + 1.49E - 3C_{i+1,j} \quad (4.22)$$

$$\text{Similarly, discretizing equation 2, } \Rightarrow C = C_{i,j} \quad (4.23)$$

$$\frac{\partial C}{\partial r} = \frac{C_{i+1,j} - C_{i,j}}{h} \quad (4.24)$$

$$\frac{\partial^2 C}{\partial r^2} = \frac{C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1}}{h^2} \quad (4.25)$$

$$\frac{\partial C}{\partial t} = \frac{C_{i,j+1} - C_{i,j}}{k} \quad (4.26)$$

with $h = 0.001$, $k = 7$

Following the procedure of treating equation (3.1), we have:

$$C_{i-1,j+1} - 3.4C_{i,j+1} + C_{i+1,j+1} = -1.18C_{i,j} - 0.2C_{i+1,j} - 0.74 \quad (4.27)$$

Equations (4.22) and (4.27) are the iterative forms of the unsteady state model equations for the macro and microporous systems. Applying the corresponding boundary conditions, nine equations result with nine unknowns, which can be evaluated simultaneously. The simultaneous equations were resolved using the inverse matrix method. To ease computation of the solution, the Microsoft Excel program was applied.

5.0 Results

5.1 Breakthrough curves

The experimental breakthrough data for the tracer, naphthalene and anthracene from a soil microcosm reactor are plotted in Figures 5.1, 5.2 and 5.3. In these figures,

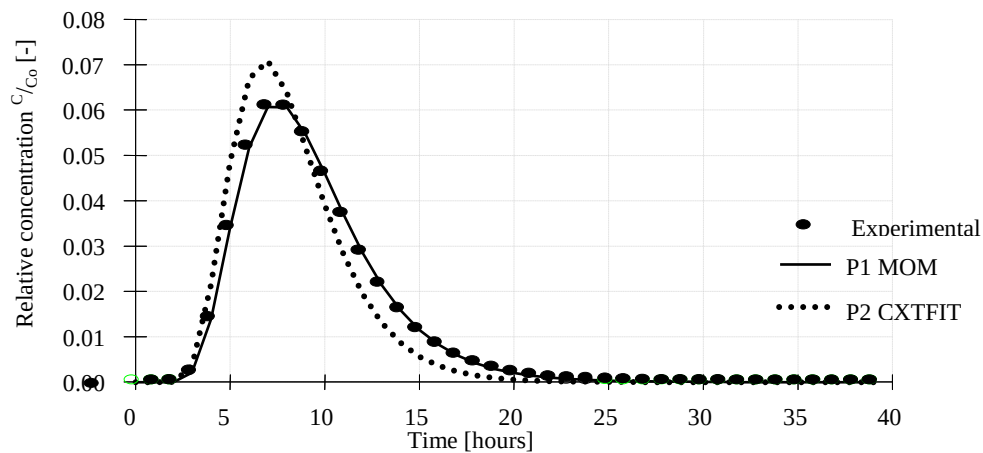


Figure 5.1: Comparison of MOM and CXTFIT simulated breakthrough curves for Tracer using experimental data.

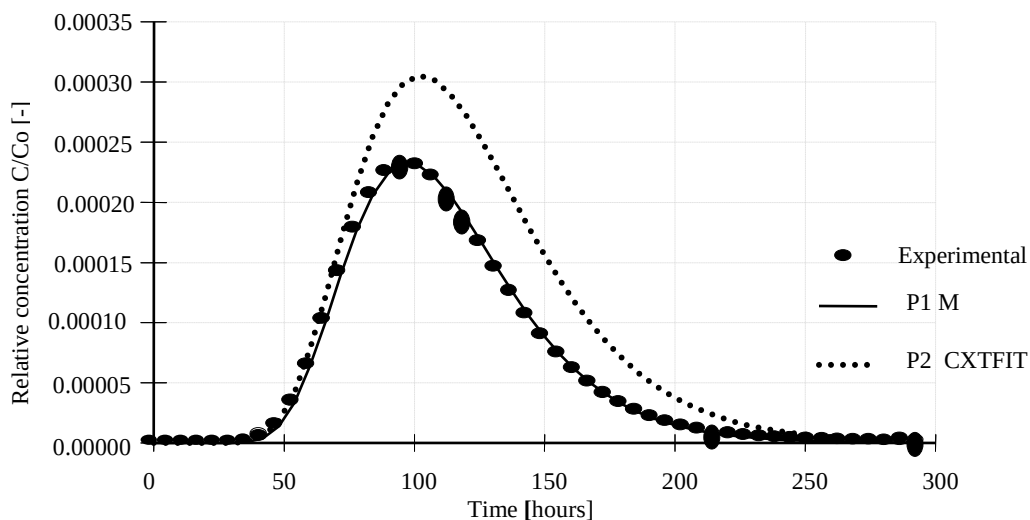


Figure 5.2: Comparison of MOM and CXTFIT simulated breakthrough curve for Naphthalene using experimental data.

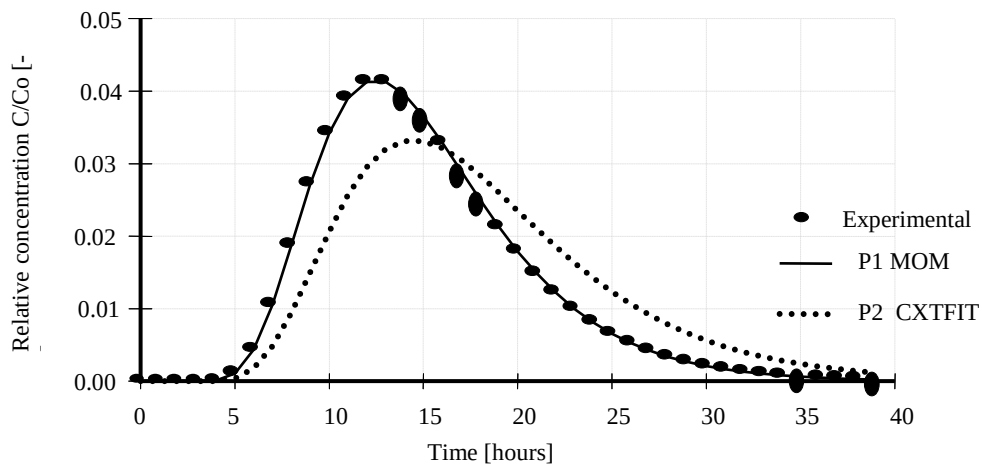


Figure 5.4: Comparison of MOM and CXTFIT simulated breakthrough curve for Anthracene using experimental data.

the dimensionless concentration of tracer and total polycyclic aromatic hydrocarbons is plotted against time. For 40 hour duration, an initial low level of normalized concentration characterized the plots $\frac{C}{C_0}$. The breakthrough data was simulated from

solutions of two analytical transport models; the nonlinear least square curve-fitting CXTFIT program and the temporal moment solutions (MOM). Results show that the MOM fits the breakthrough curve with tailing better than the CXTFIT.

Using experimental data from a sandy soil microcosm reactor, the CXTFIT curve-fitting program and the temporal moments solution were applied in the estimation of the transport parameters V (pore-water velocity) and D (dispersion coefficient), for the tracer (non-reactive solute) which serves to characterize the advection and dispersion, the first order degradation rate constant λ and the retardation factor R for naphthalene and anthracene. The summary of the results is given in Tables 5.1 and 5.2. The retardation factor is a dimensionless parameter which describes the bioavailability of naphthalene relative to anthracene and it increases with increasing solute hydrophobicity.

Naphthalene had a lower retardation factor with a corresponding higher degradation rate constant using both MOM and CXTFIT techniques. The implication of this result is significant as it affirms that the biodegradation of naphthalene and anthracene is a function of their bioavailability which is a function of the aqueous solubility, diffusivity and mobility of each PAH. Thus high retardation factor signifies a decline in degradation rate.

Table 5.1: Pore-water velocity and Dispersion coefficient obtained from methods of temporal moments and CXTFIT curve fitting program

Tracer	V(m/day)			D(m ² /day)		
	MOM	CXTFIT	ϵ	MOM	CXTFIT	ϵ
Sodium Metahexa phosphate	2.15	2.24	-0.04	2.79	2.47	0.11

Table 5.2: Degradation parameters for naphthalene and anthracene from experimental data

PAHs	R			λ (per day)		
	MOM	CXTFIT	ϵ	MOM	CXTFIT	ϵ
Naphthalene	25.77	20.23	0.21	3.54	4.22	-0.19
Anthracene	41.62	28.43	0.32	1.21	2.05	-0.69

where
$$\epsilon = \frac{MOM_{value} - CXTFIT_{VALUE}}{MOM_{value}}$$

5.2 Modelling results

The independent estimation of the constant transport parameters D_f , k_f , and D_{pi} resulted in the reduction of the dimensionality of the search process of the unsteady state model. The estimated values of these parameters for naphthalene and anthracene are shown in Table 5.3.

Table 5.3: Estimated values of the parameters for the solution of the modelling equations

CONTAMINANTS	K_F (M/DAY)	D_{pi} (M^2 /DAY)	D_F (M^2 /DAY)
NAPHTHALENE	1.924E-3	8.61E-6	7.28E-5
ANTHRACENE	1.72E-3	8.59E-6	6.10E-5

The film mass transfer coefficient k_f represents the resistance to mass transfer between the fluid phase and solid phase. The values depict that the resistance to transfer for anthracene is predominant. The pore diffusivities are indicative of a slow diffusive mechanism for anthracene. The results of the modelling equations which describe the one-dimensional convective-dispersive solute transport with linear equilibrium sorption and degradation for the macroporous and microporous systems are shown using the 3-dimensional plots of Figures 5.4, 5.5, 5.6, and 5.7. A critical appraisal of the values from the axial and radial directions of flow revealed that there was a consistent decrease in the concentration of the PAHs with time in the axial direction while in contrast, with increasing contact time, more PAHs were found within the soil particle pores than on the soil particle surface in the radial direction. This observation affirms that more microbial activities take place on the soil particle surface than within the pores. This therefore suggested that with prolonged contact time, PAHs become occluded within the micropores (fissures and cavities) of the soil particles, making them not bioavailable and thus inaccessible to microbial degradation.

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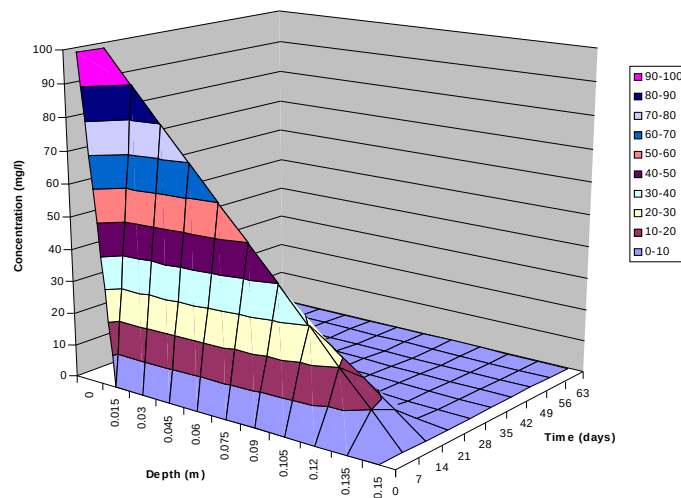


Figure 5.4: Variation of concentration of naphthalene with time and depth of soil particle

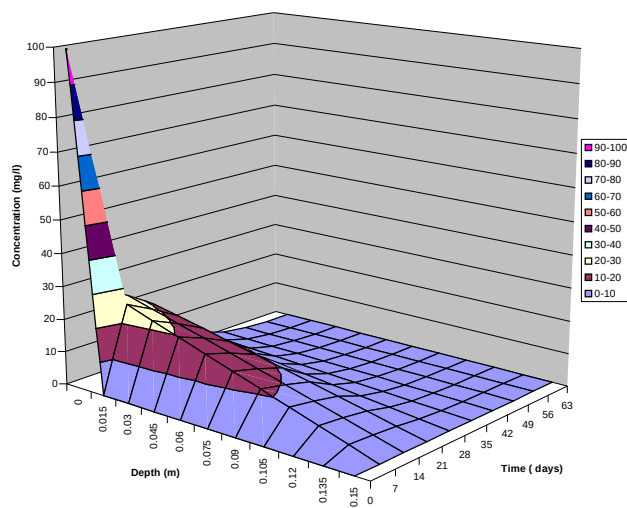


Figure 5.5: Variation of concentration of anthracene with time and depth

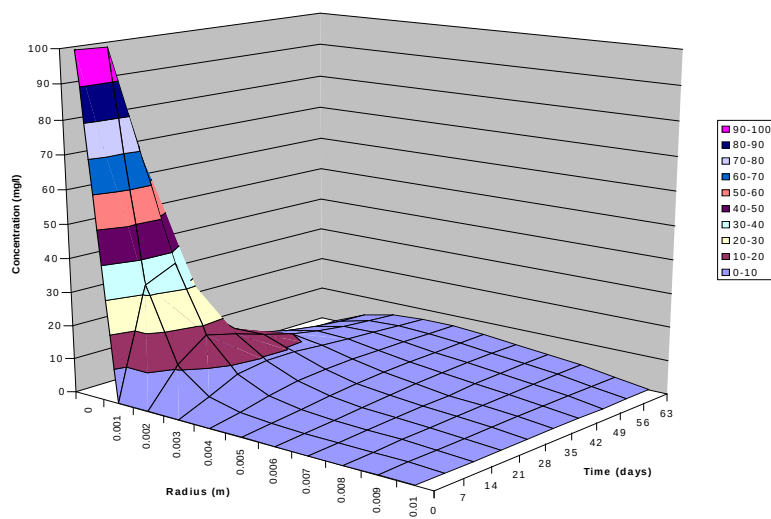


Figure 5.6: Variation of concentration of naphthalene with time and radiuts of soil particle

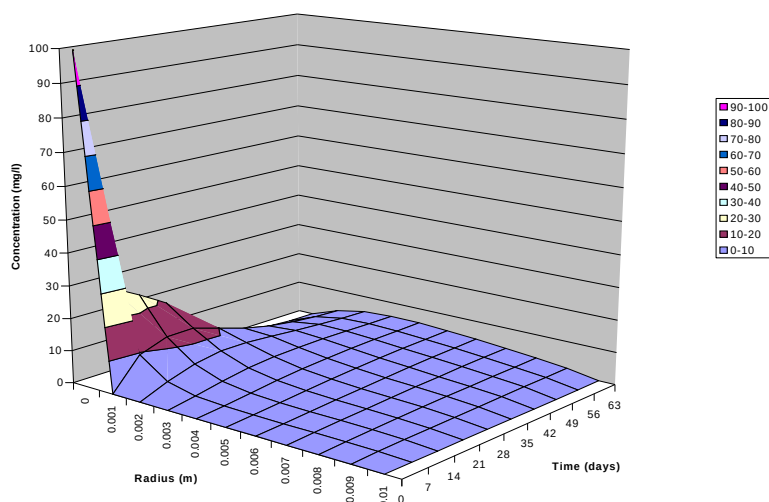


Figure 5.7: Variation of concentration of anthracene with time and radiuts of soil particle

The profiles show the surface concentration with time for naphthalene and anthracene in both axial and radial directions. Residual concentrations of the two polycyclic aromatics are shown in Table 5.4. From the table of results, the presence of the aromatics is more pronounced in the micropores of the soil particle. The summarized simulated results showed that the decay rate was faster in the macroporous system than in the microporous system and that the concentration of naphthalene was lower in both systems. These results affirmed the fact that the microbial utilization of anthracene for metabolic activities was greatly limited by its resistance to mass transfer between the fluid phase and the soil matrix occasioned by its low aqueous solubility.

Table 5.4: Residual Concentration of naphthalene and anthracene in both Axial and Radial directions

<i>PAHs</i>	<i>Axial (mg/l)</i>	<i>Radial (mg/l)</i>
Naphthalene	1.116E-5	1.478
Anthracene	7.67E-4	1.609

6.0 Discussion

The predicted breakthrough profiles for tracer, naphthalene and anthracene shown in Figures 5.1, 5.2 and 5.3 using both the CXTFIT curve-fitting program and the temporal moments solution (MOM) exhibited good agreement. The comparative analysis of the concentration breakthrough curves in the contaminant transport studies for non-reactive solute (tracer) and the experimental PAHs using the MOM and CXTFIT, presented in the profiles of Figures 5.1 to 5.3, showed that they both fit the experimental breakthrough curve; although the MOM had better fit. This was because with MOM, no assumptions about the initial conditions for the experiment were required. An experimental breakthrough time of 5hours for tracer and 17 hours for anthracene were observed. Naphthalene was completely zero. This behaviour displayed by naphthalene may be attributable to its very high diffusive mechanism through the liquid phase to solid phase. The period of low concentration is characterized by effective adsorption of the chemicals on to the surface of the soil particles.

Adsorption presents a large quantity of adsorption sites ultimately leading to high adsorption rate.

This phenomenon is followed by a sharp reduction in adsorption as indicated by the ascent of the normalized concentration profiles presented in Figures 5.1, 5.2 and 5.3. The reduction in adsorption may be due to the fact that most of the pores or sites for adsorption have become filled. These results suggest that anthracene will elute after the breakthrough of naphthalene and the tracer. A retardation factor (R) and first order degradation rate constant (λ) for naphthalene and anthracene were estimated by setting the experimentally determined moments equal to the theoretical moments as reported by [3]. In addition, the experimental data was also fitted to the analytical solutions of a transport model CXTFIT curve fitting described by [16]. The method of temporal moments (MOM) was determined from the experimental data using the trapezoidal rule of the normalized concentration-time plot. The theoretical moments from the model were derived using a Laplace transformed version of the model described by previous investigator [11]. Results are shown in Tables 5.1 and 5.2.

It was observed that the coefficient of deviation ε values for V was one order of magnitude less than the value of D , R and λ . The reason can be attributed to the fact that only the first normalized moment is required to estimate V for a non-reactive solute. Estimation of D , R and λ required both first and second normalized moments, which resulted in the observed marked deviation. This observation was found to be consistent with the reports of [10] as cited by [11] where it was noted that the higher the orders of the moments, the less stable the calculation. The MOM estimates higher values of R and D when compared with the least squares curve-fitting program. The argument is that since the MOM estimates is a function of the difference between the second moment and the first moment squared, small concentrations that are measured at times distant from the first moment (i.e. BTC tail), will have a great influence on the estimates. Conversely, CXTFIT curve-fitting program results are based on minimizing the sum of the squares deviation and the high-concentration data points dominate these. The results thus show that the first moment calculation is positively influenced by calculation in the BTC tail and that the MOM does better fitting of the tails.

The transport parameters D and V obtained from the temporal moment solutions were used for the reduction of the dimensionality of the search process. The results of the model equation for naphthalene and anthracene degradation with equilibrium sorption for the macro and microporous systems using data from experiment are depicted by the 3-dimensional profiles shown in Figures 5.4, 5.5, 5.6 and 5.7. The numerical simulation, given the initial and boundary conditions on the one hand, showed a progressive decrease in the concentration of naphthalene and anthracene with time in the axial direction, while on the other hand, showed that with increasing contact time, more of the aromatics were found within the soil particle pores. The model predicted a residual concentration shown in Table 5.4. Results of this residual concentration showed that long-term exposure of naphthalene and anthracene was characterized by their bioaccumulation and immobilization from soil particles surface towards the pores of soil particles. These observations clearly indicate that biodegradation of these contaminants occur on the soil particle surface and further affirms the fact that anthracene degradation is limited by mass transfer resistances within the microcosm reactor.

7.0 Conclusion

The temporal moment solutions were satisfactorily verified in this study using breakthrough data obtained from a soil microcosm experiment. The agreement achieved between the theoretical predictions is clearly indicated by the experimental breakthrough time.

Anthracene was found to elute after the breakthrough of naphthalene. The efficiency of the unsteady state model for macro and microporous systems is shown in the residual concentration predicted for the contaminant aromatics.

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