PYRENE MINERALIZATION IN CLAY SOIL WITH AND WITHOUT ORGANIC CARBON: THE ROLE OF ADSORPTION AND DESOPTION KINETICS EQUILIBRIA

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ABSTRACT

The kinetics of the aqueous-solids phase degradation of pyrene in clay soil enhanced with organic carbon (+C) and without organic carbon (-C) at 30°C has been investigated. The study considered the adsorption and desorption pattern in a slurry-phase system as a means of assessing the diffusion and transport of pyrene in soil. The linearized Freundlich isotherm equation was used to characterize the diffusion process.

Result of the soil type analysis showed the following particle size distribution 18.30% sand, 25.5% silt, 52.7% clay and an organic carbon content of 1.55%. A comparison of the degradation profile using the concentration-time behaviour indicated that the biodegradation of pyrene was faster by 6.67% in the soil enriched with organic carbon. Approximately, 4.33% (+C) and 2.96% (-C) of pyrene present in the clay soil at zero time given the initial concentration of 100mg/L would be utilized in a minute if the velocity of the reaction remained constant.

Equilibrium adsorption and desorption were attained in 38 and 132hours, 43 and 144hours for soil (+C) and soil (-C) respectively. The coefficient of adsorption and desorption showed that for every one minute about 0.0206mg/L and 0.0201mg/L of Pyrene would be adsorbed from solution by the soil (+C) and soil (-C) while 0.0107mg/L and 0.001mg/l will be desorbed from the soil matrix (+C) and (-C) to the aqueous phase respectively.

KEYWORDS: Organic carbon, Degradation, Adsorption, Desorption, Freundlich isotherm

Nomenclature

C_o = Initial concentration of pyrene in the bulk Liquid.

C_a = Concentration of pyrene.

r_A = Rate of change of pyrene.

V_{max} = Maximum rate

K_m = Michelis –Menten Constant

k = Reaction rate constant

K_a = Freundlich isotherm (adsorption) capacity constant

K_d = Freundlich isotherm (desorption) capacity constant

n = Freundlich constant.

R^2 = Regression Coefficient

1.0 INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of chemicals found during the incomplete combustion of coal, garbage or other organic substances like tobacco or charbroiled meat and burning jet fuel. The environmental PAHs load mostly results from combustion of fuels (Hawsam and Jones, 1998). They have also been found in emission from generators, motor vehicles, coal tar, and asphalt used in road construction as reported by (Manila and Alexander, 1991; McVecty and Hites, 1998; Marr et al, 1999; Wang et al, 1999). The chemical properties of PAH molecules are dependent in part upon both the molecular size, that is, the number of aromatic rings and molecules topology or the pattern of ring linkage (Kanaly et al, 2000).

Concerned with regards to the potential negative health effects of polycyclic aromatic hydrocarbon exposure is evident in the recent inclusion of sixteen polycyclic compounds in the USA environmental protection agency priority contamination list (Fernandez et al, 1999). Recent reports showed that very high concentrations of pyrene were found in water samples taken from Olomoro, Okpe, Abraka and Oleh in the Niger Delta region of Nigeria. (The Punch, April 15, 2005).

Extensive work has been made in the area of degradation kinetics, using the Michaelis Menten rate of degradation with time equation (Octave, 1999). The mechanisms of biodegradation of petroleum hydrocarbons depend on the structure, group of hydrocarbons, environmental conditions and microbial species. Several studies have been presented on the metabolic pathways for the degradation of these compounds (Jerina et al, 1976; Oleszczuk and Baran, 2003, Heitkamp et al, 1987; Grosser et al 1995).

Loor et al, 1996 suggested that the effect of contact time on adsorption and desorption may be more pronounced in soils with high organic carbon contents.

Extensive studies have been conducted to evaluate sorption and desorption kinetics of PAHs in soil and sediments (Peters et al, 1999; Alexander, 1995 and Rockne et al, 2002). Sorption of contaminants to mineral and organic surfaces controls contaminants bioavailability and hence the rate and extent of biodegradation.

This paper seeks to show the effect of adsorption/desorption equilibria on pyrene degradation in soil supplemented with organic carbon and that without carbon.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

The clay sample used for this study was collected from the bank of Ekpan River, close to Warri Refinery and Petrochemical Company in Delta state of Nigeria. All reagents used were of analytical grade. Distilled water was used for solution, sample preparation and dilution.

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2.2   PRESERVATION   OF   SAMPLES   AFTER COLLECTION

The bulk soil sample was collected and put in a sterile polyethylene bag. The bag containing the sample was stored in a refrigerator at a temperature of about $4^{0}C$ prior to analysis.

2.3   METHODS

Clay soil was air-dried, crushed in a smooth roll crusher (600mm in diameter and 300mm in face) and sieved through a 2mm mesh screen.

2.3.1 Organic Carbon Determination

Organic carbon content of the soil was determined using a Walkley-Black wet combustion method as described by Yujun et al (1997). The organic carbon was removed from a portion of the clay soil by mixing 500g soils with $2dm^3$ of a mixture of 0.5M Sodium hydroxide and 0.5M Sodium pyrophosphate, and agitated for 24hrs. The solution was filtered, and $2dm^3$ of 30% hydrogen peroxide was added and the mixture agitated for another 24hrs, filtered and washed to neutral pH

2.3.2 Particle Size Distribution

Mechanical analysis of the soil was carried out by the hydrometer method after the destruction of organic matter with hydrogen peroxide (Day, 1965).
50g of the air-dried soil were weighed into a $600cm^3$ beaker. $50\ cm^3$ of distilled water was added followed by 10 cm^3 of 30% volume hydrogen peroxide. The suspension was heated on a hot plate until frothing stopped and the liquid almost dried. The soil was then transferred into a cup with baffles. 100 cm^3 of water and 20 cm^3 of 20% sodium hexametaphosphate solution (algon) were added to the cup and the suspension stirred for 30 minutes. The suspension was then transferred into a 1dm^3 measuring cylinder with a jet of water from wash bottle and the volume brought to mark with distilled water.
The suspension was agitated vigorously to ensure thorough mixing and exactly 40 seconds from when agitation stopped, a hydrometer reading taken and the temperature of the suspension also recorded.
The suspension was left undisturbed on the bench. At the end of 2hours, another hydrometer and temperature reading were taken. The various particle sizes were calculated as shown below:

% Sand = 100 – Corrected hydrometer reading x 100/50
% Clay = Corrected 2 hours hydrometer reading x 100/50
% Silt – 100 – (% sand + % clay).

2.3.3 Microbial degradation of pyrene

Degradation of pyrene was carried out at $30^{o}C$ by mixing 50mg of pyrene, 500g of clay soil and 1litre of distilled water, and stirred vigorously for 30 minutes in a reactor.
Samples of 20ml aliquot were withdrawn at an interval of five days for analysis by gas chromatography equipped with flame ionization detector (FID). Nitrogen was used as the carrier gas at a pressure of 60-65psi, column temperature ranged from 40-300°C. The injector and detector temperature were 250°C and 300°C respectively.

2.3.4   Batch Adsorption/Desorption

(a) Adsorption of pyrene on clay soil with organic carbon was determined at $30^{o}C$ by mixing a concentration of 100mg pyrene, 50g soil and 250ml distilled water in a stainless steel cylindrical reactor (diameter = 11cm, length =15cm). 1cm^3 saturated solution of mercuric chloride was added to inhibit biodegradation. The slurry system was stirred continuously on a magnetic stirrer to reduce limitation to oxygen diffusion.
The   liquid   was   sampled   after 2,4,6,8,10,12,14,16,18,20,30,36,40   and   44hrs.After   the predefined time had elapsed; the samples were centrifuged prior to GC analysis.
(b) Desorption conducted by first adsorbing the pyrene on the clay soil until equilibrium was attained. This was achieved by mixing 100mg pyrene; 50g soil and 250ml distilled water; stirred and allowed to stay till equilibrium was obtained.
After equilibrium was attained, the mixture was diluted with an equal volume of distilled water, and 1ml saturated solution of mercuric chloride was added to minimize biodegradation. A 20ml   sample   was   taken   after 0,4,8,16,24,48,72,96,120,144,168   and   192hrs   centrifuged followed by GC analysis.

3.1 RESULTS

The results of the role of adsorption/desoption kinetics equilibria on the mineralization
of pyrene in the clay soil used for this study are summarized and presented in tables 1, 2 and 3; and Figures 1 through 12 below.

Table1: Physiochemical properties of clay soil used in this study.

Parameters	Soil with Carbon	Soil without Carbon
Specific gravity	2.71	2.71
%Organic carbon content	1.55	Nil
% Clay	52.70	52.70
% Silt	25.50	25.50
% Sand	18.30	18.30
Bacteria Identified		
(a) Microcosm sp	+ve	+ve
(b) Pseudomonia sp	+ve	+ve
(c) Bacillus sp	+ve	+ve
Fungi Identified		
(a) Asergillus niger	+ve	+ve
(b) Penicillum	+ve	+ve
(c) Yeast candida.	+ve	+ve

Table 2: Biokinetic parameters

Type of Soil	V_{max} (mg/l.hr)	K_m (mg/l)	k (hr^{-1})
Clay (-Carbon)	0.2324	15.513	0.02963
Clay (+Carbon)	0.0.1172	10.5	0.04325

Table 3: Freundlich isotherm data

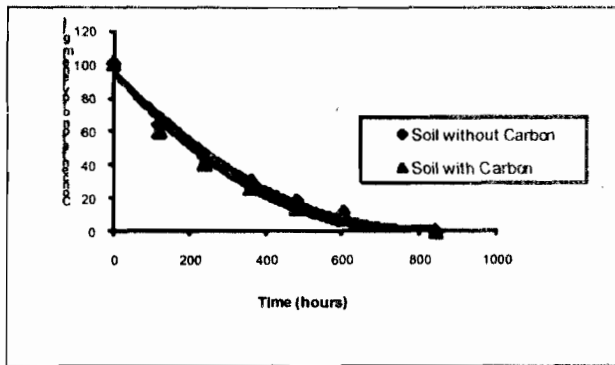| Type of Soil	Adsorption		Desorption	
	K_a	n	K_d	N
Soil (+C)	0.0206	1.0027	0.0107	1.0156
Soil (-C)	0.0201	1.0030	0.0101	1.002

Fig. 1: Degradation of Pyrene using Clay soil
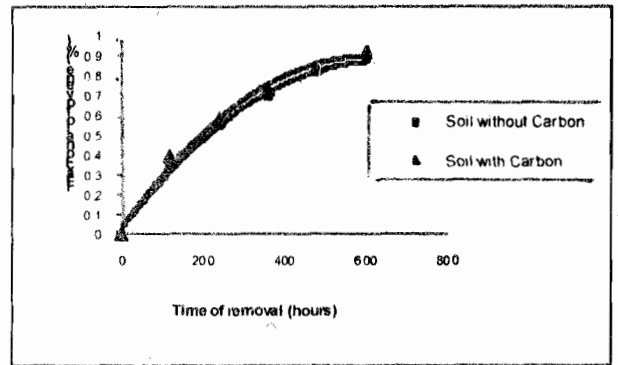with and without Carbon

Fig. 2: Fractional removal of pyrene in clay soil
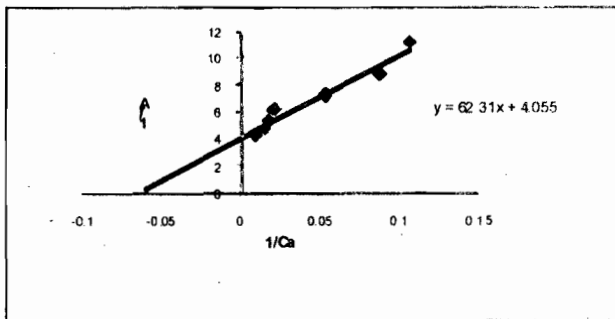as a function of time

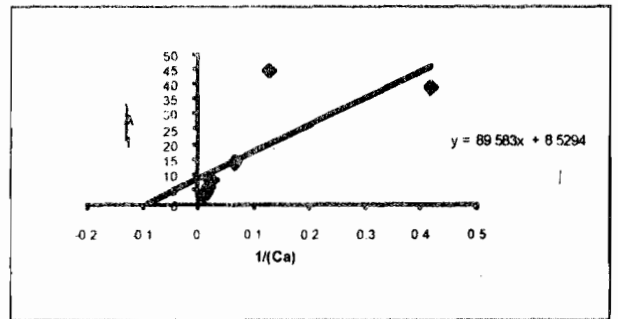Fig. 3: Lineweaver Burk plot for soil (-C)
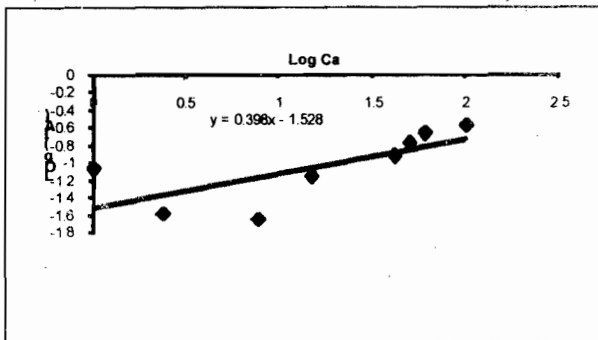

Fig. 4: Lineweaver Burk Plot for Clay(+C)

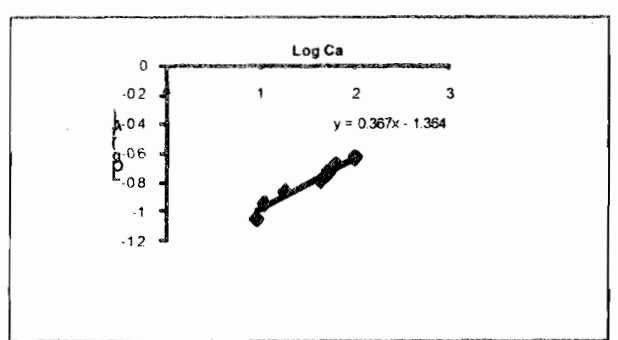Fig 5: Plot of Log (-rA) vs Log (Ca) for Soil (-C)

Fig 6: Plot of Log (-rA) vs Log (Ca) for Soil (+C)
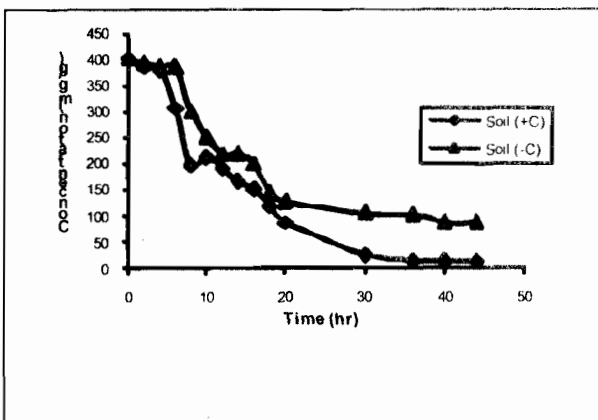

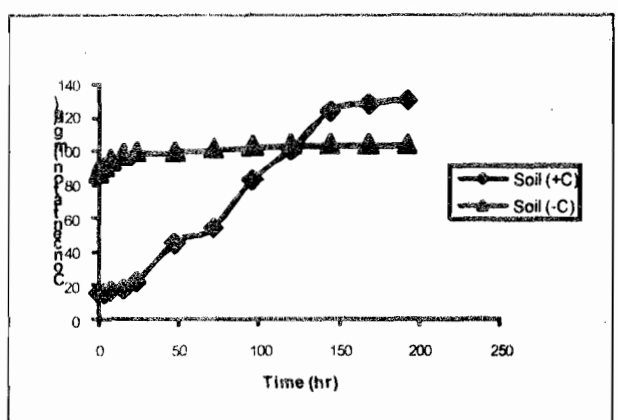Fig. 7: Adsorption kinetics of pyrene
using soil (+C) and (-C)

Fig. 8: Desorption kinetics of pyrene
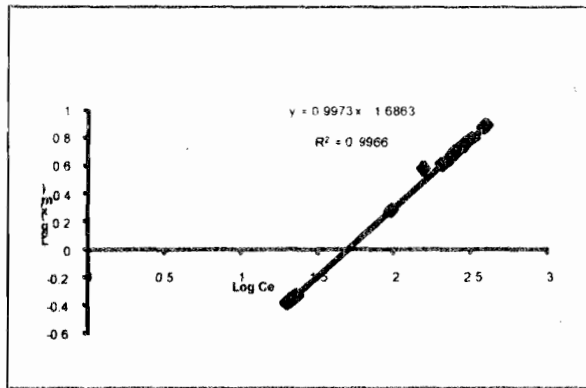using soil (+C) and (-C)

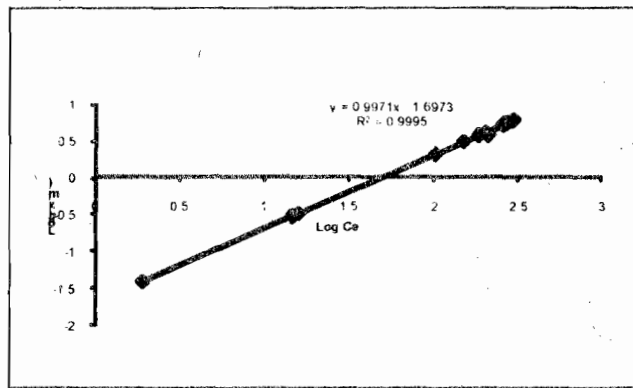**Fig. 9: Freundlich isotherm (Adsorption) for Soil (+C)**

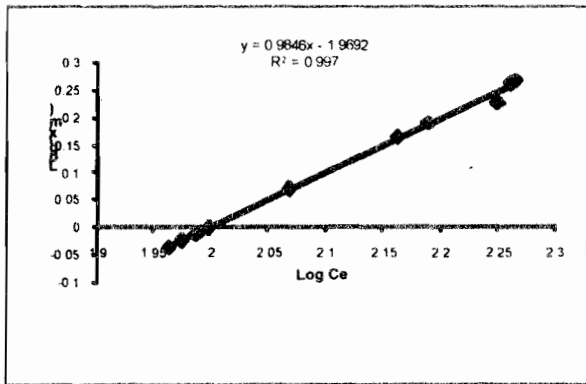**Fig 10: Freundlich isoherm (Adsorption) for soil (-C)**

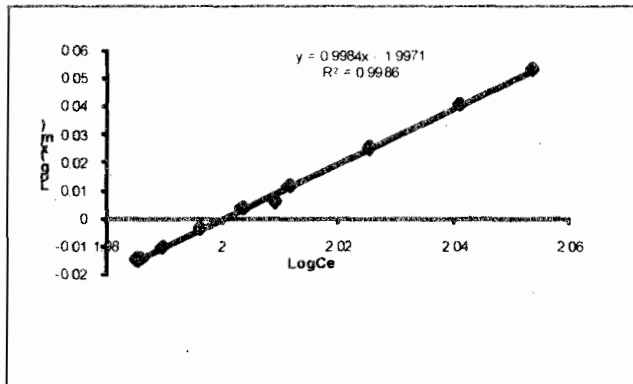**Fig. 11: Freundlich isotherm (Desorption) for soil (+C)**

Fig.12: Freundlich isotherm (Desoption) for soil (-C)

3.2   DISCUSSION

The result obtained showed that the percentage (%) organic carbon content was found to be 1.55%. A low nitrogen and a low to moderate available phosphorus in the soil accounted for the low nutrient level. Hence there was the need to supplement the soil with nutrients such as straw, saw dust and poultry dung. A Microbial Population Numeration (MPN) study carried out in the soil, indicated the presence of both bacteria (microcosm sp, pseudomonia sp and bacillus sp) and fungi (Aspergillus niger, Penicillum and yeast candida).

After impacting the soils with pyrene a rapid and exponential decrease in the concentration was observed for both soil type as shown in Figure 1. The degree and extent of this decrease differed between the soil types.

A faster mineralization of pyrene with time was noted in soil (+C). This observation suggests that microbial degradation was significantly enhanced in the presence of organic carbon. Organic matter (carbon) promotes microfauna, by creating openings in the soil, which improves infiltration and storage of cations in neutral and alkaline soils. The overall effect is the binding of heavy metals and preventing them from interfering with microbial activity.

The percentage fractional removal $\dfrac{C_o - C}{C_o}$ profiles shown in

Figure 2, were similar in shape but differed in the quantities removed. A sharp increase in the percentage removal was observed with increasing contact time. Approximately, 75% and 70% of pyrene present in the clay soil (+ carbon) and (- carbon) had been degraded at the end of one half the contact time of 360 hrs.

The percentage fractional removal can be attributed to contributions of hydrophobicity and diffusion through intraparticle pores or restricted diffusion in organic matter.

By applying the differential method of analysis and the Michaelis-Menten kinetics on the experimental data, the biokinetic parameters (V_{max} and K_m) were estimated. The V_{max} describes the maximum attainable velocity of the reaction in relation to the concentration of the total enzyme catalyzing the degradation. The Michaelis-Menten constant K_m, represents a valuable tool in microbial-degradation study, as it is a measure of the strength of the enzyme-substrate (ES) complex (Segel, 1975). The biokinetic parameters (K_m and V_{max}) obtained from the kinetics via line-weaver burk reciprocal plot are shown in Table 2 and Figures 3 and 4 respectively for the two soil types. A high K_m indicates a weak binding while a low K_m is indicative of strong binding between the enzyme and substrate. The estimated K_m values suggest that there is a weak ES complex between pyrene and enzyme catalyzing its degradation in the clay soil without carbon.

The physical significance of the rate constant k, obtained from Figures 5 and 6 is that, it approximates the fraction of the substrate present that is converted to product per small increment of time. Thus, from Table 2, about 4.33% and 2.96% of the pyrene present at zero time in the clay soil (+carbon) and soil (-carbon) respectively would be utilized in a minute if the velocity of reaction remained constant. This result affirms that biodegradation is faster in the presence of organic carbon.

The adsorption and desorption kinetics equilibria of pyrene was characterized by a fast step, followed by a slow almost constant step as shown in Figures 7 and 8.

The results showed that adsorption equilibrium was attained at 38 and 43hrs while desorption equilibrium was achieved after 132 and 144 hours for soil (+C) and (-C) respectively. This implies that the process of desorption of the chemical from the soil matrix is very slow and as such it is rate-limiting, being the only kinetically significant step in the sequence of reaction.

Equilibrium adsorption/desorption on the external surface and the internal pores of the particles was described using the Freundlich isotherm equation. Results in Table 3 showed that for every one minute about 0.0206mg/L and 0.0201mg/L of Pyrene would be adsorbed from solution by soil (+C) and soil (-C) respectively, while 0.0107mg/L and 0.001mg/L will be desorbed from the soil matrix (+C) and (-C) to the aqueous phase respectively. High values of K_a and K_d therefore suggest increased amount of pyrene that will be adsorbed and released for mineralization.

CONCLUSION

Microbial degradation of pyrene will take place naturally in clay soil. The rate was however found to be enhanced by the presence of organic carbon.

The desorption step showed the lowering of the aqueous phase concentration of pyrene due to resistance to mass transfer and hindered pore diffusion mechanisms. The desorption step was found to be rate limiting, being the only kinetically significant step.

The estimated K_m suggests that there is a weak binding between pyrene and the microorganisms catalyzing its degradation in clay soil without organic carbon.

The implication of this research work is significant. The estimated adsorption/desorption capacities (k_a and k_d) provide useful information on the transport of pyrene in the different clay soil used for this study.

The knowledge derived from the transport parameters, form he basis of the degradation reaction, which helps to facilitate the effective clean up of soils contaminated with pyrene.

REFERENCE

Alexander, M., 1995. "Sequestration and bioavailabilty of organic compounds in soil", in: Bioavaialabilty and biodegradation kinetics protocol for organic pollutant compounds to achieve environmentally acceptable endpoint during bioremediation. Annals of the New York Academic of Sciences. The New York Academic of Sciences, New York, 829, 36-61.

Day, O.R., 1965. "Particle fractionation and particle size analysis" in: Methods of soil analysis, Am. Soc. Agron., Madison, Wisonson, 9 ; 545-567.

Grosser, R.J., Warshowsky, D. and Vestal, J.R., 1995. "Mineralization of polycyclic and n-Heterocyclic aromatic compounds in hydrocarbon-contaminated soil", Environ. Toxicol. Chem. 14(151): 375-382

Heitkamp, M.A.and Cermiglia, C. E., 1987. "The effects of chemical structure and exposure on the microbial degradation of polycyclic aromatic hydrocarbon in fresh water and estuarine ecosystems" Environ. Toxicol Chem. 6: 535-546.

Howsam, M. and Jones, K.C., 1998. "Sources of PAH in environment" The handbook of environmental chemistry. A.N. Neilson edition, 3: 137-174.

Jerina, D.M., Seander, H., Yagi, H., Well, M.C., Davey J., Mahadevan, V. and Gibson D.T., 1976. "Dihydrodiolsfrom anthracene and phenanthrene". J. Am. Chem. Soc., 98:5988.

Kanaly, R.A. and Harayama, S., 2000. "Biodegradation of high molecular-weight polycyclic aromatic hydrocarbons by bacteria" J. Bacteriol., 182: 2059-2067.

Loor Y, Storm, P.F. and Farmer, W.J., 1996. "The effect of sorption on phenanthrene bioavailability" J. of Biotechnol. 51: 221-227.

Manila V.B, and Alexander, M., 1991. "Factors affecting the microbial degradation of phenonthrone in soil", Appl. Microbial. and Biotechnol. 35(3): 401-405.

Marr, L.C., Kirchstetter, T.W., Harley, K.A., Mignal , A.H. Hering, S.U. and Hommod S. K., 1999. "Characterization of polycyclic aromatic hydrocarbon in motor vehicle fuel and exhaust emission" Environ. Sci. Technol. 33, 3091-3099.

McVecty B. D and hits R. D., 1998. "Atmospheric deposition of polycyclic aromatic hydrocarbon to water surfaces, a mass balance approach", Atmos. environ. 22(3) 511-536.

Octave, L.,1999. "Chemical Reaction Engineering", John Wiley & Son Inc. New York, 3rd edition, 36-76, 611-619.

Oleszczuk, P. and Baran, S., 2003. "Degradation of individual polycyclic aromatic hydrocarbons (PAHs) in soil polluted with aircraft fuel" polish J. Environ. Studies, 12(4): 431- 437.

Peters, C.A., Knights, C.D. and Brown, D.G., 1999. "Long term composition dynamics of PAH-containing NAPLs and Implication for risk assessment". Environ. Sci. Technol. 33: 4499 - 4507

Rockne, K.J., Shor, L.M., Young, L.Y., Taghon, G.L. a.id Kosson, D.S., 2002. "Distributed Sequestration and release of PAH in weathered sediment: The role of sediment structure and organic carbon properties" Environ. Sci. Technol., 36: 2636-2644.

Segel, I. H., 1995. "Biochemical calculations" John Wiley and sons. Inc; New York, 2nd edition, 234-245.

The punch Newspaper, April 15, 2005. "Pyrene found in water samples in the Niger Delta Region" 3-4.

Warg, Z; Fing, M; Cody, Shu, Y.Y; Sigouin, L;Lnadriaut, M and Lambert, P., 1999. "Quantitative charaterization of PAHs in burnt residue and sooth samples and differentiation of pyrogenic PAHs" Environ. Sci. Technol. 33: 3100-3109.

Yin, Y., Allen, H.E, Huang, C P, Spark, D.L, and Sanders, P.F , 1997. "Kinetics of Mercury(II) Adsorption and Desorption on soil", Environ. Sci. Technol. 31: 496-503.