A Mathematical Model Incorporating the Influence of Biodegradation on the Fate of a Simulated Oil Spill in a Brackish Aquatic System

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Research Article

ABSTRACT

Aims: To address the limitation in the Nigerian Oil Spill Model (NOSM) which models biodegradation using the first order decay process in which the rate of oil biodegraded is proportional to the initial mass and an empirical decay coefficient. It does not monitor the total biomass of the microorganisms involved in biodegradation. It is not a reflection of natural systems which is a combination of first, second and third order reactions.
Study Design: Cross-sectional study.
Place and Duration of Study: Eagle Island (Brackish water) behind the Rivers State University of Science and Technology, Port Harcourt, Rivers State, Nigeria between July and September, 2009.
Methodology: Monod biodegradation kinetics is used. Crude oil serves as the substrate for microorganisms. Here, there is stimulation of the destruction of substrates, consumption of electron acceptors (oxygen, nitrate) and the growth of biomass. Substrate is biodegraded by microorganisms in the aqueous phase or by biomass present as micro colonies (Molz et al., 1986). In order to simulate this model, MATHLAB/SIMULINK was used. This powerful software package offers an array of numerical methods that can be used for modeling simulation of non-linear differential equations PLOT, amongst the main functions of MATHLAB was used.
Results: From the proposed model, it was observed that biodegradation augments when there was increase in the number of bacterial population. This was quite conspicuous in the delay of crude oil breakdown that occurred because the microorganisms that degrade the substrate must grow first of all and increase in number. When the biomass was sufficient, the crude oil was quickly biodegraded. There was growth in the biomass as the microorganisms utilized the electron acceptors (oxygen and nitrate).

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Conclusion: The modification of the biodegradation component in the NOSM shows the involvement of microorganisms and use of electron acceptors which is a reflection of natural systems. This proposed model addresses the limitation in NOSM where oil biodegraded is proportional to the initial mass of oil and an empirical decay coefficient.

Keywords: Biodegradation; proposed model; biomass; crude oil.

1. INTRODUCTION

The frequency of oil spills around near-shore marine, fresh water and brackish water ecosystems present a growing concern. Oil spill accidents bring serious environmental impacts because it is long lasting especially through food chain to the whole ecological system. The   composition of oil changes from time to time (Rheinheimer, 1991). The heavy residues of oil form tar balls, ranging in size from less than 1mm to 10-20cm in diameter, and degrade extremely slowly (Clark, 1992).

Oil spillage is categorized into four groups: Minor, Medium, Major and Disaster (Ntukekpo, 1996). The minor   spill takes place when the oil discharge is less than 25 barrels in inland waters or less than 250 barrels on land, offshore or coastal waters that do not pose threat to public health or welfare. In the case of the medium spills, the spill must be 250 barrels or less in the inland water or 250 to 2,500 barrels on land, off-shore and coastal waters. For the major spill, the discharge to the inland waters is in excess of 2500 barrels on land, offshore or coastal waters. The disaster refers to any uncontrolled well blow-out pipeline rupture or storage tank failure which poses an imminent threat to the public health or welfare (Ntukekpo, 1996).

Biodegradation is slow oil loss due to the ingesting and metabolizing of oil by various aquatic microorganisms. Microorganisms with hydrocarbon-degrading ability are ubiquitous in the aquatic environment although they are higher in number in oil-polluted sites. The number of oil-degraders in fresh water sediments has been shown to increase by several orders of magnitude in the weeks following an oil spill (Horowitz et al., 1977; Heitkamp et al., 1984).

The environmental concern over oil spills has led to the development of mathematical models to simulate the transport and fate of oil slicks. These models can either be used on a real-time basis to reduce the environment impact assessment or as scenario models during training and planning.

The Nigerian Oil Spill Model includes a first order decay process in which the oil biodegraded is proportional to the initial mass and an empirical decay coefficient.

The proposed biodegradation model is a higher order model that involves the stimulation of the destruction of the crude oil, consumption of electron acceptors and growth of biomass. This is a more realistic picture of biodegradation in natural systems because of the involvement of microorganisms and electron acceptors which are the major factors in biodegradation (Mackay and Mc Auliffe, 1988).

2. MATERIALS AND METHODS

2.1 Water and Sediment Samples Sources and Collection

Water and sediment samples were collected from Eagle Island (Brackish water) behind the Rivers State University of Science and Technology, Port Harcourt, Rivers State, Nigeria. Physicochemical analyses of the water and sediment samples were determined prior to crude oil contamination in a simulated environment (Fig 1). The solid phase biodegradation option adapted for Nigeria condition (DPR, 1997) was employed. River Water served as the liquid phase while the solid phase was sediment from the brackish aquatic environment. Water troughs made of glass materials were used for the tests; with dimensions: 1.5m length x 1m width x 0.3m depth. Each water trough had an outlet situated 16cm from the bottom of the trough. They were covered with black polyethylene paper on the sides and on top to prevent photo degradation and rapid evaporation after values required for spreading, evaporation, etc. had been obtained.

Fig. 1. Solid phase continuous flow biodegradation system

2.2 Crude Oil

Bonny light crude oil obtained from Nigerian National Petroleum Corporation (N.N.P.C.) Port Harcourt, was employed in this study.

2.3 Chemical Reagents

The following chemical reagents: Manganese Sulphate solution, Alkaline-Iodide-Azide reagent, Silver nitrate solution, Potassium Chromate indicator solution, Standard Sodium Chloride solution, Potassium dichromate solution, Concentrated Sulphuric acid, Ferrous ammonium Sulphate solution, Ferroin (indicator solution), anhydrous sulphate solution, etc. employed in this study were products of Aldrich Chemical Co, Milwauke, USA, BDG Chemicals, Poole, England and Sigma Chemical Company, St. Louis Missouri, USA.

2.4 Preparation of Test Concentrations Treatment

Sediment was mixed with the crude oil to obtain the following concentrations; 5,000mg/kg, 50,000mg/kg and 100,000mg/kg.

For the positive biodegradation control, the same concentrations were prepared using Olive oil and for the negative control, a subsample of each concentration treatment of sediment and crude oil was removed and poisoned with sodium azide.

2.5 Physicochemical Analyses

The pH of the test water was determined using the Jenway pH meter (3015 model).

Azide modification method as described in (APHA, 1998) was employed for the determination of dissolved oxygen while conductivity was determined using a WTW electronic conductivity meter model, Germany. The mercury thermometer was used to determine the temperature. Salinity was determined   by employing Argentometric method (APHA, 1998). For the sediment samples, nitrate, total organic carbon (TOC) and total petroleum hydrocarbon (TPH) were determined monthly for 90 days (APHA, 1998).

2.6 Bacteriological Analyses

The total heterotrophic bacterial count was performed in duplicates on nutrient agar plates using the spread plate method (APHA, 1998). Plates were enumerated after 48hrs of incubation. Vapor phase transfer method (Okpokwasili et al., 1988) was used in estimating the population of hydrocarbon-utilizing bacteria. Modified mineral salt medium (mineral C) of Mills et al., (1978) was inoculated with the river water and sediment samples. Plates were enumerated after 7 days of incubation at room temperature.

2.7 Methodology for Modeling

In order to simulate this model, MATHLAB/SIMULINK was used. This powerful software package offers an array of numerical methods that can be used for modeling simulation of non-linear differential equations. PLOT, amongst the main functions of MATHLAB was used. It implements a variation of the numerical method to solve partial differential equations (PDE) and least square analyses which is used to perform non-linear optimization for determining the parameters in the biodegradation model that best match the experimental data sets.

2.8 Determination of Fate of Oil Spill Using NOSM Method

2.8.1 Evaporation

Mackay evaporative exposure formula developed by (Mackay, 1980) was used. It is mostly used to calculate the evaporation rate of oil. Evaporation depends on the type of oil, spill area, oil slick thickness, vapor pressure and mass transfer coefficient. These are in turn composition of the oil, wind speed and temperature.

2.8.2 Dissolution

Mackay and Leonine algorithm for dissolution of oil is used. The method of Cohen et al., (1980) is applied. Dissolution accounts for a negligible fraction of the mass balance of the oil. It is a function of oil slick area, dissolution mass transferability and oil solubility in water.

2.8.3 Mechanical Spreading

Fay's spreading theory of 1971 was used. In Fay's theory, oil spill is considered to pass through 3 phases. In the first phase, only gravity and inertial forces are important. In the second phase, gravity and viscous forces dominate. The third phase is governed by the balance between surface tension and viscous forces.

2.8.4 Shoreline deposition

NOSM simulates the shoreline deposition as an exponential decay function. The movement of the oil slick in the model actually represents the movement of the centroid of the slick. The amount of oil that can be deposited onshore is a function of the area of the shore exposed to tide and wave action. This model is based on a simplified version of Reed et al., (1989).

2.8.5 Sedimentation

This process occurs when the specific gravity of oil increases over that of the river water. Nigerian Oil Spill Model can model sedimentation as a 'constant rate' process. The oil sedimentation algorithm is described in French et al., (1994), ASA (1996) and Kirstein et al., (1985).

2.8.6 Emulsification

Nigerian Oil Spill Model formula on emulsification is based on a function of evaporative losses and change in water content which is based on Mackey et al. (1982).

2.8.7 Advection

This is the main mechanism that governs the drifting of suspended oil and surface of oil slick. The advection of surface oil is caused by combined effects of surface currents and wind drag.

2.8.8 Nigerian Oil Spill Model for biodegradation

Nigerian Oil Spill Model models biodegradation as the oil biodegraded proportional to the initial mass and an empirical decay coefficient.

2.8.9 Proposed biodegradation model

Monod biodegradation kinetics was included in this model. Inhibition of biodegradation by electron acceptors toxic to microorganisms; biodegradation reactions in both the aqueous and sediment phases and first order abiotic decay reactions were features included in this model. The model simulates the biodegradation of crude oil as a pseudo-component using average biodegradation kinetic parameters. Crude oil served as the substrate (carbon and/or energy sources) for microorganisms.

It stimulates the aerobic destruction of the crude oil, the development of an oxygen deficient zone down gradient of the spill. Since nitrate is present in the water, the model can use electron-acceptor inhibition functions to switch off aerobic biodegradation of crude oil where oxygen concentration is sufficiently low. Consumption of electron acceptors (oxygen, nitrate, etc.) and the growth of biomass are also stimulated.

Substrates were biodegraded by microorganisms in the aqueous and sediment phases or by biomass present as micro colonies (Molz et al.*,* 1986).

2.9 Statistical Analysis

Results were subjected to statistical analysis employing the student t-test at 95% and 99% probability levels (Finney, 1978) and least square regression analysis.

3. RESULTS AND DISCUSSION

Table 1 shows some physicochemical parameters of the liquid phase of the Solid Phase Continuous Flow System (SPCFS). The FMEnv (1991) acceptable limits for natural aquatic systems is between 6 -9 and the pH fell with this range. Conductivity is strongly influenced by the concentration of dissolved solids. The conductivity level was within the permissible limits of FMEnv, 1991. The sulphate, nitrate and salinity levels were all within the acceptable limits (FMEnv, 1991).

Table 1. Physicochemical parameters of the liquid phase of SPCFS

Parameters	Values	Methods
pH	7.14	Jenway pH meter (3015 model)
Conductivity(μs/cm)	800	WTW electronic conductivity
Dissolved oxygen(mg/l)	6.80	Azide modification method (APHA,1998)
Sulphate(mg/l)	6.19	Colorimetric method (APHA,1998)
Nitrate(mg/l)	6.53	Spectrophotometric method (APHA,1998)
Salinity(mg/l)	9.75	Argentometric method (APHA,1998)

The results of the percentage decrease of total organic carbon of Bonny light crude, Olive Oil (positive control) and negative control are presented in Figs. 2a, b and c.
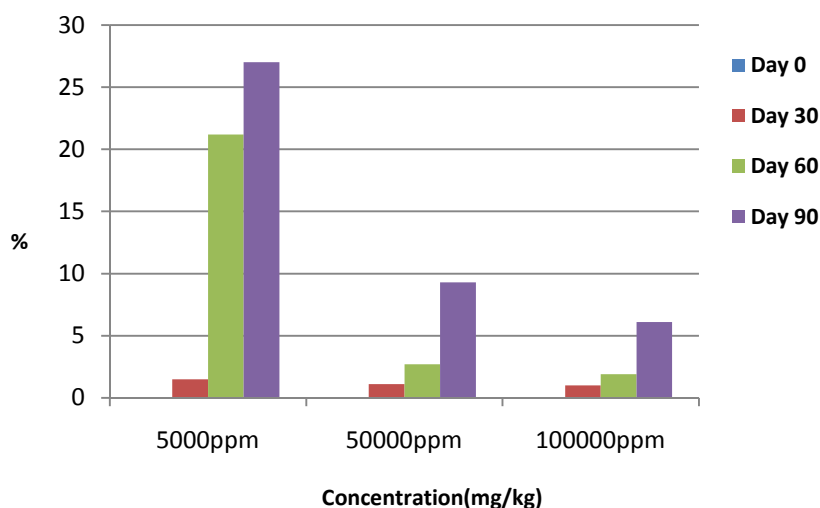

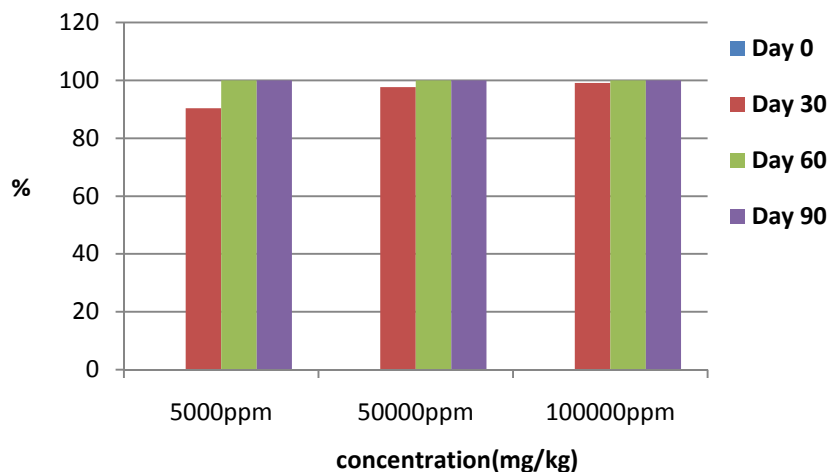**Fig. 2a. Percentage decrease of TOC in bonny light crude oil**

Fig. 2b. Percentage decrease of TOC in olive oil (positive control)
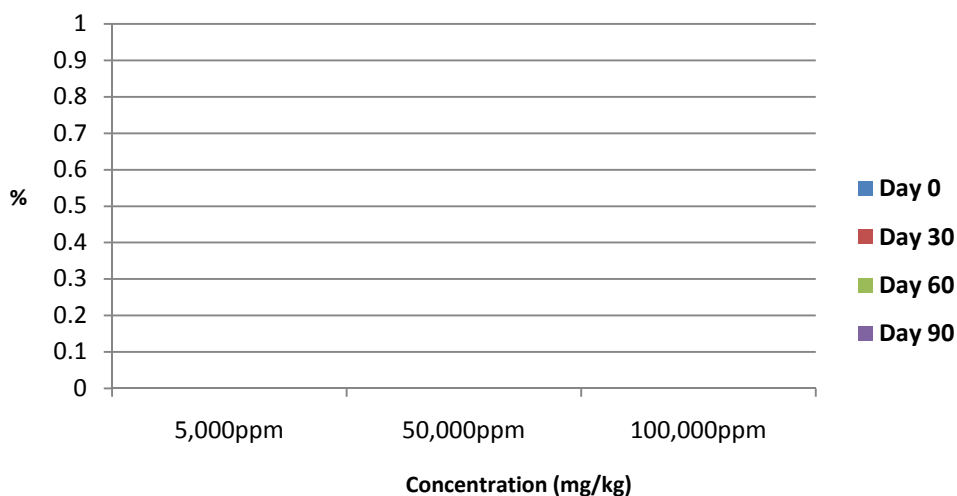

Fig. 2c. Percentage decrease of TOC in negative control

Results showed a significant decrease in the total organic carbon (TOC) at 5% probability level at 5,000ppm. But for the positive control (Olive Oil) by the 90th day for all concentrations, degradation was complete (100%). In the negative control, there was no significant decrease in the percentage of total organic carbon and total petroleum hydrocarbon for the mixture of Bonny light crude oil and sodium azide throughout the degradation period.

The TOC result tallied with the gas chromatographic analysis (total petroleum hydrocarbon) shown in figs 3a-3f. In the test sediment, between day 0 and the 90th day, 30.6% of the hydrocarbon content was biodegraded.100% of the hydrocarbon content in the positive control was biodegraded by the 90th day. In the negative control, by the 90th day, there was no significant hydrocarbon content biodegraded**.**
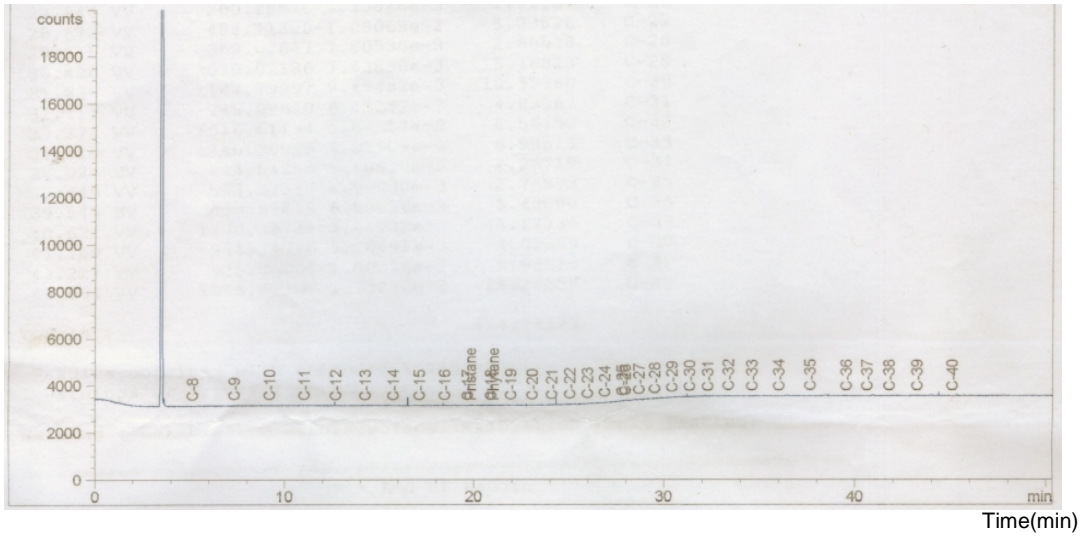
Fig. 3a. Total petroleum hydrocarbon in 5,000ppm of crude oil on day 0
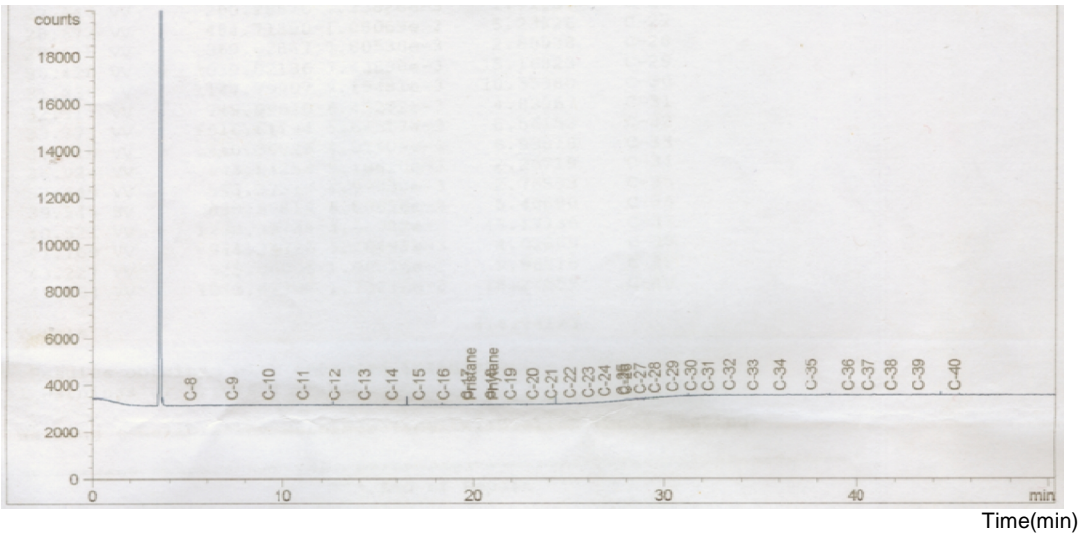

Fig. 3b. Total petroleum hydrocarbon in 5,000ppm of crude oil on day 90.
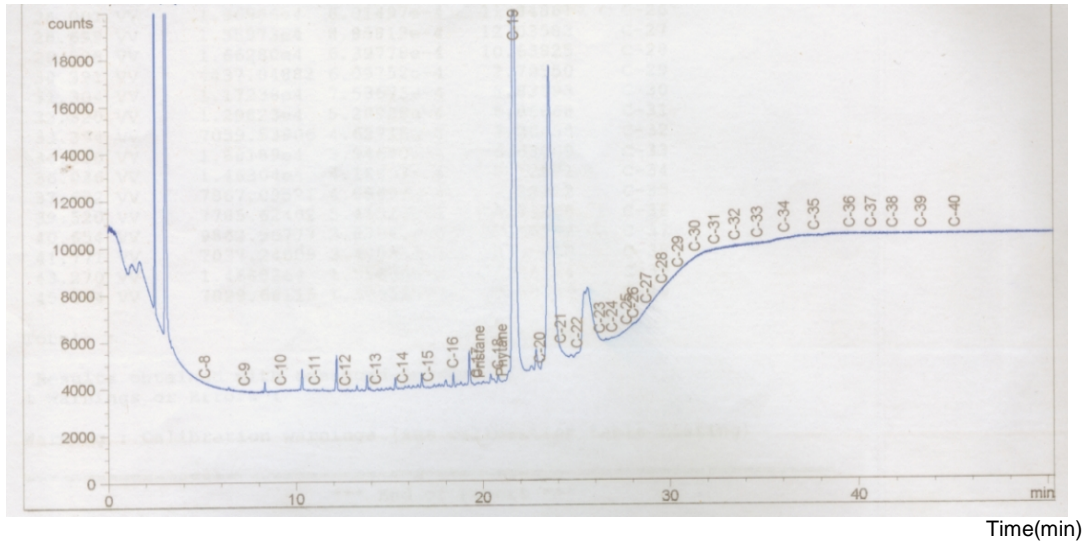
Fig. 3c. Total petroleum hydrocarbon in 100,000ppm of olive oil (positive control) on day 0
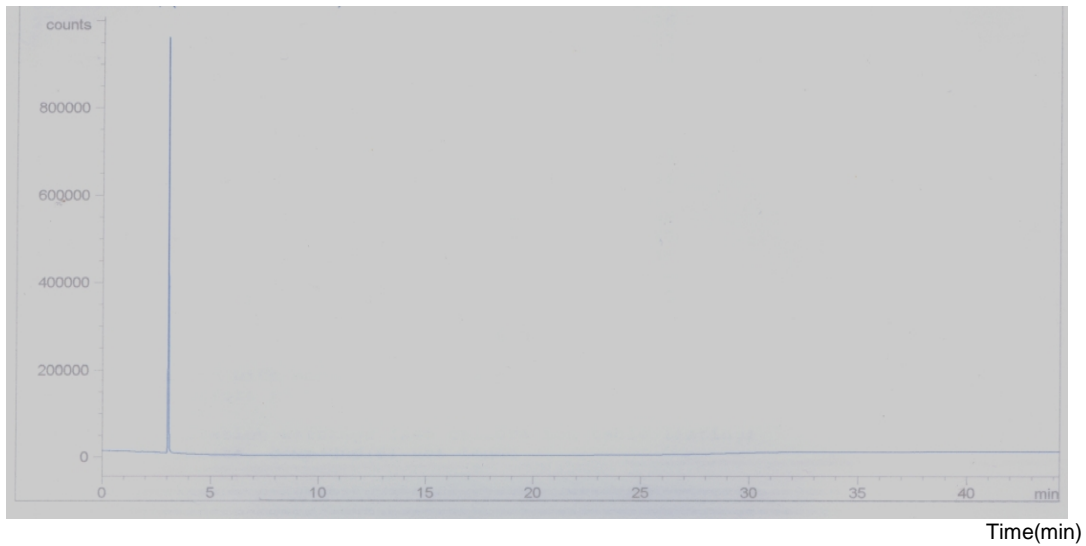

Fig. 3d. Total petroleum hydrocarbon in 100,000ppm of olive oil (positive control) on day 90
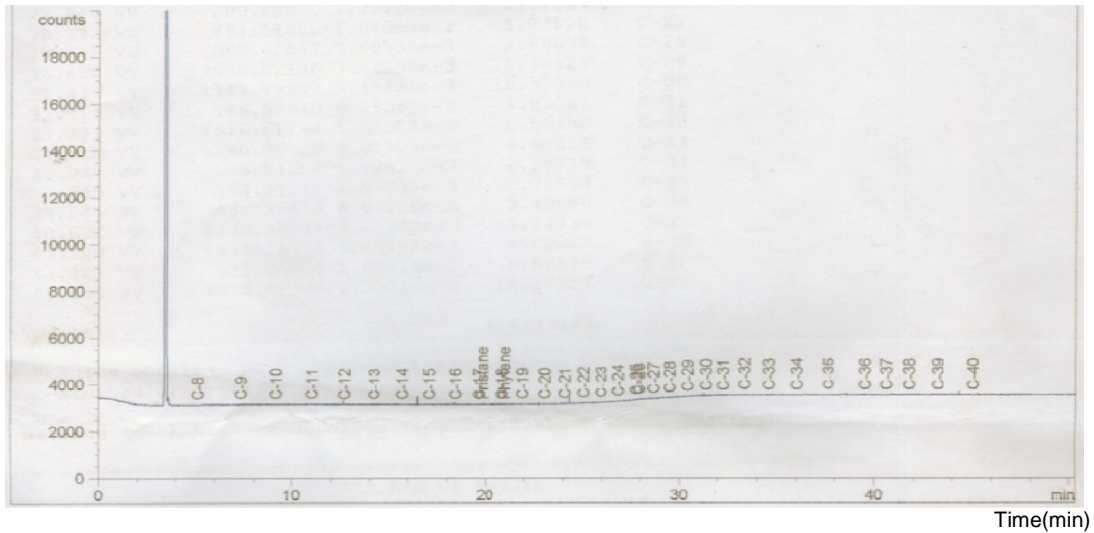
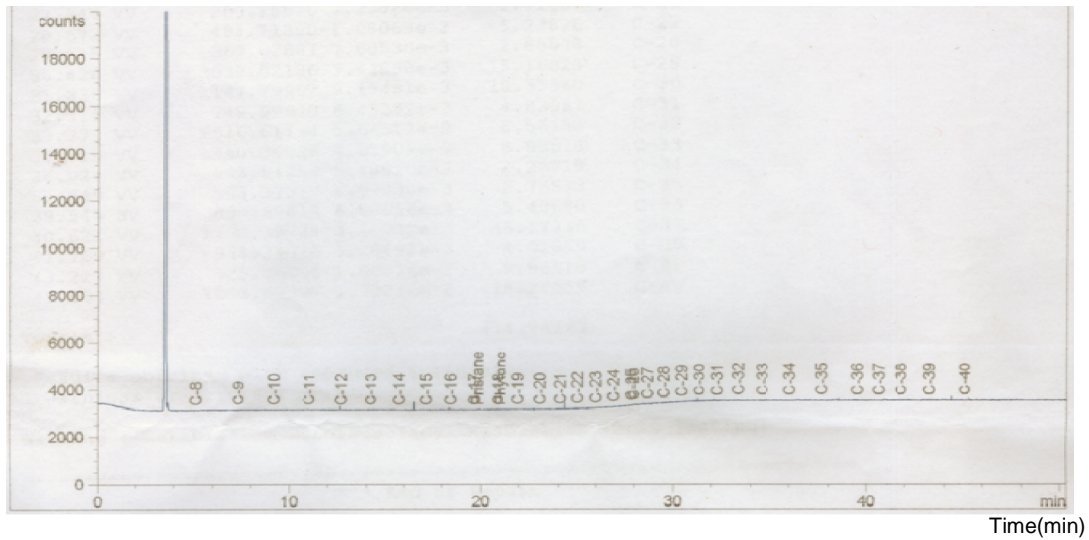**Fig. 3e. Total petroleum hydrocarbon in 5,000ppm of negative control on day 0**

Fig. 3f. Total petroleum hydrocarbon in 5,000ppm of negative control on day 90

Figs. 4a, 4b and 4c show the hydrocarbon utilizing bacteria counts in the sediments incorporated with Bonny light crude oil (test system), olive oil (positive control system) and Bonny light crude oil poisoned with sodium azide (negative control system). The Hydrocarbon utilizing bacteria of a sample represent the fraction of the heterotrophic bacteria that can derive their energy from the oxidation of the hydrocarbon. If the test sample is toxic or contains very little amount of biodegradable organic carbon, the hydrocarbon utilizing bacteria counts would be low (Odokuma and Okpokwasili, 1993, 1997). The Hydrocarbon utilizing bacterial counts were higher in the positive control than in the test sample containing Bonny light crude oil. In the negative control, very low counts were observed due to the toxicity of the sodium azide to the Hydrocarbon utilizing bacteria.
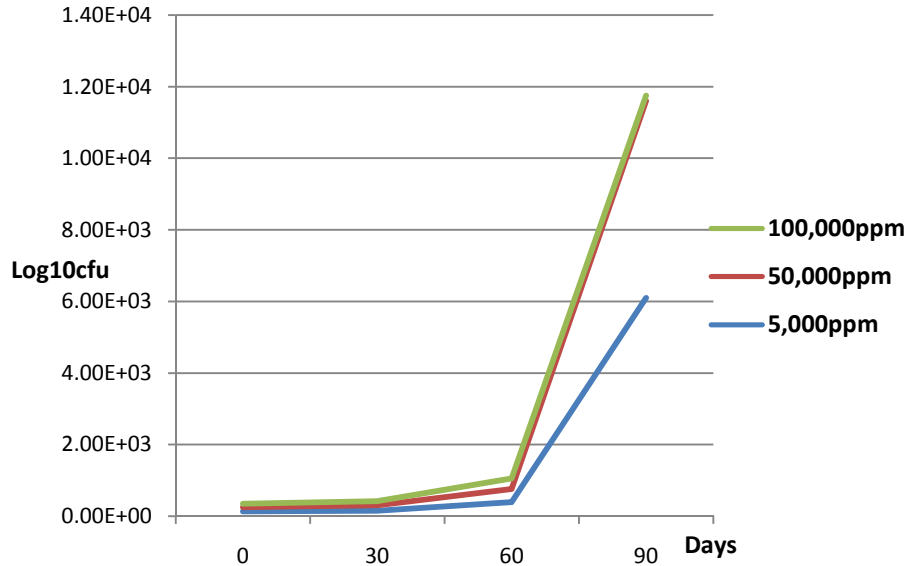
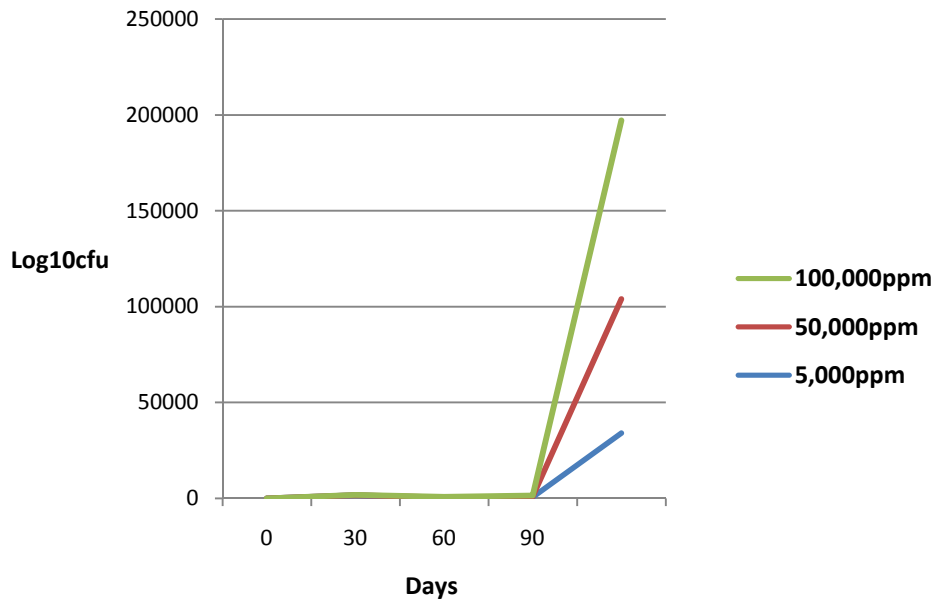**Fig. 4a. Hydrocarbon utilizing bacterial count in the test system**

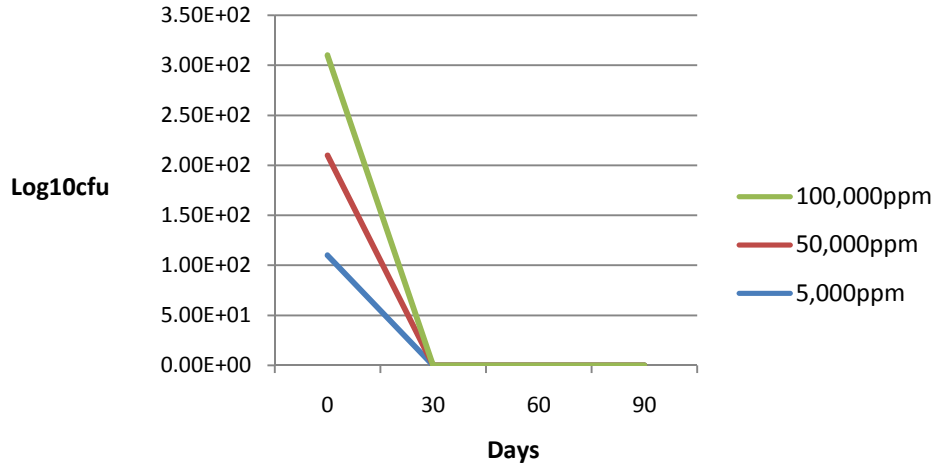**Fig. 4b. Hydrocarbon utilizing bacterial count in positive control system**

Fig. 4c. Hydrocarbon utilizing bacterial count in negative control system

Figs. 5a, 5b and 5c show the Total Heterotrophic bacteria counts in the sediments incorporated with Bonny light crude oil (test system), olive oil (positive control system) and Bonny light crude oil poisoned with sodium azide (negative control system). The total Heterotrophic bacteria of a sample represent the total population of bacteria that can derive their energy from the oxidation of all forms of biodegradable organic matter present in that sample.
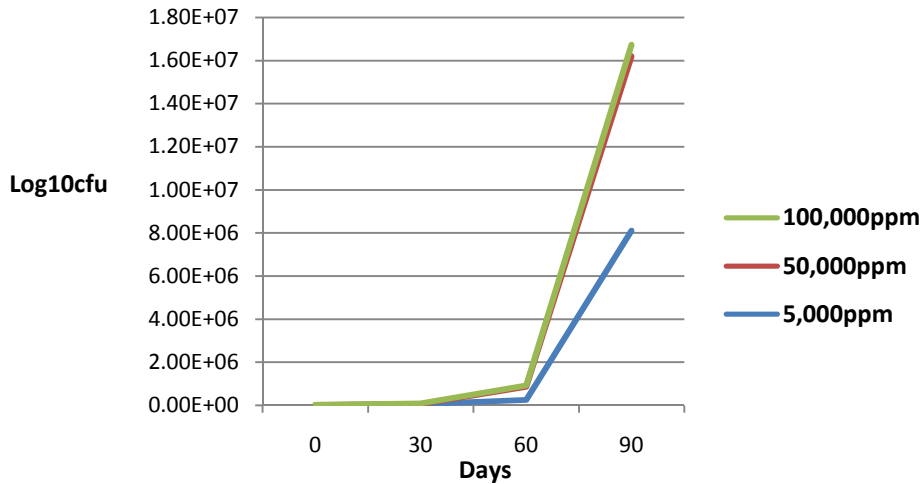

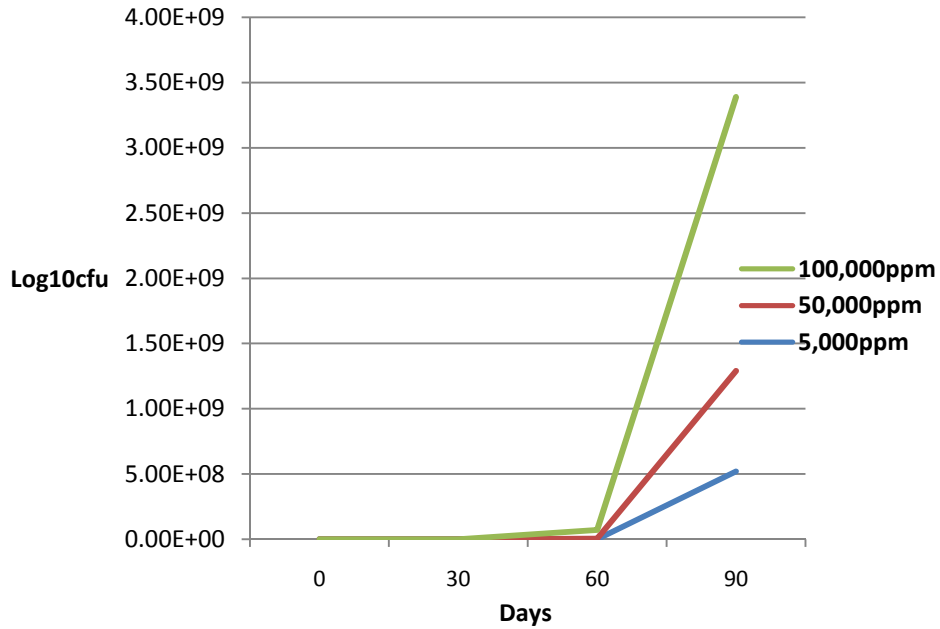**Fig. 5a. Total heterotrophic bacterial count in test system**

Fig. 5b. Total heterotrophic bacterial count in positive control system
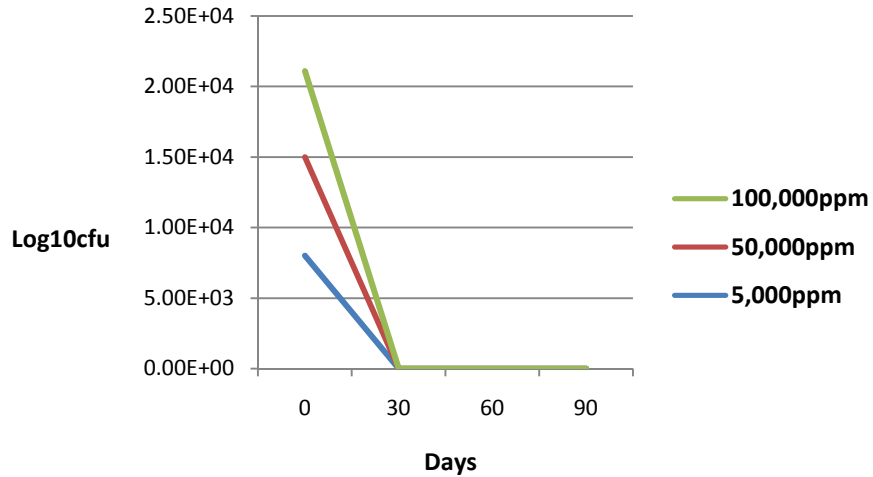

Fig. 5c. Total heterotrophic bacterial count in negative control system

At lower concentrations (5,000ppm) there was significant increase at 5% probability level in the total heterotrophic bacteria (THB) with increasing degradation period in the test system. At higher concentrations, 50,000ppm to 100,000ppm, there was no significant increase in the total heterotrophic bacteria. In the positive control system, there was significant increase at 5% probability level in the THB in all the concentrations (5,000ppm, 50,000ppm and 100,000ppm) with increasing degradation period. In the negative control system, for all the

concentrations, THB was observed only on day 0 and the sodium azide killed the entire microbial flora after then.

Evaporation is a function of many variables. (1) Wind speed at 10m above water surface (2) spill area (3) surface temperature (4) initial vapor pressure of oil among other variables.

$$F = \frac{1}{C}\left[InPo + In\left(CK_E t + \frac{1}{Po} \right) \right] \quad \text{...} \quad (1)$$

Where $F = K_E t$ is the evaporative exposure term which varies with time and environmental conditions
$K_E = K_M A V_m (RTV_o)$;
$Km = 0:0025\ U_{wind}^{0.78}$ is the mass transfer coefficient in m/sec.
U_{wind} is the wind speed in m/s
A = Spill area in m^2
V_m = Molar Volume in cubic meters per mol.
R = Gas constant, 82.06×10^{-6} atm m^3 mol^{-1} K^{-1}
T = Surface temperature of oil in degree Kelvin which is generally close to the ambient temperature in degrees Kelvin
Po=Initial vapor pressure
Vo = Initial Spill volume in cubic meter.

The initial vapor pressure, Po in atm at the temperature, T_E is
In Po = 10.6 (1- $^{To}/_{TE}$)
Where To = Initial boiling point in ^0K, the constant, C can be determined by the relationship,
C = constant. C value and initial boiling point, T_o are calculated at $T_E = 283^0K$ for various types of oils.

Through curve fittings (numerical analysis) C and T_o at T_E = 2830k can be calculated C = 1158.9 API$^{-1.1435}$
$T_o = 542.6 - 30.275\ API + 1.565\ API^2 - 0.03439\ API^3 + 0.0002604\ API^4$.

The results in Figs. 6a and b show the evaporation model with area of spill and time. Evaporation rate was 0.02469% at 900seconds.

Dissolution is a function of oil slick area, dissolution mass transferability and oil solubility in water.

Total Dissolution Rate, N is calculated by:

$$N=KAsS \quad \text{...} \quad (2)$$

Where N is the total dissolution rate of the slick in g/hr.; K is the dissolution mass transfer coefficient in m/hr., A_s is the slick area in m^2 and S is the oil solubility in water. The result in Fig. 7 shows dissolution with time.

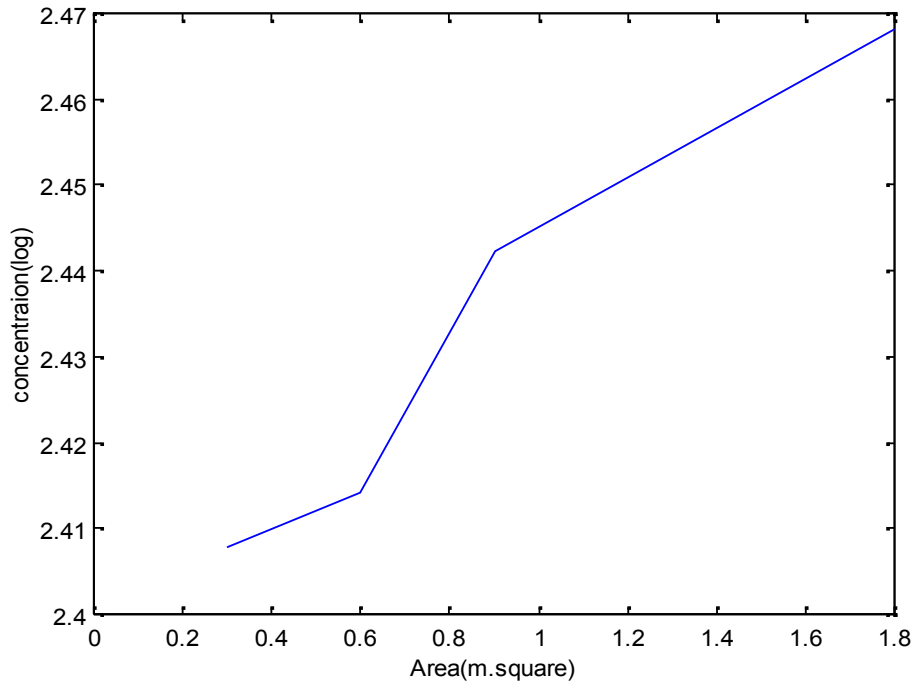In our study, the rate of dissolution at 900 seconds was 0.00357%.

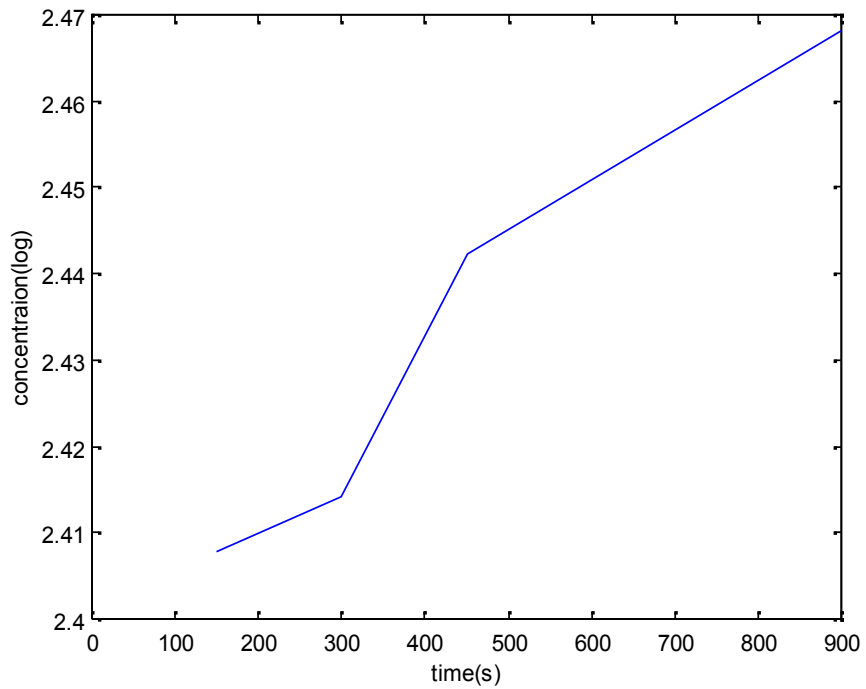**Fig. 6a. Evaporation model showing rate of evaporation with area of spill**

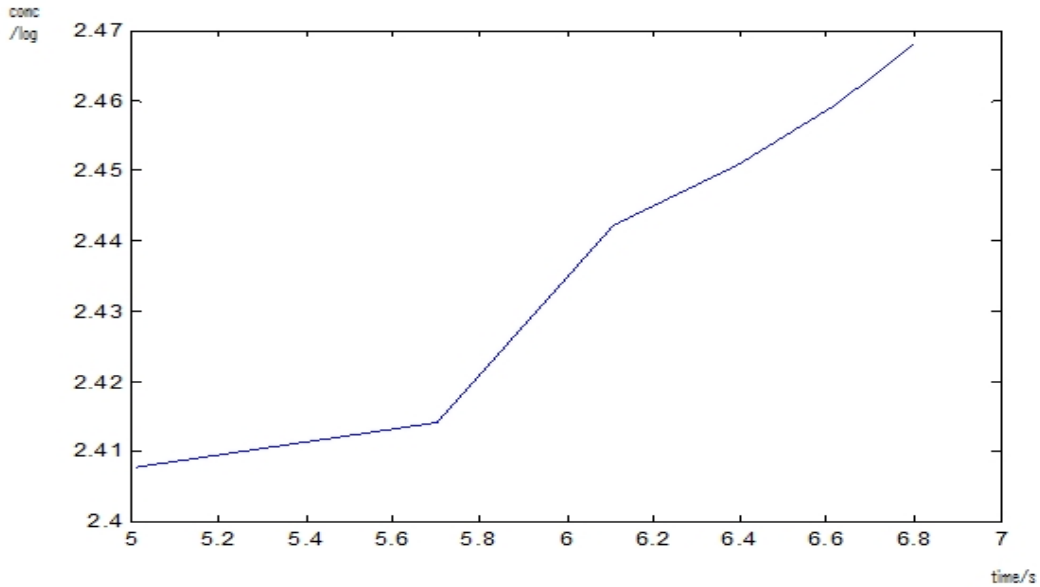**Fig. 6b. Evaporation model showing rate of evaporation with time**

Fig. 7. Dissolution model showing rate of dissolution with time

In mechanical Spreading, 3 phases are considered during the spreading of the oil The slick. Spreading is assumed to be radial.

Spreading phase	Formulae (radial)	
Gravity – Inertia	$1.14\left(\Delta g \forall t^2\right)^{\frac{1}{4}}$	.... (3)
Gravity - Viscous	$0.98\left(\Delta g \forall^2 t^{\frac{3}{2}} V^{-\frac{1}{2}}\right)^{\frac{1}{6}}$	.... (4)
Surface tension - Viscous	$1.60\left(\dagger^2 t^3 p^{-2} w V^{-1}\right)^{\frac{1}{4}}$	.... (5)

$= 1 - (e_o/e_w)$
V = Kinetic Viscosity (constant) 1.14×10^{-6} $m^2 S^{-1}$ or stoke (st)
g = 9.8m/s
t = time of spill
$\forall$ = total volume of crude oil
e_w = water density (1.0)
e_o = oil density
= time step

The result in fig. 8 shows the initial spread of oil. The overall surface area of the slick increased with time. Jeffery, 1973; Clark and Macleod, 1977, Shen et al., 1987 reported an increase in the overall surface area of the slick during the early stages of an oil spill in water, thereby enhancing mass transfer via the evaporation and dissolution processes.
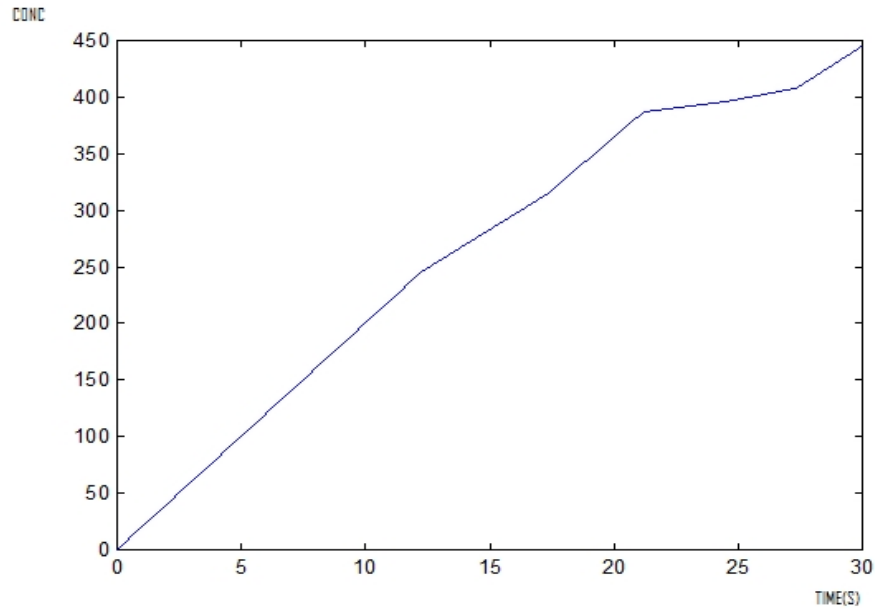
Fig. 8. Mechanical spreading model showing initial spread of oil slick with time

The equation for emulsification is presented below but no results are achieved due to lack of data necessary to give information about it. Nigerian Oil Spill Model's formulation on emulsification is based on a function of evaporation losses and change in water content. It is as follows:

$$Y = C_3 \left[1 - \exp\left\{ \frac{-2 \times 10 - 6}{C_3 \{1 + W\} 2t} \right\} \right] \quad \text{... (6)}$$

Where;

Y =   Fractional water content
C_3=   Mousse viscosity constant (final fraction water content) 0.7 for crude oils.
W = Wind speed (m s-1).

Mousse formation causes an increase in viscosity which may be computed by the Mooney equation:

$$\sim = \sim_0 \exp\left[\frac{2.5Y}{\{1 - C_3 Y\}} \right] \quad \text{.. (7)}$$

Where; μ_0 = Parent oil Viscosity (cP). Buchana et al. (1988) calculates the parent oil viscosity by μ_0 =224A ½ where A = Asphaltene content (%).

The equation for shoreline deposition is presented below, but no results are achieved due to lack of data necessary to give information about half – life of the shoreline in which the oil that reaches the coastline is deposited.

$$\frac{\Delta\forall_b}{\forall_b} = 1 - 0.5\Delta + /\} \quad\text{.. (8)}$$

Where,

$\Delta\forall_b$ = Vol. of beached oil entrained into the sea during each of time step.

$\forall_b$ = volume of oil on the beach.

= half-life.

= time step.

The equation for advection-diffusion (Venkatesh, 1988) is presented below but no results are achieved due to lack of data necessary to give information about it. The diffusive part of the equation represents spreading of the oil itself and the convective term represents the advection of oil by current and winds (Paladino et al., 2000). The governing equations for the motion and spread of the oil on the surface water can be written as a conventional advection diffusion equation:

Model Equation for Advection – Diffusion;

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(U_S C_S) + \frac{\partial}{\partial y}(V_S C_S) = \frac{\partial}{\partial z}\left(Kx\frac{\partial C_S}{\partial x}\right) + \frac{\partial}{\partial y}\left(Ky\frac{\partial C_S}{\partial y}\right) +$$
$$\left(\Gamma_1 V_b C_v - {}_w C_y + Kz\frac{\partial C_S}{\partial z}\right) - xC_S - S_C - S_d + M_S(x,y) - D_S(x,y) \quad\text{............................ (9)}$$

Where x, y, z and t are space and time variables; z = vertical co-ordinate measured downward from the water surface; Cs = local oil concentration on water surface layer per unit area, C_v = the volumetric oil concentration of oil in the suspended layer per unit; volume of water; U_s and V_s are the components of different velocities in x and y directions respectively; kx, ky and kz are the diffusion coefficients in the x, y and z directions respectively; $_1$ = coefficient representing probability in oil droplet reaching the water surface; V_b = the buoyant velocity of suspended oil parcels, = coefficient describing the rate at which the surface oil is dispersed into the water column, S_d and S_E are the rate of dissolution and evaporation per unit area of the surface slick respectively; Ms = effect on the distribution of surface oil by shoreline disposition.

Sedimentation is usually not important for mass balance calculations unless the concentration of suspended matter is high (> 100mg/l). Nigerian Oil Spill Model can model sedimentation as a 'constant-rate' process.

Nigerian Oil Spill Model formulation on biodegradation is based on the initial mass of the oil and an empirical decay coefficient which is based on a first order decay process.

$$-\frac{dm}{dt} \Gamma t$$

$$-\frac{dm}{dt} = kt$$

$$m = (m_0)\exp(-kt) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (10)$$

Where: m = Mass of the oil
m_0 = Initial Mass of the oil
k = Empirical decay coefficient
t = Time.

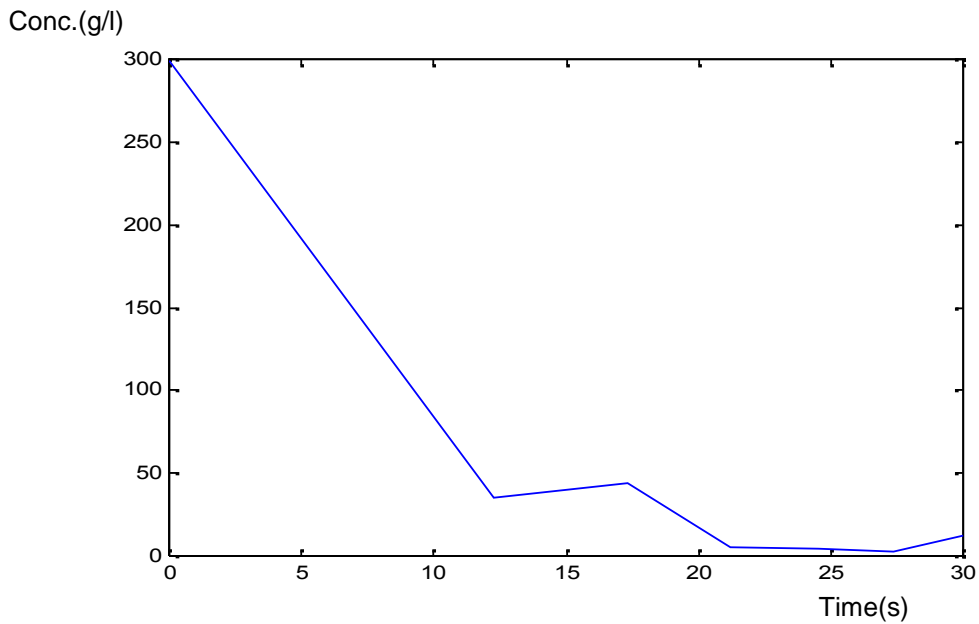Figure 9 shows NOSM followed the first order decay pattern.

Conc.(g/l)

Fig. 9. NOSM showing only reduction of substrate with time

Fig. 10 shows the conformity of our input data to NOSM in fig. 9. It is the modeling of 1st order kinetic derived from NOSM expression of biodegradation. It followed the normal course of the first order decay pattern which shows the substrate (crude oil) as the only important factor in biodegradation with time. It is over simplistic because the total biomass (microorganisms) and involvement of electron acceptors which are reflections of natural systems were not taken into cognizance.
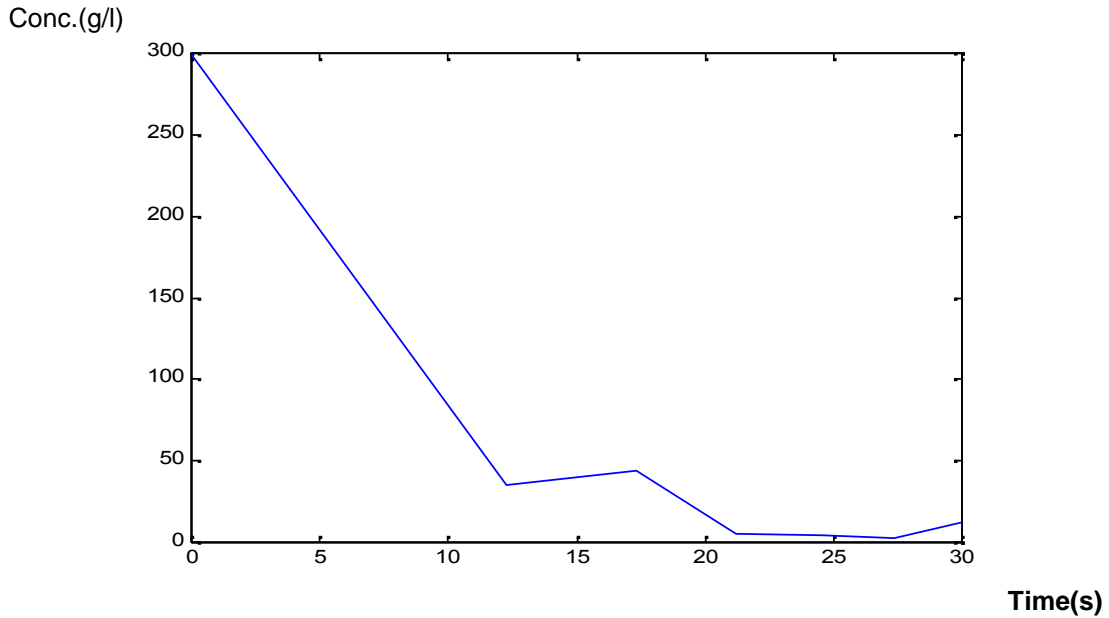
Conc.(g/l)

Time(s)

Fig. 10. Modeling of 1ˢᵗ order Kinetic derived from NOSM showing only reduction of substrate with time

Biodegradation is the major fate of oil spill (Mackay and McAuliffe, 1988), hence, a higher order model that takes into cognizance the total biomass of microorganisms and the electron acceptors involved in biodegradation is required.

The proposed biodegradation model is a higher order model as follows:

Substrate loss in bulk fluid

$$\frac{\partial C_i}{\partial t} = \sum_{k=1}^{X_k} \frac{C_i}{\left[\sim_{\max} X_k \left(Ks\left(1 + \sum_{j=1}^{X_k} \frac{C_i}{Ks}\right) + C_i\right)\right]}$$

Substrate loss in biomass

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{X_k} \left(\frac{-BX_K}{m(C_1 - C_2)}\right) - \sum_{j=1}^{Xs} \left(\sim_{\max} \left(\frac{C_i}{K_s\left(1 + \sum \frac{C_i}{Ks}\right)}\right)\right)$$

Where:
C_1 = Concentration of Species in the bulk liquid (Mass, C/Volume of aqueous phase)
X_k = Concentration of biomass

Xs = Concentration of substrate
C_1 = Initial Concentration of crude oil
C_2 = Final Concentration of Crude oil
Ks = Monod half Saturation Constant
m = mass of single colony (mass/colony)
t = time

Greek letters
μ_{max} = Monod maximum growth rate
   = Surface area of a single bacterial colony available for mass transfer

Subscripts
i = substrate
j = electron acceptor
k = biological species
Subscripts, i,j, k refers to metabolic combinations of substrate, electron acceptors and biological species.

From our study, Fig. 11a shows a reduction of the concentration of substrate with time. The rate of destruction of the crude oil by the microorganisms' occurred as there was a steady drop in the substrate concentration with time. Figure 11b shows a slight reduction of dissolved oxygen which indicates the use of oxygen for the growth of the biomass. The microorganisms were utilizing the oxygen in the environment with increase in time which shows the presence of aerobic microorganisms. Fig. 11c shows the increase of the biomass with time as they utilized the substrate and electron acceptors until 10minutes when there was slight decline in the growth of the microorganisms (Molz et al., 1986). Fig. 11d shows slight increase in nitrate concentration until 8 minutes when there was reduction all through. Nitrate, an electron acceptor was utilized by some microbes (facultative anaerobes) for growth especially when there was a drop in oxygen.
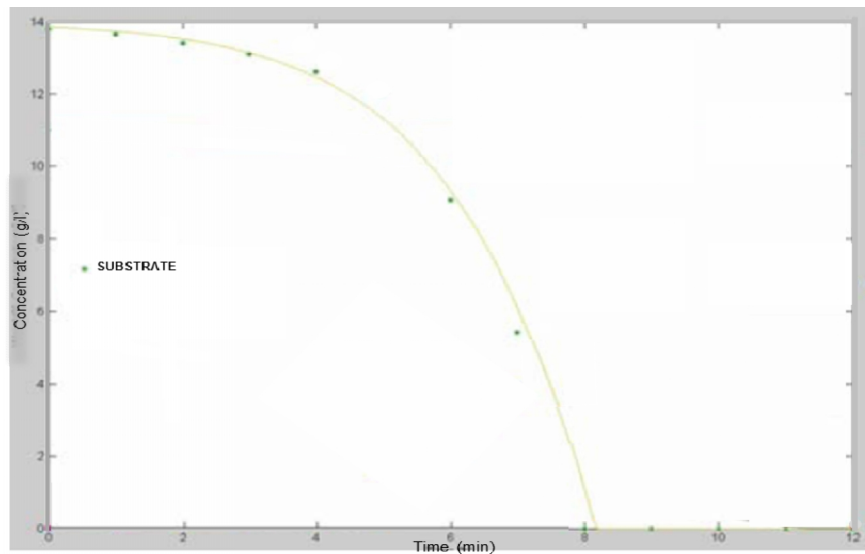

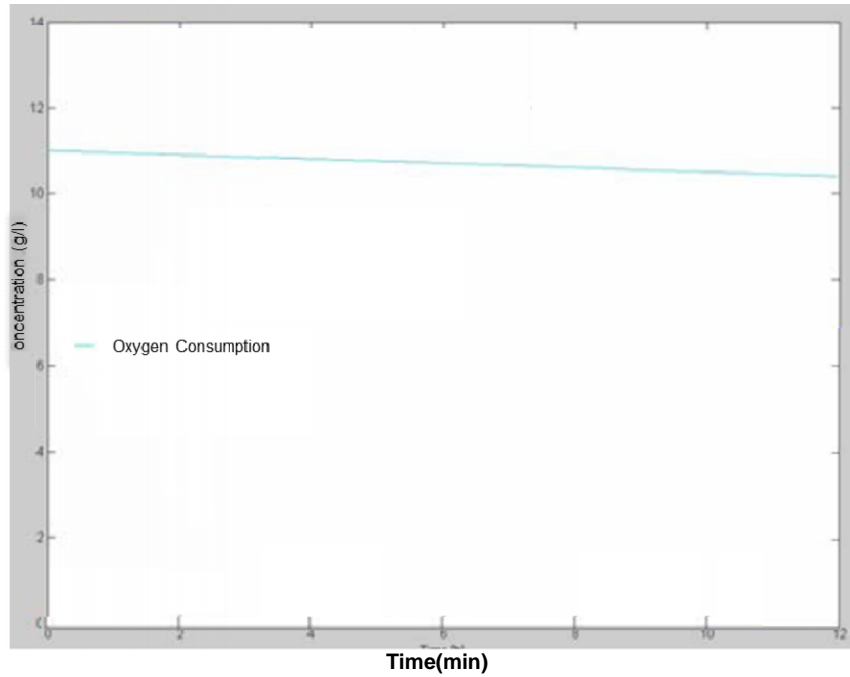**Fig. 11a. Proposed biodegradation Model showing Substrate –time graph**

Fig. 11b. Proposed biodegradation Model showing Dissolved Oxygen –time graph
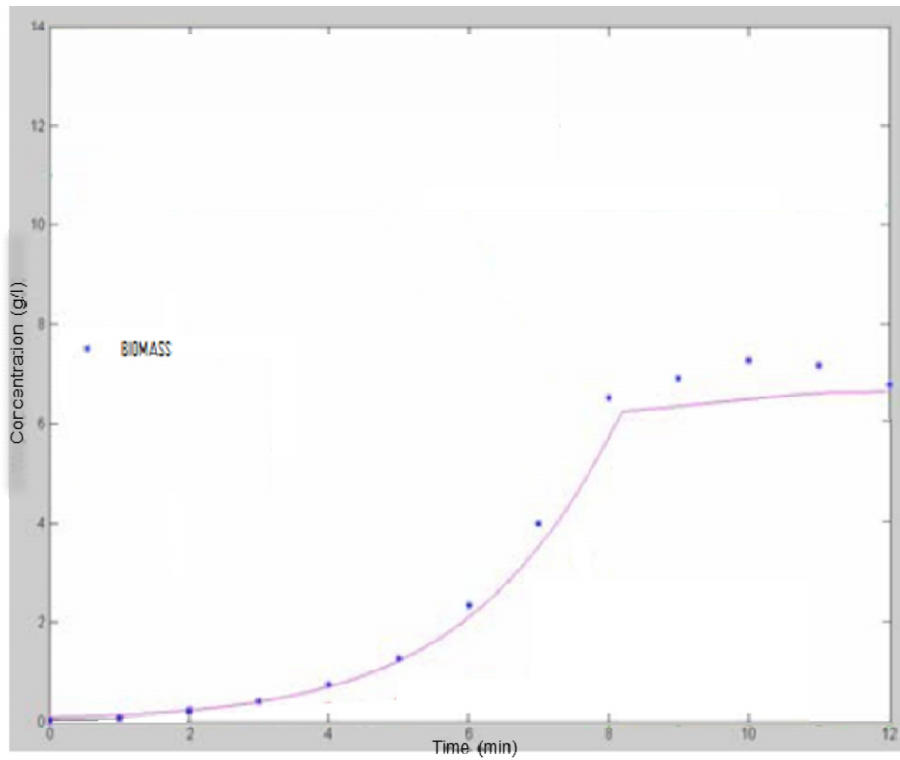

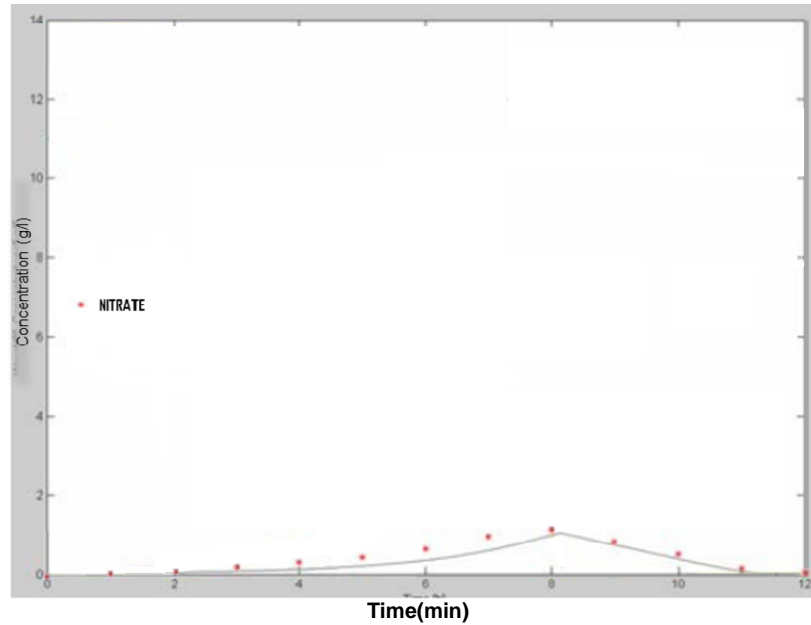**Fig. 11c. Proposed biodegradation model showing biomass- time graph**

Fig. 11d. Proposed biodegradation model showing nitrate-time graph

Fig. 12 shows the proposed biodegradation model coupled with substrate, biomass, nitrate and dissolved oxygen. From the proposed model, it was discovered that biodegradation augments when there was increase in the number of bacteria population. This was quite conspicuous in the delay of crude oil breakdown that occurred because the microorganisms that degrade the substrate must grow first of all and increase in number. When the biomass was sufficient, the crude oil was quickly biodegraded. This coupled proposed model is a more realistic picture of natural systems because of the involvement of the major factors involved in biodegradation (microorganisms and electron acceptors).
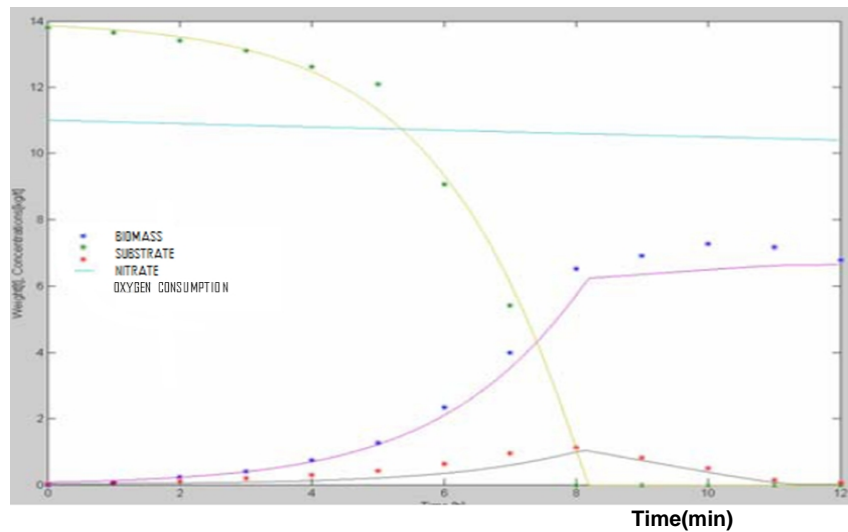

Fig. 12. Proposed biodegradation model showing coupled substrate, dissolved oxygen, biomass and nitrate.

4. CONCLUSION

The modification of the biodegradation component in the NOSM shows the involvement of microorganisms and use of electron acceptors (major factors of biodegradation) which is a reflection of natural systems. This proposed model addresses the limitation in NOSM where oil biodegraded is proportional to the initial mass of oil and an empirical decay coefficient.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

American Public Health Association. (1988). Standard Methods for the Examination of water and waste water 16th (ed). American Public Health Association, New York.

Applied Science Associates Inc. (ASA). (1996). Technical Manual for spill impact modeling (SIMAP), Version W1.0.

Atlas, R.M. (1995). Petroleum biodegradation and oil spill bioremediation. Marine Pollution Bulletin, 31, 178-182.

Clark, R.B. (1982). Biological effects of oil pollution. Wat. Sc. Tech., 14, 1185 – 1194.

Cohen, Y.D., Mackay, W., Shiu, Y. (1980). Mass transfer rate between oil slick and water. The Canadian Journal of Chemical Engineering, vol. 58.

Clark, R.C., Macleod, W.D. (1977). Inputs, transports and concentrations. In effect of petroleum on Arctic and subarctic marine environments and organisms. Vol. 1: Nature and Fate of Petroleum, ed. D.C. Mulins, Academic Press. Pp. 91-222.

de Blanc, P.C.K. Sephernoori, G.E, Jr., Mc Kinney, D.C. (1996). Investigation of numerical solution techniques for biodegradation equations in ground water flow model, proceedings of the XI international conference on computational methods in water resources, Cancun, Mexico, July 22 – 26, (1996).

Department of Petroleum Resources. (1997). Guidelines for the laboratory determination of biodegradability of chemical under Nigeria conditions. DPR draft Biodegradability Test Protocol.

Fay, J.A. (1971). Physical processes in the spread of oil on a water surface, in proceedings of the joint conference on prevention and control of oil spill. American Petroleum Institute, P. 463 – 467.

Finney, D.J. (1978). Statistical methods in biological assay 3rd (ed). Charles Griffin. London. PP 1 – 252.

French, D. Howlett, Mendolsohn, D. (1994). Oil and chemical spill impact model system descriptions and application, P 815-835 in: Seventeenth Arctic and Marine Oil Spill Prog Technical Seminar vol. 2.

Hang, O.P., Evensen, Martinsen, E.A. (1989). Oil models for the South China Sea, Technical Report No. 70. Det Norslse Meterorologiske Institutt.

Heitkamp, M.A., Johnson, B.T. (1984). Impact of an oilfield effluent on microbial activities in a Wyoming River. Can. J. Microbiol. 30, 786-792.

Horowitz, A., Atlas, R.M. (1977). Response of microorganisms to an accidental gasoline spillage in an Arctic freshwater ecosystem. Appl. Environ. Microbiol., 33, 1252-1258.

Jeffrey, P.G. (1973). Large scale experiments on spreading of oil at sea and its disappearance by natural factors, Proc. Joint EPA, AI, USCG conf. on prevention and control of oil spills. Pp 469-474.

Kirsten, B., Clayton, J.R., Clary, C., Payne, T.R., McNabb, D., Fauna, G., Redding, R. (1985). Integration of suspended particulate matter and oil transportation study, Mineral Mgt. services, Anchorage, Alaska.

Mackay. D., Paterson, S., Madeau, S. (1980). Calculation of the evaporation rate of volatile liquids. In Proceeding: National Conference on control of Hazardous Material Spills, Louis Ville Kentucky, P. 361-368.

Mackey, D., Buist, J., Mascarehas, R., Paterson, S. (1980a). Oil Spill Processes and Models. Report E-8 Environment Protection Services, Ottawao Canada.

Mackey, D.S., Paterson, Trudel, K. (1980b). A mathematical model of oil spill behavior. Department of Chemical and Applied Chemistry, University of Toronto, Canada.

Mackey, D., Shiu, W.Y., Hossain, K., Stiver, W., McCurdy, D., Peterson, S. (1982). Development and calibration of an oil spill behavior model, report NO. CG – D – 27-83, USA Coast Guard, Research and development Centre, Croton, CT.

Mackey, D., Mc Auliffe, C.D. (1988). Fate of hydrocarbons discharged at sea. Oil Chem. Pollut., 5(1), 1-20.

Mills, A.L., Brevil, C., Colwel, R.R. (1978). Enumeration of Petroleum Degrading Marine and Estuarine Micro Organism by the most Probable Number Method Candian journal of microbiology, 24, 552-557.

Molz, F.J., Widdowson, M.A., Benefield, L.D. (1986). Simulation of microbial growth dynamics couple to nutrient and oxygen porous media. Water Resources Research. 22(8), 1207 – 1216.

Ntukekpo, D.S. (1996). Spillage: Bane of petroleum, ultimate water technology & environment.

Odokuma, L.O., Okpokwasili, G.C. (1993). Seasonal Ecology of hydrocarbon – utilizing microbes in the surface waters of a river. Environmental Monitoring and Assessment 27, 175-191.

Odokuma, L.O., Okpokwasili, G.C. (1997). Seasonal influences of the organic pollution monitoring of the New Calabar River. Nig. Environmental Monitoring and Assessment, 45, 34-56

Okpokwasili, G.C., Amanchukwu, S.C. (1988). Petroleum hydrocarbon degradation by *Candida* species. Environ. Int., 14, 243-247

Paladino, E.E., Maliska, C.R. (2000). Mathematical modeling and numerical simulation of oil spill trajectories on the sea, Fed. Univ. of Santa Carina, Brazil.

Reddy, G.S. (1997). Aspects of a computational model for predicting the flow and pollutant transport in Rivers, Estuaries and Seas, Proceedings of the 3rd International conference on computer modeling of seas and coastal regions (COASTAL ENGINEERING 97) Lacoruna, Spain.

Reddy, G.S. and Brunet M. (1997). Numerical prediction of oil slick movement in Gabes Estuary. Transoft International, EPINAY/SEINE, Cedex, France.

Reed, M.E., Gundlach, Kana, T. (1989). A coastal zone oil spill model: development and sensitivity studies. Oil and Chem. Pollution, 5, 411-449.

Rheinheimer, G. (1991). Aquatic micro biology 4th (ed). John Wiley and Sons, New York.

Shen, H.T., Yapa, P.D., Petroski, M.E. (1987). A simulation model for oil slick transport in lakes. Water Resources Research, 23(10), October, 1949-1957.

Stiver, W., Mackey, D. (1984). Evaporation rate of spills of hydrocarbon and petroleum mixtures: Evaporation science and technology. vol. 18, American Chem. Society, Washington, D. C. Pp. 834 – 440.

Tkalich, P., Huda, M.K., Gin, K.H. (2003). A multi phase oil spill model. Journal of Hydraulic Research, 41(2), 115 – 125.

Venkatesh, S. (1988). The oil spill, behavior model of the Canadian Atmospheric Environment Service, p+ 1. Atmosphere Ocean, vol. 26, Pp. 93 – 108.