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EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF CRUDE OIL PHYSICAL PROPERTIES ON ITS DIFFUSION RATE IN SOIL MEDIUM

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ABSTRACT

In this work, the effects that crude oil kinematic viscosity (ratio of dynamic viscosity to density) had on the longitudinal and vertical diffusion rate of crude oil once spilled onto soil medium had been advanced. Six crude oil of varying viscosity obtained from different oil facilities in Nigeria's Niger Delta were spilled onto loamy-sand soil. The result of the study shows that EG-3 crude oil with the lowest kinematic viscosity (0.0526 m^2/s) exhibits the highest diffusion rate as a result of its low sorptive capacity in the soil tested, while UT crude sample with the highest kinematic viscosity (0.4392 m^2/s) exhibits the lowest diffusion rate. The longitudinal diffusion rate was almost negligible as it is controlled purely by molecular diffusion. The vertical diffusion rate of all crude oil investigated was significant as a result of advective flow in addition to diffusive flow. Correlation models were developed from the experimental result as function of crude oil kinematic viscosity. The correlation model equations are:

Longitudinal - $$L(x,t) = \left(1.6482 - 1.789\left(\frac{\mu_p}{\rho_p}\right)\right)t^{0.38}$$

Vertical - $$L(y,t) = H(y,t) = \left(2.7706 - 2.6812\left(\frac{\mu_p}{\rho_p}\right)\right)t^{0.56}$$

These models when incorporated into conventional soil transport equations can correctly predict the diffusion rate of crude oil of varying physical properties in soils of known physical properties.

INTRODUCTION

Spilled crude oil, like any other contaminant, participates in various chemical, physical and biological transformation processes in the receiving media. These transformations need to be considered during soil and groundwater analyses. The presence of spilled petroleum and other contaminants in the groundwater in many agricultural areas of the Niger Delta has raised concerns on the hazardous effects of such compounds on human health and the quality of the environment (Sprague *et al*. 2000; Ayotamuno and Kogbara, 2007). The transport/diffusion rate of spilled crude oil in soils is a function of the properties of the soil, the chemistry of crude oil and its characteristics in liquid phase (Laird *et al.* 1994; Uzoije, 2008; Oghenejoboh *et al*. 2009). Contaminants that are not soluble in water are termed non-aqueous phase liquids (NAPLs). Those with a density less than unity are known as light non-aqueous phase liquids (LNAPLs), while contaminants with

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density greater than unity are referred to as dense non-aqueous phase liquids (DNAPLs) (Palmer and Johnson, 1989a; Palmer and Johnson, 1989b; Wilson *et al*. 2001; Rahbar, 2003). Crude oil belongs to the family of LNAPLs. Though, immiscible with water, petroleum does slowly dissolve in water. As a result of this slow dissolution of petroleum in water, there is mass transfer across the existing interfaces (Grathwohl, 2000; Robinson, 2003). The slow dissolution of spilled petroleum in soils poses long-term danger to groundwater source, hence the need to study the fate and transport of spilled petroleum in soils medium (Khachikian and Harmon, 2000; Oghenejoboh *et al*. 2008a; 2008b; 2009)

Physical and chemical properties of spilled crude oil strongly influence its fate and transport in soils (Uzoije, 2008). These properties affect its distribution among the four phases in which it exist in soil (De Jonge *et al*. 1997; Oghenejoboh *et al*. 2009). The four phases are: gaseous (vapour) phase, aqueous (dissolved in pore water) phase, solid (adsorbed on the surface of particles) phase and free petroleum pool. The most significant of these properties are the crude oil viscosity and density (Omole *et al*. 2009). Viscosity, which describes a fluid's resistance to flow, is caused by the internal friction developed between molecules within the fluid. For most practical applications, viscosity can be considered to be a qualitative property in that, the higher a fluid's viscosity, the more resistive it is to flow. Fluids with low viscosity are often referred to as "thin", while higher viscosity fluids are described as "thick". Thinner fluids move rapidly through the subsurface than thicker fluids. Density, on the other hand, refers to the mass per unit volume of a substance and is often presented as specific gravity (ratio of a substance's density to that of some standard substance, usually water). The densities of all Nigerian crude petroleum are generally less than 1.0 gm/cm^3 and typically range between 0.78 to 0.98 g/cm3. Density varies as a function of several parameters, most notably temperature. However, in most subsurface environments, the temperature (and hence the density) remains relatively constant. It is important to know the density of petroleum at a spill site, as this is usually required for estimating the volume of petroleum spilled.

In this paper, experiments are carried out to determine simultaneous diffusion rate of six crude petroleum samples of different physical properties obtained from the Niger Delta fields of Nigeria in top (loamy-sand) soil, the results of the experiments were correlated with the crude oil kinematic viscosity. These correlation models can be incorporated into soil transport equations in developing predictive models for the simulation of diffusion of crude petroleum once spilled into soil medium.

MATERIALS AND METHODS

SOIL ANALYSIS

The soil sample used for the experiment was obtained from a cassava farmland in the oil producing community of Eket in Akwa Ibom State of Nigeria's Niger Delta. Physical properties of the soil analysed were: total porosity, texture, pH, organic matter content and water content. Using the result obtained from the soil texture analysis, the soil was then classified by means of the soil triangle. The soil texture was determined using the hydrometer method of Day (1965). The total soil porosity was calculated from measured values of the bulk density and particle density

where η is soil total porosity, ρ_b is $\left(i.e.\ \eta = 1 - \frac{\rho_b}{\rho_p}\right)$ ty and ρ_p is the particle density. The organic matter content was determined using the Walkley-Blake method (Nelson and Summers, 1982). The soil pH was measured using a Pye Unicam model MK2 pH meter from a 1-5 soil/water weight solution, while the water content was determined by placing the saturated soil sample in a forced air oven at 105 ^oC until a constant weight of dried soil was obtained. The water content of the soil was then calculated as the difference between the weights of the saturated and dried soils.

CRUDE OIL ANALYSES

Six crude oil samples - Afiesere (AF), Utorogu (UT), Eriemu (ER), Obigbo North (OBN), Evwreni (EW) and Egim-3 (EG-3), all obtained from Shell Petroleum Development Company Limited facilities in Delta and Rivers States of Nigeria were analysed and used for the diffusion rate experiments. Crude oil physical properties of interest, analysed for, were viscosity, density and water content. The crude oil viscosity for the six samples was measured using the Redwood viscometer according to ASTM Standard methods. The densities were measured by weighing a cylinder filled with exactly 50mL of the crude oil to be tested after noting the weight of the empty, clean cylinder. The density of the crude oil was then determined as:

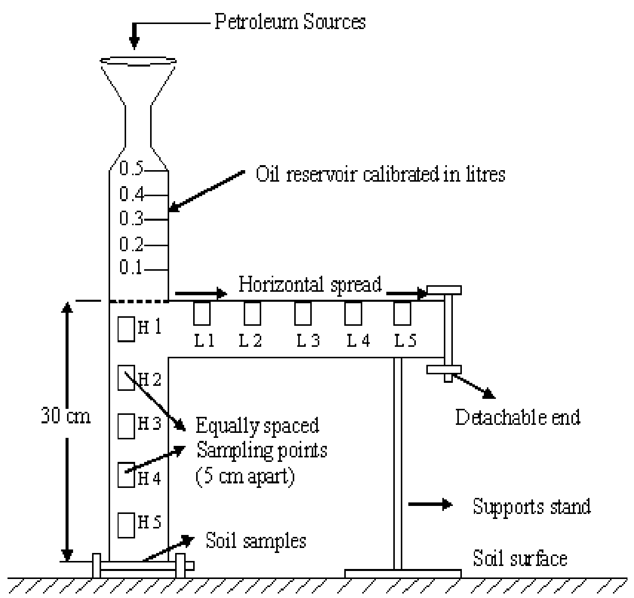
$$Pb = \frac{\text{(mass of empty cylinder + crude oil) - (mass of empty cylinder)}}{\text{(Volume of crude oil)}}$$

The distillation method was used for the determination of the water content of the crude oil samples. The distillation column was assembled with a drying tube containing desiccant inserted at the end of the condenser to prevent condensation of atmospheric moisture in the condenser. A 100mL graduated measuring cylinder was filled slowly with the petroleum sample to avoid the entrapment of air, adjusting the level as closely as possible to appropriate graduation. The content of the cylinder was carefully poured into the distillation flask and the cylinder rinsed five times with 20mL of xylene (equivalent to of the capacity of the graduated cylinder) and the rinsing added to the flask. The cylinder was thoroughly drained to ensure complete sample transfer. Heat was then slowly applied to the flask for 30 minutes initially to prevent bumping and possible loss of water from the system, after which, heating was regulated to achieve distillate discharge into the condensate trap at the rate of 2 to 5 drops per second. Distillation was continued until there was no visible water in any part of the apparatus except in the trap. After the volume of water in the trap was observed to be constant for 5 minutes, heating was discontinued and the trap and its contents, allowed to cool to 20 ^oC. Any water adhering to the sides of the trap was dislodged with a Teflon scraper and transferred to the water layer. The volume of water in the trap was read through the graduation in the trap. The volumetric percentage water content of the crude oil sample was then calculated as:

$$\text{Volume \%} = \frac{\text{(volume of water in trap (mL)) - (xylen : blank (mL) x 100\%}}{\left(\frac{\text{mass pf petroleum sample (g)}}{\text{density of petroleum sample (g/mL)}}\right)}$$

DIFFUSION RATE EXPERIMENT

The apparatus for these experiments was specifically designed to promote a uniform simultaneous one-dimensional flow regime of crude petroleum in both the vertical (downward) and horizontal (along soil surface) in soils. It was fabricated with galvanized stainless steel sheet, coated inside with anti-rust, oil resistant paint to prevent reactions between the steel and active chemical components present in petroleum. This fabricated laboratory apparatus consisted of a graduated petroleum reservoir capable of holding 500cm^3 (0.5litres) of petroleum. Five equally spaced sampling points are placed 5cm apart along the vertical (labelled H1 – H5) and horizontal (labelled L1 – L5) wings of the apparatus respectively. Loading of soil samples into the apparatus is done by means of a detachable plate at each end of the apparatus. Loamy-sand (topsoil) and six crude oil samples discussed in the preceding sections were used for the diffusion rate experiment. Other materials used include graduated cylinders, Spectron 70 UV-Spectrophotometer, sampling syringe (plunger



type) and air tight sampling plastic containers.

Diffusion rate experimental apparatus

The vertical and horizontal wings of the apparatus were loaded with the loamy- sand soil obtained for the experiment through the detachable ends by means of a heavy square iron bar of almost the same dimension as that of the apparatus. The compaction was done in such a way that there was a negligible loss in soil porosity as determined from the bulk density of the compacted soil. After replacing the detachable ends, 500cm3 (0.5 litre) of one of the crude oil sample was introduced into the petroleum reservoir. The experimental set-up was then left in the unit operations laboratory of Chemical and Petrochemical Engineering Department of the Rivers State University of Science and Technology, Port-Harcourt for 25 days. Three sets each of contaminated soil samples were collected in plastic sample bottles using a 5ml open-end syringe according to standard procedures (Beneski, 2000), every 5 days from the sampling points marked L1-L5 and H1-H5.

One set of samples were analysed immediately in the laboratory, while the remaining two sets were sent to commercial laboratories for analyses for the purpose of integrity check. The spectron 70 UV-Spectrophotometer was used to measure the absorbance of the contaminated soil and the absorbance converted to TPH concentration by means of a TPH calibration curve. Similar experiments were performed for each of the six crude oil samples at the same volume of 0.5 litres. All the experiments were laboratory based under room temperature.

RESULTS AND DISCUSSIONS

SOIL AND CRUDE OIL ANALYSES

The results of the soil and crude oil analyses are presented in Table 1 and 2 below-

Table 1 Result of soil analyses

Soil Texture:	Sand	(%)	92.80
	Silt	(%)	5.20
	Clay	(%)	2.00
Soil class			Loamy sand
Bulk density		(g.cm^3)	1.24
Particle density		(g/cm^3)	2.65
Total porosity		(-)	0.53
pH			5.60
Organic matter content		(%)	2.47
Total hydrocarbon content		(%)	0.00
Water content		(%)	58.11

Table 2 Results of Crude oil analyses

Crude Petroleum Samples	Density (ρ) kg/m3	Viscosity (μ) kg/m-h	Water Content (θ) %
Afiesere (AF)	956.34	63.6	0.00
Utorogu (UT)	940.86	413.2	10.04
Eriemu (ER)	966.22	71.7	5.60
Evwreni (EW)	938.24	64.6	0.02
Obigbo North (OBN)	995.82	243.4	10.64
Egim-3 Well Head (EG - 3)	886.36	46.6	0.02

DIFFUSION RATE

The results of the diffusion rate experiments for the six crude petroleum samples in the soil under consideration in the longitudinal and vertical directions are shown in Figures 1 and 2.

The diffusion rate of all the crude oil samples in the longitudinal direction follow the Gaussian distribution and tend to converge few centimeters from the point of spill. This may probably be due to the fact that the longitudinal diffusion is controlled only by molecular diffusion (Alshawabkeh and McGrath, 1999). Diffusion, a relatively slow process, takes place in an environment where viscous force dominates (i.e. very low Reynolds number). The diffusive transport of spilled crude oil in the longitudinal direction is not Brownian in nature; rather it is due to individual probabilistic motion of particles leading to diffusion as in the case of transport through waste containment as demonstrated by Shackelford and Daniel (1991). Gaussian concentration profiles as highlighted by Baeumer et al. (2001), are symmetric, and spread out from the centre at a rate proportional to the square root of time, and have tails that diminish rapidly as one move farther away from the point of spill. However, many tracer tests produce concentration profiles that are highly skewed and spread out from the point of spill faster than the square root of time with heavy tails; this phenomenon is referred to as superdiffusion (Haggerty and Gorelick, 1995; Haggerty and Gorelick, 2000; Brusseau, 1992). This phenomenon however, does not describe our experimental results in the horizontal direction. The vertical diffusion rate on the other hand, though Gaussian, shows evidence of advective flow in addition to diffusive flow. The diffusive flow is as a result of concentration gradient while the advective flow is due to the effect of gravity and capillary forces. The effect of gravity is more pronounced on liquid with low viscosity. This is seen from the trend exhibited by the six petroleum samples as shown in Figure 2

As can be seen from Figures 1 and 2, the diffusion rate of spilled crude oil in soils medium is a function of the crude oil physical properties especially, the density and viscosity. Kinematic viscosity (i.e. the ratio of the fluid dynamic viscosity to its density) is an important measure of a contaminant's sorption and hence its mobility in porous media such as soil. Egim-3 (EG-3) crude oil sample with the lowest kinematic viscosity of 0.0526 m2/h exhibits the highest diffusion rate both longitudinally and vertically as a result of its low sorptive capacity (poorly sorbed). On the other hand, Utorogu (UT) crude oil sample with the highest viscosity (0.4392 m2/h), has the highest sorptive capacity (highly sorbed) and therefore exhibits the lowest diffusion rate. Research has shown that a highly sorbed contaminant is relatively immobile and will not be leached or transported great distances from the point of release with little chance of meeting human receptors other than those in the vicinity of the spill or release (Oghenejoboh et al., 2008a).. A contaminant with a low kinematic viscosity is strongly sorbed to the organic carbon in the substrate and hence less available and less likely to be volatilized or biodegraded. From the result of the soil analysis presented in Table .1, it can be seen that the soil used in this work has high soil organic matter (SOM) of 2.47%. This explains the sorption trend of the six crude oil samples in the soil since sorption of hydrophobic organic substances (e.g. crude oil) is to the natural organic matter present in the soil (Seth et al., 1999), and therefore less mobile. Another important soil property that affects sorption and hence

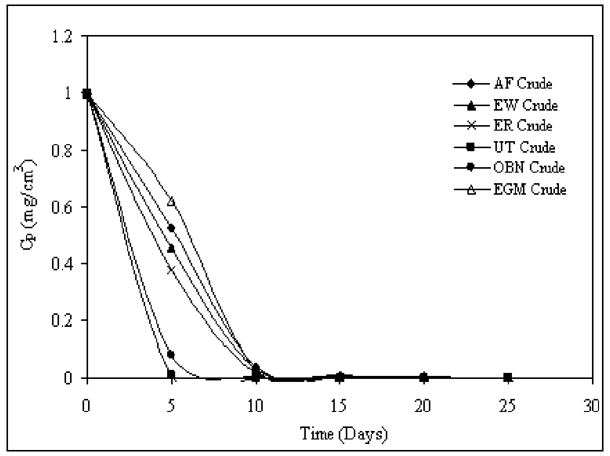


Fig. 1 Longitudinal diffusion rate of six crude oil samples in loamy sand soil

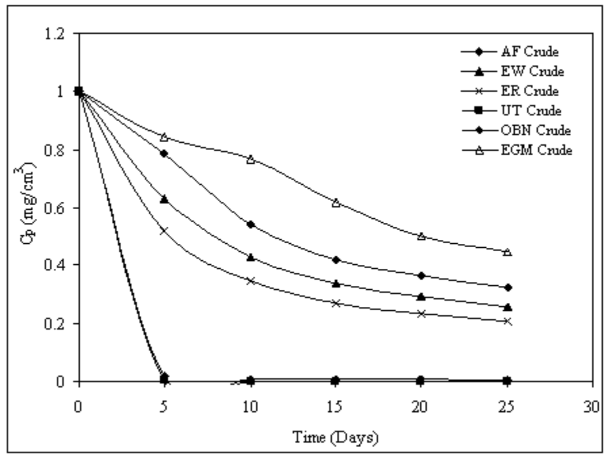


Fig. 2 Vertical diffusion rate of six crude oil samples in loamy sand soil

its diffusion rate is the texture of the transporting soil. Soils with high percentage of clay possess high surface area and retains significant amount of high kinematic viscosity contaminants thereby inhibiting free migration of the contaminant. This may account for the retarded mobility or facilitated transport of UT and OBN crude oil samples in the vertical directions (Reddi and Inyang, 2000).

CORRELATION OF ALTERNATE DIFFUSION RATE MODELS

The extent of diffusion of the experimental results of the six crude oil samples into loamy- sand soil presented in Figures 1 and 2, were correlated with time applying the product-moment statistical formula implemented on Polymath 3.0.1® non linear regression program (Shacham and Cutlip, 1995). The relationship between the diffusion rate of the crude oil samples at $L(x,t) = M_x t^{n_x}$ olume of 0.5 litres were correlated as follows:

$$H(y,t) = M_y t^{n_y}$$ (1)

(2)

where M and n are constants depending on the petroleum sample and its properties, L(x, t) is the longitudinal length diffused and H(y, t) is the vertical depth diffused by the crude oil over time

From the analysis it was observed that both Mx and My for the six petroleum samples decreases as the viscosity increases, while n_x and n_y were constant at 0.38 and 0.56 respectively for all six crude oil samples. A plot of M versus petroleum samples' kinematic viscosity (i.e. μ_p/ρ_p) was generated for both spatial directions. Diffusion rate in both directions were linearly correlated with negative slopes of –2.6812 and -1.789 for the vertical and longitudinal directions respectively as depicted in Figures 3 and 4

From Figure (3) and (4), M was correlated with kinematic viscosity as follows:

Longitudinal: $$M = 2.7706 - 2.6812\left(\frac{\mu_p}{\rho_p}\right)$$ (3)

Vertical: (4)

$$L(x,t) = \left(1.6482 - 1.789\left(\frac{\mu_p}{\rho_p}\right)\right)t^{0.38}$$

Substituting Equations (3) and (4) into Equations (1) and (2) gives

Longitud' '
(5) $$H(y,t) = \left(2.7706 - 2.6812\left(\frac{\mu_p}{\rho_p}\right)\right) t^{0.56}$$

Vertical: (6)

$$\frac{dH(y,t)}{dt} = U = 0.56\left(2.7706 - 2.6812\left(\frac{\mu_p}{\rho_p}\right)\right) t^{-0.44}$$ led ive

of Equation (6) to give

(7)

Equations (5), (6) and (7) correctly predicts diffusion rate of spilled crude oil of different physical properties in soil medium of known physical properties when substituted into the solutions of the conventional 1 – dimensional, purely diffusive and advective-diffusive soil transport equations.

CONCLUSION

Experimental investigations on the effects of crude oil physical properties on longitudinal and vertical diffusion rate in soil of known properties had been presented. It is shown that the diffusion rate in both spatial directions is strongly influenced by the crude oil kinematic viscosity. Crude oil with high kinematic viscosity exhibits low diffusion rate as a result of its high sorptive capacity, while crude oil with low kinematic viscosity is lowly sorbed in soil and hence exhibits high diffusion rate. Correlation models which are able to predict the diffusion rate of crude oil of various properties when substituted into 1 – dimensional soil transport equations have been developed from the experimental results. These models which are currently being tested for global application will form the basis for another submission.

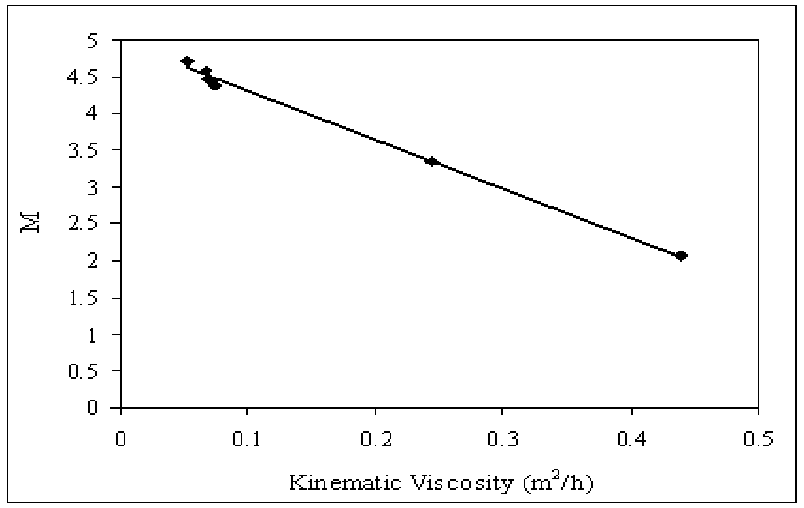


Fig. 3 Plot of M versus kinematics viscosity of petroleum spilled into loamy-sand soil in the vertical spatial direction

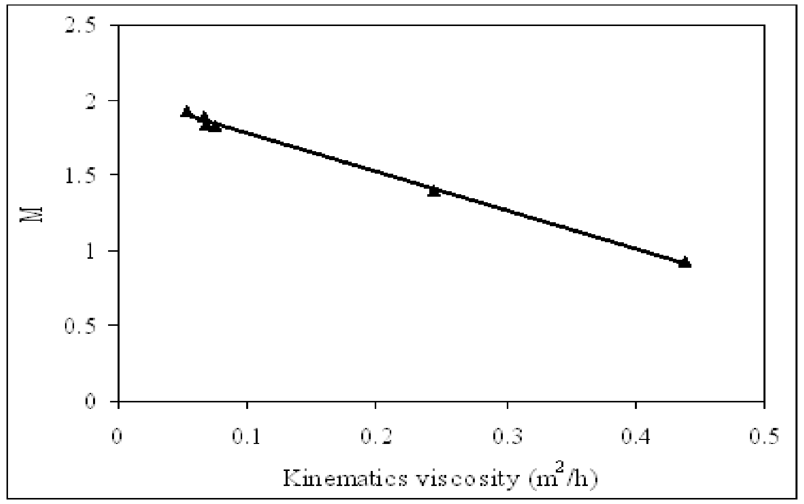


Fig. 4 Plot of M versus kinematics viscosity of petroleum spilled into loamy-sand soil in the longitudinal direction

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