Modeling of Vertical Transport of Hydrocarbons of Crude Oil Spills in Non-Convective Water Bodies Supported by Suspended Sediments: Case of Parts of the Nigerian Niger Delta Mangrove Swamps

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ABSTRACT

Crude oil spill is a major source of water pollution. In water with wave and tides, the environment could be self-cleaned. This kind of environment has enjoyed tremendous research attention over the years with plethora of models available for the forecasting, monitoring and management of residual petroleum presence in impacted environments. On the other hand, parts of the Nigerian Niger Delta mangrove swamp contain stagnant water with suspended sediments. The heavy load of suspended sediments has the capacity to adsorb oil and dissolved hydrocarbon components. This paper reports on the development of models for the vertical transport and concentrations of petroleum hydrocarbon components at different strata of the water column by suspended sediments adsorption using governing equations of transport and mass transfer. The developed models were validated with data obtained from simulated stagnant water that was polluted with crude oil.

Keywords: crude oil spill, hydrocarbons, Mangrove Swamp, models, sediments

INTRODUCTION

Over the years, several efforts have been made to effectively review existing information on oil spill transport mechanisms as well as development of predictive mathematical models for water bodies (Giya and Jimoh, 2010; Jimoh and Alhassan, 2006; Njubenuwu and Abowei, 2008; Njubenuwu, 2014; Susu et al., 1997). These efforts have enhanced the practice and helped in the identification of available knowledge gaps oil spill management and research (Chao et al., 2001; Garcia-Martinez and Flores-Tovar, 1999; Lonin, 1999; Tkalich, 2006; Wang et al., 2005). One of such knowledge gaps is the low research attention in oil spill transport mechanism in non-turbulent water bodies (stagnant water) as found in some parts of the Niger Delta region of Nigeria and more importantly, the role of suspended sediments resulting from dead vegetation in the transport of whole oil and hydrocarbon components after an oil spill. The need for a shift in attention or focus is borne out of a careful observation of the existing oil spill models which show that a majority of them are focused on horizontal distribution of whole oil, weathering and the general fate of spilled oil in rivers and seas that are characterized by flow, high turbulence and effect of wind (Bragg and Owen, 1995; Le Floch et al., 2002; Owens and Lee, 2003; Owens et al., 2003; Page et al., 2000). Even in occasions where the vertical transport trajectories were considered, the focus was on particulate transport occasioned by the breaking of the oil slick into oil particles by waves that could be stabilized by the presence of suspended sediments, which, depending on density difference with the water, begin to sink and even re-suspend (Boufadel et al., 2020; Imanian et al., 2017; Li et al., 2018; Röhrs et al., 2018, 2019).

This gap has led to a dearth of information both in practical modeling approach and empirical data availability on the transport and behavior of spilled oil in non-flowing water bodies particularly mangrove swamps with relatively static water and the role of suspended sediments that are in the water arising from decaying vegetation as can be found in some parts of the oil rich Niger Delta region of Nigeria (Odisu, 2020; Odisu et al., 2020).

Directing attention to the Nigerian Niger Delta region has become extremely important because parts of its swamps contain water bodies with very low or even no observable flow and laden with heavy load of suspended sediments and vegetation. Also, the region experience high level of crude oil exploration, production and transportation activities leading to accidental and deliberate oil spill with attendant environmental consequences.

Odisu et al. (2020) has shown that in the event of an oil spill in this kind of aquatic environment, the transport and overall fate will be totally different from what is obtained for open water with wave and wind. The research also showed that besides diffusion
of dissolving petroleum hydrocarbon components through the bulk of the water, their transport will also be supported by the simple principle of dissolved oil components-sediment partitioning. This therefore makes existing models un-amenable to cases of relatively static water bodies in these parts of the Nigerian Niger Delta mangrove swamps.

This paper reports the application of the fundamental governing equations of transport and mass transfer in modeling the transport of whole oil and dissolved components supported by suspended sediment in a stagnant water body with consideration to adsorption of whole oil onto sediment, dissolution of petroleum hydrocarbon components from the oil slick into the water-oil interface, diffusion of dissolved components through water, adsorption of a fraction of the diffusing components by suspended sediments which may lead to sinking and sedimentation or trapping within the water column depending on density difference.

The reliability of the model developed was verified using data from a simulated oil spill site typical of parts of the Niger Delta mangrove swamp with static water and monitored for ten (10) months. The result obtained were analyzed including calculation of the R² values case by case. Results obtained are as shown in the result section.

**MODEL DEVELOPMENT**

The model development was based on a stagnant water body system with suspended sediments as a result of dead vegetation as shown in the schematics in **Figures 1 to 4**.

The general conservation equation expressed in Equation 1 and based on **Figure 4** serve as the basis for the mathematical description of the transport of hydrocarbon component from the oil slick on the surface (bulk) into the oil water interface and then the water column.

\[
\text{Rate of accumulation (of dissolved aliphatic or aromatic hydrocarbons)} = \text{Amount in} - \text{Amount out} + \text{net amount introduced by source}
\]  

Equation 1

Identifying the mass flux as a summation of both the convective and diffusive fluxes, Equation 1 is then expressed as;

\[
\begin{align*}
\text{(Rate of accumulation of aliphatic or aromatic hydrocarbons in the water column)} &= (\text{Net inflow rate of aliphatics or aromatics by convection}) \\
&+ (\text{Net inflow rate of aliphatics or aromatics by diffusion}) \\
&+ (\text{Net source of aliphatics or aromatics by dissolution from oil bulk}) \\
&+ (\text{Net source of aliphatics or aromatics by biodegradation})
\end{align*}
\]  

Equation 2
Figure 2. Spread of the oil layer

Figure 3. Slick covered water body
Consideration is here given to the conservation law of the quantity $\psi$ within the fixed macroscopic volume $V$ bounded by the fixed macroscopic surface area $A$ as expressed in Equation (3).

$$\frac{\delta}{\delta t} = \rho \psi dV = - \int_A (\rho \sigma \nu \cdot n \cdot a - \int V \cdot f) + \int V \cdot dV$$  \hspace{1cm} (3)

The convective and diffusive transport terms can be rewritten as a volume integral using Gauss' theorem and the Equation can then be assembled in a single volume integral:

$$\int_V \left( \frac{\delta(\rho \nu)}{\delta t} + \nabla \cdot (\rho \sigma \nu + \nabla J) - \Phi \right)$$  \hspace{1cm} (4)

$$\frac{\partial(\rho \psi)}{\partial t} + \nabla \cdot (\rho \sigma \psi + \nabla J) - \Phi = 0$$  \hspace{1cm} (5)

For the peculiarity of this work, we assume that the convective transport term or convective flux reduces to zero, that is there is no transport due to convection or bulk flow because the water body under consideration is a relatively stagnant one. The Equation will therefore reduce to the form

$$\frac{\partial(\rho \psi)}{\partial t} + \nabla \cdot (\nabla J - \Phi) = 0$$  \hspace{1cm} (6)

As mentioned earlier, the source term is a contribution from the dissolution of hydrocarbon (aliphatics and aromatics) from the bulk (oil sleek), and the biodegradation of the hydrocarbons by microbial activities. Equation (5) can also be represented as Equation (7)

$$\frac{\partial \sigma}{\partial t} = D \frac{\partial^2 \sigma}{\partial x^2} - \Phi$$  \hspace{1cm} (7)

The hydrocarbon supply into the water-oil interface is represented as

$$\frac{dm}{dt} = A \frac{D}{d} \left( c_s - c_i \right)$$  \hspace{1cm} (8)

The biodegradation of dissolved hydrocarbon process could be represented by a multi-substrate Monod model where multiple growth substrates are available to oil degrading microbes.
However, Vilcaez et al. (2013) in an attempt to formulate the theoretical work first tried both multi-substrate and sole-substrate models for the degradation of soluble oil. They reported that the outcome for both sole and multiple substrate models were very close. Therefore, because the kinetic coefficients for sole-substrate models are typically more available from total petroleum hydrocarbons (TPH) biodegradation measurements or oxygen uptake measurements than those for multi-substrate models, for simplicity, the sole-substrate model is used for all hydrocarbons pseudo-components as shown in Equations (9), (10) and (11).

\[ r_b = \mu_{max} \frac{c}{k_s + c} B \]  
\[ r = \frac{1}{V} r_b \]  
\[ r = \frac{1}{V} \mu_{max} \frac{c}{k_s + c} B \]

Therefore, the relative mass flux or diffusive mass is defined as

\[ J_c = \rho_c (v_c - v) = \rho_c v_{c,d} \]

where \( J_c \) is approximated for binary mixtures by Fick's law to be

\[ J_c = -\rho D_e w_c \]

The minus sign accounts for the mass flux of species \( c \) in the direction of decreasing concentration

\[ J_c = J_c^g + J_c^o + J_c^σ + J_c^r = \rho_c v_{c,d} \]

However, as stated earlier, the convective flux term is assumed to be zero making the system static. As such, the available flux will be principally due to diffusion.

It is also to be noted that the transport of hydrocarbons into the bulk of the water is principally through diffusive mass transfer with a proportion of the diffusing hydrocarbon getting adsorbed by suspended sediments that are available all around the water column.

Therefore, from Equation 6,

\[ \nabla (\nabla J) \text{ can be represented as } \nabla (\nabla J)_{\text{water}} + \nabla (\nabla J)_{\text{sediment}} \]
Where \( \nabla (V_f)_{\text{sediment}} \delta q_i = k_{Ld}(q^* - q_t) \)

\[
\frac{\partial (\rho \psi)}{\partial t} = -\nabla (V_f) + \left( \frac{dm}{dt} - r_{oil} \right)
\]

It therefore implies that for situations when the model seeks to establish the total hydrocarbon availability in sediment alone, \( \nabla (V_f)_{\text{water}} \) reduces to zero,

\[
\frac{\partial (\rho \psi)}{\partial t} = -\nabla (V_f)_{\text{sediment}} + \left( \frac{dm}{dt} - r_{oil} \right)
\]

For total aliphatic hydrocarbon in sediment, we have

\[
\frac{\partial c_{ali}}{\partial t} = -\nabla (V_f)_{\text{sediment}} + \left( \frac{dm}{dt} - r_{ali} \right)
\]

While for total aromatic hydrocarbons in sediment

\[
\frac{\partial c_{aro}}{\partial t} = -\nabla (V_f)_{\text{sediment}} + \left( \frac{dm}{dt} - r_{aro} \right)
\]

While the above three Equations are for total aliphatic and aromatic hydrocarbons, they can also be used to represent individual aliphatics and aromatics like n-octane, pristane, naphthalene and anthracene. Thus,

\[
\frac{\partial c}{\partial t} = k_{ad}(q^* - q_t) + k_{dis}(c_s - c_t) - r_{oil}
\]

\[
\frac{\partial c (ali)}{\partial t} = k_{ad (ali)}(q_{(ali)}^* - q_t (ali)) + k_{dis (ali)}(c_s (ali) - c_t (ali)) - (k_{bio-w (ali)} c_{(ali)}) + k_{bio-sed (ali)}
\]

\[
\frac{\partial c (aro)}{\partial t} = k_{ad (aro)}(q_{(aro)}^* - q_t (aro)) + k_{dis (aro)}(c_s (aro) - c_t (aro)) - (k_{bio-w (aro)} c_{(aro)}) + k_{bio-sed (aro)}
\]

From Equation (5),

\[
\frac{\partial (\rho \psi) = -(\nabla (V_f)_{water} + \nabla (V_f)_{sediment}) + \left( \frac{dm}{dt} - r_{oil} \right)}{\partial t}
\]

\[
\frac{\partial c (ali)}{\partial t} = D_{ali} \frac{\partial^2 c_{ali}}{\partial x^2} + k_{ad (ali)}(q_{(ali)}^* - q_t (ali)) + k_{dis (ali)}(c_s (ali) - c_t (ali)) - (k_{bio-w (ali)} c_{(ali)}) + k_{bio-sed (ali)}
\]

\[
\frac{\partial c (aro)}{\partial t} = D_{aro} \frac{\partial^2 c_{aro}}{\partial x^2} + k_{ad (aro)}(q_{(aro)}^* - q_t (aro)) + k_{dis (aro)}(c_s (aro) - c_t (aro)) - (k_{bio-w (aro)} c_{(aro)}) + k_{bio-sed (aro)}
\]

Recall that \( C_{xt} = C_w + C_{sed} \)

\[
C_w = D \frac{\partial^2 c}{\partial z^2} - k_s (q^* - q_t) + k_d (c_s - c_t) - k_{bio} c
\]

and \( C_{sed} = C_{xt} - C_w \)

Hai-Long et al. (2011), developed partial differential equations to represent each of these model components as shown by Equation (29) to (32)

\[
\frac{\partial^2 c}{\partial z^2} = \frac{\partial^2 c_s}{\partial z^2} + \frac{\partial c_s}{\partial z} = \frac{\partial}{\partial z} (AhD_z \frac{\partial c}{\partial z})
\]

\[
k_{ad}(q^* - q_t) = \frac{\partial}{\partial z} (AhC_s) + \frac{\partial C_s}{\partial z} + \frac{w_s}{h} AhC_s - \frac{P_r}{h} AhC_s
\]

\[
= \frac{\partial}{\partial z} (AhD_z \frac{\partial C_s}{\partial z}) + K_sK_p Ah \Theta C_d - K_p Ah \Theta C_d - K_p Ah \Theta C_s
\]

\[
k_{dis}(c_s - c_t) = + \frac{\partial C_d}{\partial z} = \frac{\partial}{\partial z} (AhD_z \frac{\partial C_d}{\partial z}) + K_sK_p Ah \Theta C_d - K_p Ah \Theta C_d
\]

**METHOD OF SOLUTION**

In solving the model, the following pathway was followed as shown in the flow chart below:
The method of solution based on the above flow chart involves a development of a manual solution of the model using the manual finite element method and then a Matlab program was developed. The essence of the Matlab is to automate the process, increase the accuracy and post processing of solutions in terms of graphs. In the manual solution only six (6) elements were used for discretization whereas over a hundred (100) were used in the Matlab solution. This also applied to the time step.

The manual finite element solution involves the following steps
- Discretization of the domain into a collection of preselected finite elements
- Selection of the element equations for all typical elements in the mesh, element interpolation function and then the element matrices was computed
- Assembly of the equations to obtain the equations of the whole problem
- Imposition of the boundary conditions of the problem
- Solving the assembled equations

While the Matlab program development involved the following steps
- Specification of the constants and initial boundary conditions
- Generating the interpolation function (shape function)
- Carrying out integration and obtaining the coefficient matrix for F,M and K
- Substitution of constants and domain values into the coefficient matrix generated
- Assembling the matrix and varying out row reduction based on boundary condition
- Using alpha family of approximations, the equations were solved applying iterative approach
- Finally, tabulating the solution for each iteration and plotting the graphs

**MODEL RESULT**

**Model Validation**

The models (Equations 27 and 28) developed and their response patterns were tested using data obtained from a simulated oil spill. The spill site was prepared by spilling 60 litres of crude oil sourced from a flow station in Delta State, Nigeria with viscosity of 13.5 cp on a simulated mangrove swamp of 8m long, 5m wide and 1.5m deep typical of parts of the Niger Delta region of Nigeria. The volume used was such that could cover the entire surface uniformly. Samples were then collected using an improvised depth sampler after every 30 days for a period of 10 months at depths of 0.25m, 0.5m, 0.75m and 1.0m. Details of the experiment and procedure have been well documented by Odisu et al. (2020) and Odisu (2020). The validity was further strengthened by calculating the $R^2$ case by case.

**Figures 5 to 9** show the experimental result matched with the model result for the transport of aliphatics adsorbed by sediments alone for the first 5 months.
Figure 5. Total aliphatic transport by sediment adsorption for varying depth and fixed time of one month for experiment and model

Figure 6. Total aliphatic transport by sediment adsorption for varying depth and fixed time of two months for experiment and model
Figure 7. Aliphatic transport by sediment adsorption for varying depth and fixed time of three months for experiment and model.

Figure 8. Aliphatic transport by sediment adsorption for varying depth and fixed time of four months for experiment and model.
Figures 5 to 9 show the plots for aliphatic hydrocarbon concentration occasioned by suspended sediments transport from top to bottom of the water column for the experimental and predicted (model) for months one to five (others not shown here). The plots of month one to five at depth 0.25m to 1.0m show a good reflection of the experimental plots by the model plots. There was basically no case of remarkable departure. Also, the calculated $R^2$ using the model responses and the experimental result for the aliphatic concentration distribution by sediment transport at depths of 0.25m, 0.5m, 0.75m and 1.0m were 0.78, 0.81, 0.71 and 0.72 respectively. The $R^2$ values obtained are observed to be lower than those obtained for the case of aromatic hydrocarbon transport as reported in the aromatic section below. This may be as a result of assumptions and constants adopted which seem to have favored the aromatic transport better than the aliphatics. Nonetheless, they still fall within the regime of acceptable correlation values. Thus, it can be safely implied that the model developed has the capacity to give a good prediction of the aliphatic hydrocarbon transport by suspended sediment along the water column of a calm water body situated in a mangrove swamp.

Figures 10 to 14 show the result of model and experimental match for first months for aromatic hydrocarbon transport by sediment adsorption across the water column.
Figure 10. Total aromatic hydrocarbon transport by sediment adsorption for varying depth and fixed time of one month for experiment and model

Figure 11. Total aromatic hydrocarbon transport by sediment adsorption for varying depth and fixed time of two months for experiment and model
Figure 12. Aromatic hydrocarbon transport by sediment adsorption for varying depth and fixed time of three months for experiment and model

Figure 13. Aromatic hydrocarbon transport by sediment adsorption for varying depth and fixed time of four months for experiment and model
Figures 10 to 14 show the plots for aromatic hydrocarbon transport by suspended sediments from top to bottom of the water column for the experimental and predicted results. As was highlighted in the case of aliphatics above, the plots from month one to five (others not shown) at depth 0.25m to 1.0m show a good reflection of the experimental plots by the model plots. There was basically no case of remarkable departure of the curves. Also, the R² values calculated for aromatics hydrocarbon transported by suspended sediments using the model responses as well as the experimental results were 0.99, 0.97, 0.94 and 0.98 for 0.25, 0.5m, 0.75m and 1.0m respectively. These imply that the model developed has the capacity to give a good prediction of the aromatic hydrocarbon concentration occasioned by adsorption onto suspended sediment and transported along the water column. Unlike the case of the aliphatic hydrocarbons with relatively lower R² values, those for the aromatics suggest that the conditions and assumptions adopted better fit for aromatics possibly than aliphatics. It is even more encouraging that the models developed are able predict aromatic hydrocarbon transport relatively well because environmental research attention and focus are more on aromatics than on aliphatics considering the potential of aromatics to cause more harm to both the environment and life therein (Abowei, 1996; Akpofure et al., 2000).

CONCLUSION

The relatively low research attention accorded to stagnant water bodies of the mangrove swamps particularly in parts of the Nigerian Niger Delta have led to poor understanding of the transport mechanisms of hydrocarbons in such water bodies with resultant poor management of oil spill cases in this area. This led to the development of a predictive model using basic transport and mass transfer equations for quantifying petroleum hydrocarbon pseudo components and here applied to aliphatics and aromatics transported through water by sediment adsorption from depth to depth down the water column. The models developed were then evaluated for fitness using data collected from a simulated mangrove spill site. The result show that the models are adequate and sufficiently robust to predict the aliphatic concentration in water and sediments from depth to depth of a stagnant water column in a mangrove swamp.

NOMENCLATURE

\( \frac{\partial (\rho \psi)}{\partial t} \) - Change in concentration with respect to time (Transient term)

\( \nabla \cdot (\rho u \psi) \) - Convective transport term

\( \nabla \cdot j \) - Diffusive transport term

\( \Phi \) - Source term

\( \textbf{v} \) - Fluid velocity
\[ \rho \] - Mixture density
\[ \psi \] - Conserved quantity
\[ J \] - Diffusive flux
\[ \kappa \] - Solubility term
\[ c_i \] - Mass concentration of aromatics/aliphatics in the bulk of the crude oil at a given time
\[ r \] - Rate of microbial growth (cells/L – h),
\[ r_{\text{out}} \] - Rates of degradation of hydrocarbon pseudo groups (mg-oil/L – h) and oxygen consumption (mg-O_2/L – h), respectively,
\[ \mu_{\text{max}} \] - Maximum rate coefficient (h\(^{-1}\)),
\[ C_{\text{ori}} \] - Total hydrocarbon concentration (mg/L),
\[ K_s \] - Half saturation constant (mg/L)
\[ B \] - Concentration of microbes (cells/L) in the bulk fluid.
\[ (\text{Y}_{\text{al}}) \] - Microbial biomass produced per mass of hydrocarbon biodegraded
\[ w_c \] - Mass fraction
\[ \rho_c \] - Fractional density
\[ x_c \] - Fractional mole fraction
\[ \mathcal{C} \] - Total concentration
\[ D_c \] - Mass diffusion coefficient or diffusivity (m\(^2\)/s)
\[ C_{z,T} \] - Total hydrocarbon components dissolved and diffusing in water column
\[ C_{\text{water}} \] - Hydrocarbon components in water alone
\[ C_{\text{sed}} \] - Hydrocarbon components in sediments alone

**STATEMENT OF NOVELTY**

Models for predicting the vertical transport of dissolved petroleum hydrocarbon components (not whole oil) by suspended sediments after an oil spill in non-turbulent water bodies as found in parts of Nigerian Niger-Delta have been developed. This is the first practical attempt to model transport of spilled oil categorized into its components in such environment with emphasis on the role of suspended sediment without wave action.

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