Residual Contamination at Seabed due to Vertical Transport of Oil

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Abstract

A one-dimensional, numerical model describing the fate and vertical transport of oil spilled on the surface of a water body is presented. The model simulates the movement of oil through a control volume that extends the full thickness of the water column. The model includes the processes of emulsification, dissolution, and biodegradation of the oil in the water column. Vertical forces (weight, buoyancy, and drag) on an individual oil droplet are also included.

The time-dependent release of oil droplets from the sea surface into the water column, controlled by the energy dissipated at the sea surface by waves and other parameters, is modeled stochastically. Droplets may change density and/or size due to emulsification, dissolution, and biodegradation once introduced to the water column. Collision with suspended solids may cause droplets to fall to the seafloor, this motion being resisted by the buoyant and drag forces. The model provides a description of the fraction of oil present in each phase or region of the model: on the surface, at the seafloor, or dissolved, suspended or biodegraded in the water column. A hypothetical case study is presented illustrating application of the model and the influence of the application of a chemical dispersant. This example shows that the fraction of oil reaching the seafloor may increase significantly when chemical dispersants are used. The findings of this study can be refined provided site data are available to better describe the processes affecting the modeled oil droplets. Extension to two- or three-dimensions is also feasible, introducing the processes of advection and dispersion.

1   Introduction

Following an oil spill in the open sea, properties of the spilled oil and conditions at the sea surface determine the fate of the oil. Most oil spill accidents are accompanied by high winds and rough sea conditions where oil particles undergo complex physical and chemical processes at the sea surface. The dominant processes are evaporation, emulsification, dispersion, spreading, dissolution, oxidation, biodegradation and sedimentation (Figure 1).
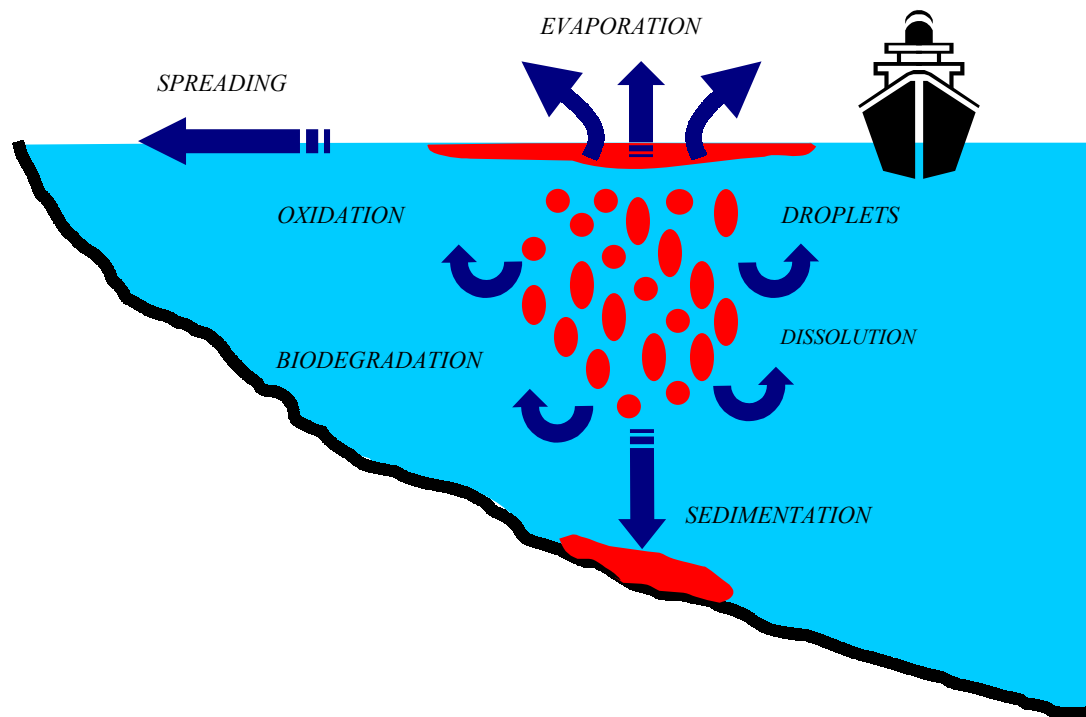
Figure 1. Physical Processes Related to Behavior of Oil in Water

Advection and diffusion of the oil slick at the water surface have been studied by several investigators (Bruheim et al., 1997; Sobey and Barker, 1997; Kazezyılmaz et al., 1998). Others have assessed the subsequent level of contamination in submarine sediments and influences on aquatic biota (Johnston, 1992; Alabdali et al., 1996; Maasoud et al. 1996; Almuzaini and Jacob, 1996; Barakat et al., 1997). Al-Rabeh et al. (1991) demonstrated numerically that 80 days after the 1991 Al-Ahmedi oil spill in the Arabian Gulf, 15% of the oil was either suspended in the water column or deposited on the sea bed. Thorpe (1995) estimated that 20% of the oil released from the 1993 Braer oil spill off the Shetland Coast reached the bottom sediments. Based on a random walk model for the vertical mixing of oil, Turrell (1994 and 1995) argued that the unaccounted for 44% of the Brear spill was mixed into the water column. Despite the fact that the fraction of oil reaching the seafloor may be significant, little is known about the vertical motion of oil and consequently, questions related to the residual contamination at the sea bottom remain open.

2   Fate and Transport Processes

This paper focuses on the vertical motion of oil from the sea surface to the seafloor. The main driving force for the downward motion of oil is recognized as the attachment of oil droplets to particles suspended in the water column. Li and Garrett (1998) investigated the relationship between oil droplet size and upper ocean turbulence and introduced a formula for the maximum droplet size based on the pressure and viscous shear regimes. Ivanov et al. (1999) examined the lifetime of oil droplets attached below an oil-water interface as a function of droplet diameter and found that flocculation in an oil-water emulsion is significantly affected by the interfacial deformation in the contact zone between the droplets.

A one-dimensional, transient, numerical model to describe the vertical migration of oil to the seabed following an oil spill at the surface is presented in this paper. The model consists of three components: a stochastic oil droplet generation model at the sea surface, a vertical oil transport model based on force balance for individual oil droplets, and a mass balance and fate model to describe the transformation of oil droplets as they are transported vertically through the water column. Results reveal important parameters of the process, and the ultimate fraction of oil reaching the seafloor.

At the present stage, external specification of hydrodynamic forcing is required. Coupling with a multi-dimensional hydrodynamic model to address three-dimensional transport of oil in the water column is feasible. Emphasis is presently placed on processes, to facilitate integration with a two- or three-dimensional hydrodynamic model.

The droplet generation model assumes that oil droplets of variable diameters are released from an oil slick at the sea surface into the water column due to wind and wave action. The rate of droplet formation and the size distribution of the particles are modeled stochastically because of the complex processes involved in the break-up of small oil droplets from the main oil slick. The expected value of oil droplet release is assumed to decrease with time to reflect the dissipation of the surface oil slick due to evaporation and dispersion at the sea surface.

As the oil droplets are transported vertically, individual oil particles undergo dissolution biodegradation, and emulsification. Dissolution and biodegradation cause the diameter of the oil droplet to decrease with time. Emulsification of water and oil molecules increases droplet size and causes the density of the droplet to approach that of water. The model assumes that the oil droplets can collide and get attached to solids in the water column. Because the density of oil is almost always lower than that of water, this process is considered to be the main process for the vertical migration of oil to the sea surface. The model also assumes that the seabed acts as an infinite sink for the oil.

The forces acting on a discrete oil particle are its weight, the buoyancy force due to the differences in density between sea water and the oil droplet, and the drag force. Stokes' law is assumed to be valid for the computation of the drag force on individual oil droplets. Under the action of buoyancy, oil droplets that do not get attached to heavier solid matter in the water column will drift back to the sea surface.

3   Model Description

The computational domain extends from just below the surface slick to the seafloor. The model consists of three components: a droplet generation model that describes the formation of oil droplets at the sea surface, a vertical oil transport model based on force balance for individual oil droplets, and a particle tracking mass conservation model for oil in the water column.

3.1 Droplet Generation Model

Due to wind and wave action after a spill, discrete oil droplets are generated at the sea surface. The rate of droplet generation (in units of droplets per unit time per unit area) at the sea surface is denoted by:

$$\dot{N}_s(\phi, t)$$

where ϕ is the diameter of the oil droplet, and t is time. The factors that affect the generation of droplets from an oil slick include the energy dissipation rate, and water-oil interfacial tension and the ratio of oil to water viscosity. In this study the rate of droplet generation is assumed to be a normally distributed process with mean and variance determined from the existing field conditions. Furthermore, to account for evaporation the rate of droplet generation was assumed to decrease with time, until the complete depletion of the surface slick.

Moreover, the mean diameter of the generated droplets at the surface can be defined in terms of the relationships presented by Li and Garrett (1998) who identified two mechanisms responsible for the generation of droplets. When the droplet Reynolds number is large, the pressure force of turbulent flows is the cause of droplet breakup (Hinze, 1955). Alternatively, when the droplet Reynolds number is small, the shear caused by the local velocity gradient will be responsible for the breakup of the oil droplets.

3.2 Fate and Transport Model

We consider a time interval Δt and a control volume of unit surface area and height H extending from just below the surface plume to the seafloor. The fate and transport model tracks the number of droplets of diameter ϕ - or the droplet size density distribution- at all times t. To facilitate the tracking of particles within the control volume, droplets are grouped together into K small intervals of diameter. Accordingly, the model will estimate the number of droplets within each diameter interval as a function of time:

$$N_k(\phi, t) \qquad \phi_k \leq \phi < \phi_{k+1}$$
for all $k=1, \ldots, K$

Given the droplet size distribution, the non-dissolved mass of oil in the water column is readily calculated from the droplet size, fraction of oil in droplet, and density of oil.

The mathematical representation of each of the processes affecting the concentration of oil in the water column is discussed below.

3.2.1 Emusification of Oil and Water

Emulsification is the process by which water and oil molecules bond together to form larger, continuous oil/water mixtures. These emulsions occur provided certain constituents in the oil, such as asphaltenes and resins, as well as sufficient mechanical energy are present (Bobra et al., 1992). As the molecules bond together, the mass fraction of oil $\eta(t)$ decreases while the density of the water/oil droplet approaches that of water. The viscosity ratio and oil-water interfacial tension change, and in turn affect the rate and size of water-oil droplet generation. A first-order rate law is often employed to model emulsion formation (Fingas, 1995). Consequently, the decrease in oil fraction due to emulsification is assumed to have the following functional form:

$$\eta(t) = e^{-\omega t}$$
(1)

where ω is the parameter controlling the rate of formation of emulsions. The initial oil fraction is unity, and then approaches zero asymptotically. Note also that emulsification causes no change in the mass of oil in the control volume. However, the change in the diameter and density of the droplet associated with emulsification will affect the buoyancy and, consequently, the transport of the droplet.

3.2.2 Dissolution

Oil consists of numerous compounds that have different solubility. The actual rate of dissolution of each of these constituents is primarily a function of the chemical composition of the oil. Dissolution at the time scales encountered in oil spill problems is generally not significant. Thus dissolution has been approximated as a droplet surface phenomenon with a rate of dissolution per unit surface area, δ [$M/L^2/T$]. The corresponding rate of change in mass of one droplet due to dissolution is:

$$\frac{dM}{dt} = -\delta \eta(t) \pi \phi^2$$
(2)

where $\pi \phi^2$ is the surface area of the droplet

3.2.3 Biodegradation

Biodegradation plays an important role in the transformation of hydrocarbons through their metabolism by living organisms into mineralized end products. Biodegradation is a complex fate process because of the diversity of the bacteria and the wide range of metabolic processes that can occur. As a result, biodegradation kinetics become strongly dependent on field conditions, which include the composition of hydrocarbon, the availability of oxygen or other electron acceptors, and temperature. In this study, the biodegradation rate is assumed a first-order process:

$$\frac{dM}{dt} = -\beta M \qquad (3)$$

where β [1/T] is the biodegradation parameter. For simplicity, the biodegradation rate is assumed to be independent of time or the size of the droplets.

3.2.4 Droplet collision and attachment to sediments

Attachment of oil droplets to sediments in the water column is recognized to be the main transport mechanism to the sea bottom. The collision and attachment of a droplet to sediments is assumed to be a stochastic process with probability of attachment per unit time p_a. This probability is assumed to be a function of the sediment concentration in the water column and their rate of movement, which in turn are function of the sediment size, the rate of energy dissipation, water depth and density of the sediments and wave charcateristics. The number of droplets of size group k that gets attached to sediments and transported to the sea bottom in time Δt is:

$$p_a N_k(\phi, t)\Delta t \qquad (4)$$

3.2.5 Buoyancy

The forces acting on a discrete oil droplet are its weight, the buoyancy force , and the drag force. In general, time-averaged vertical currents are very small and consequently are ignored here. Because the density of oil is generally lower than that of sea water, the droplet will tend to drift up to the sea surface. For small droplet Reynolds numbers, the drift velocity upwards is given by Stokes Law:

$$V(\phi) = \frac{g\phi^2\left(1 - \dfrac{\rho_d}{\rho}\right)}{18v} \qquad (5)$$

where
g gravitational acceleration
ρ absolute density of sea water
ρ_d absolute density of the droplet
v kinematic viscosity of sea water

In a short time interval Δt, the fraction of droplets of size ϕ and at time t that would be transported back to the surface of the sea due to buoyancy is:

$$(1 - p_a \Delta t) N_k (\phi, t) \frac{V(\phi) \Delta t}{H} \tag{6}$$

where (1-$p_a\Delta t$) is the probability that the droplet does not get attached to a sediment in the column.

3.2.6   Droplet size distribution

Considering the control volume of unit surface area and height H, the change in the number of droplets with diameter ϕ that are present in the control volume is:

$$\partial N_k (\phi, t) = \dot{N}_s (\phi, t) \partial t - (1 - p_a \partial t) N_k (\phi, t) \frac{V(\phi) \partial t}{H} - p_a N_k (\phi, t) \partial t \tag{7}$$

The above expression is written for the kth diameter interval. Similar expressions are written for all sediment sizes, k=1, …K.

The above equation does not include the effect of dissolution and emulsification within the water column because these processes do not affect the number of droplets in the water column. However, these processes do affect the diameter of individual particles. Their effect is given by the following differential equation:

$$\frac{\partial M}{\partial t} = -\delta \eta(t) \pi \phi^2 \tag{8}$$

where M is the mass of an individual droplet and the terms on the right hand side of the equation is the dissolution term. It is assumed that biodegradation would not affect the number or size of droplets. For a droplet with diameter ϕ, M is defined as:

$$M = \eta(t) \rho_o \frac{\pi}{6} \phi^3 = e^{-\omega t} \rho_o \frac{\pi}{6} \phi^3 \tag{9}$$

 Substituting Equation (9) into Equation (8) yields:

$$e^{-\omega t} \rho_o \frac{\pi}{2} \phi^2 \frac{\partial \phi}{\partial t} - \omega e^{-\omega t} \rho_o \frac{\pi}{6} \phi^3 = -\delta e^{-\omega t} \pi \phi^2 \tag{10}$$

After simplification, the above expression can be written as:

$$\frac{\partial \phi(t)}{\partial t} = \omega \frac{\phi(t)}{3} - \frac{2\delta}{\rho_o} \tag{11}$$

3.2.7 Mass distribution

In this section expressions for the mass of oil released at the sea surface, present in the water column, dissolved, biodegraded, transported to the sea surface due to buoyancy, and attached to sediments are written in terms of the droplet size distribution, $N_k(\phi,t)$ for all $k=1$, ..., K.

The mass of oil released at the sea surface is related to the rate of droplets released at the sea surface:

$$M_{released}(t) = e^{-\beta t} \sum_{k=1}^{k=K} \rho_o \eta(t) \left(\frac{\pi}{6} \phi_k^{\;3} \right) \dot{N}_{s,k}(\phi,t) \Delta t \tag{12}$$

where the term $e^{-\beta t}$ accounts for the continuous biodegradation that occurs from the time of the spill.

The mass of oil dissolved in the entire control volume in the time interval Δt is:

$$M_{dissolved}(t) = e^{-\beta t} \sum_{k=1}^{k=K} \delta \eta(t) \left(\pi \phi_k^{\;2} \right) N_k(\phi,t) \Delta t \tag{13}$$

The mass of oil that would be transported to the bottom of the sea in the time interval Δt is:

$$M_{attached}(t) = e^{-\beta t} \sum_{k=1}^{k=K} \rho_o \eta(t) \left(\frac{\pi}{6} \phi_k^{\;3} \right) p_a N_k(\phi,t) \Delta t \tag{14}$$

The mass of oil that would be transported back to the sea surface in the time interval Δt is:

$$M_{bouyancy}(t) = e^{-\beta t} \sum_{k=1}^{k=K} (1 - p_a \Delta t) \rho_o \eta(t) \left(\frac{\pi}{6} \phi_k^{\;3} \right) N_k(\phi,t) \frac{V(\phi)\Delta t}{H} \tag{15}$$

The mass of oil remaining in the water column at time t is:

$$M_{column}(t) = e^{-\beta t} \sum_{k=1}^{k=K} \rho_o \eta(t) \left(\frac{\pi}{6} \phi_k^{\;3} \right) N_k(\phi,t) \tag{16}$$

Finally, biodegradation affects the entire mass of oil that is released into the control volume, irrespective of its fate. Consequently, the mass of oil that is biodegraded during time Δt is:

$$M_{bio\,deg\,raded}(t) = \beta \left(M_{column}(t) + M_{released}(t) + M_{dissolved}(t) + M_{attched}(t) + M_{bouysncy}(t) \right) \Delta t \tag{17}$$

4   Model Application and Discussion

The model was used to evaluate the transport of oil to the sea bottom after the application of chemical dispersants on the surface slick. Generally, chemical dispersants are sprayed on oil slicks to reduce the oil water interfacial tension, which in turn enhances the oil's dispersion and speeds up the cleanup of the surface spill.

Based on the model developed (Li and Garrett, 1998), at energy dissipation rates expected in breaking waves, oil droplets with maximum diameter on the order of a few hundred microns are generated. When chemical dispersants are used to treat surface slicks, the maximum droplet diameter for the same energy dissipation rates is on the order of tens of microns.

Two model simulations were performed based on hypothetical data. The first simulation assumes that the generated droplets at the sea surface are normally distributed with a mean of 100 microns and standard deviation of 20 microns. This droplet size distribution corresponds approximately to an energy dissipation rate of 10 m^2/s^3 in the absence of surface dispersants.

The second case study simulates similar conditions as the first except the presence of chemical dispersants. The droplet size distribution is assumed to be normally distributed with a mean of 10 microns and standard deviation of 2 microns. This corresponds approximately to the same energy dissipation rate as in the first simulation. The smaller droplet size is due to the application of chemical dispersants . All other parameters were held constant. The water depth is assumed to be 10 m. Droplets are assumed to be released into the water column for a period of 5 days. The rate of droplet generation (kg/day) is assumed to vanish linearly in the 5-day period. The first biodegradation rate used in both cases is 0.07 day^{-1}, which is based on first-order degradation rates for fuel hydrocarbons reported by Bedient et al. (1999). The characteristic time for the emulsification exponential function is 10 days. The dissolution rate of the oil into the water was assumed to be equal to 3 x 10^7 kg/m^2/day. This value is dependent on many factors including the composition of the oil, temperature and degree of turbulence in the water column. As the results show, this value leads to a negligible amount of dissolution in the time frame considered. The average probability of a droplet colliding with a sediment particle and eventually getting transported to the sea bottom is assumed to be 0.003 day^{-1}. As noted in Section 3.2.4, this probability is function of sediment concentrations and their rate of movement in the water column. Typical vertically averaged sediment concentrations in shallow waters are in the order of 10^{-2} to 10^{-5} m^3/m^3. The probability value of 0.003 day^{-1} means that in a one-day period the probability of an oil droplet getting attached to a sediment is 0.003.

The main purpose of these two simulations was to evaluate the effect of chemical dispersants on the vertical migration of oil. Figure 2 shows the droplet size distribution at t=0 and 25 days later for both cases considered. For the droplet diameters expected when no chemical dispersants are applied, the buoyancy effect is relatively high, especially for

droplets with diameters larger than 60 microns. As a result, only smaller droplets remain in the water column, while the larger droplets are transported back to the sea surface. For the case with chemical dispersants, the shift in the droplet size distribution is relatively small, suggesting that a smaller fraction of the droplets would drift back to the sea surface.

Figures 3 and 4 show the oil mass distribution for the two cases analyzed. For the case without dispersants, about 99% of the oil mass travels back to the surface, with only about 0.044 % of the oil released into the water column reaching the sea bottom. When dispersants are used, the fraction of oil that travels back to the sea surface drops to about 45 %. The mass of oil in the column constitutes a bigger portion of the total mass of oil released. It also remains dispersed for much longer duration than the droplet release duration. This in turn increases the probability of a droplet colliding with a sediment particle and being transported to the sea bottom. As a result, the fraction of oil reaching the sea bottom is about 2 %, which is about 50 times larger than the previous case. This order of magnitude calculation suggests that the use of chemical dispersants may increase significantly the transport of oil to the sea bottom.
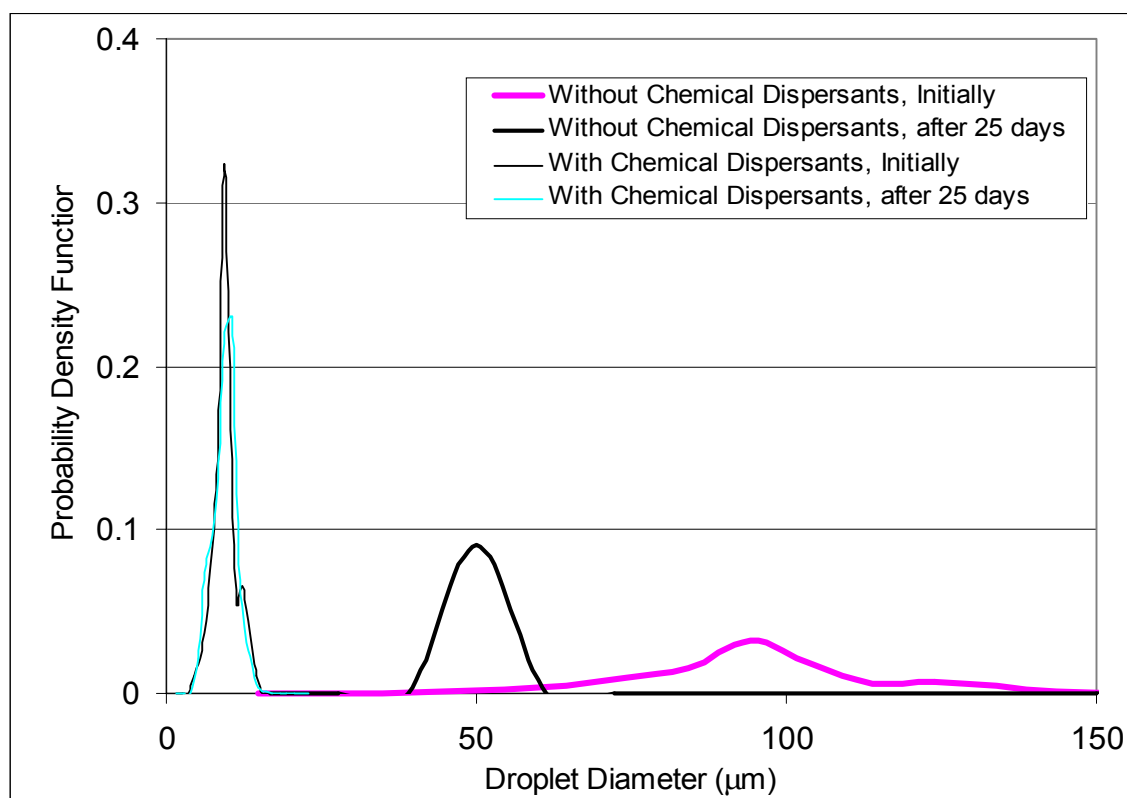

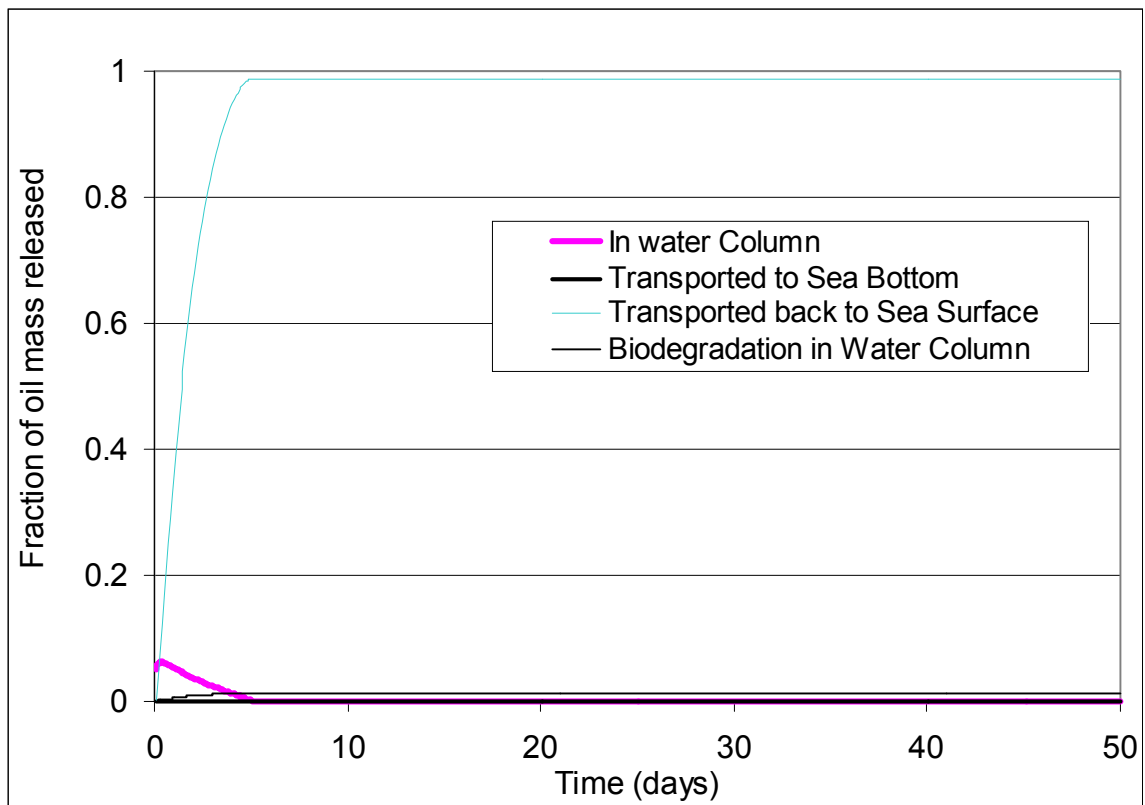**Figure 2. Droplet size distribution in the water column at t=0 and t=25 days for the two cases considered.**

Figure 3. Fate and Transport of Oil when no chemical dispersants are used
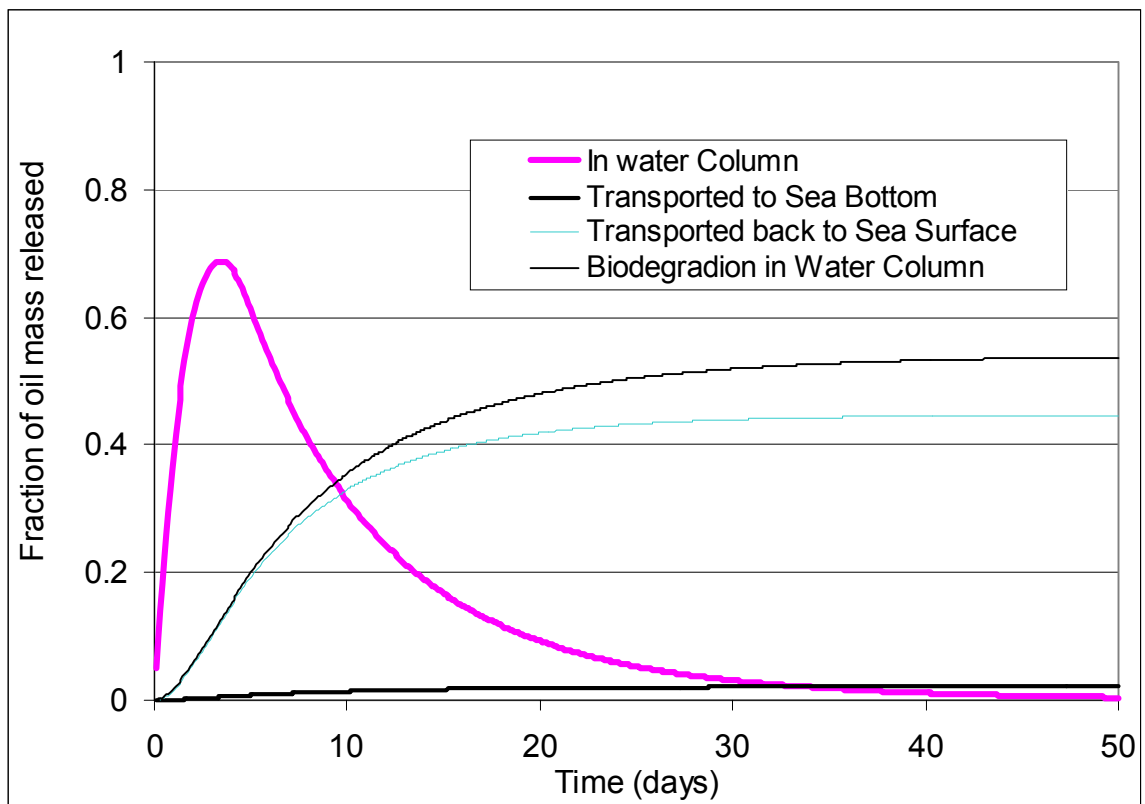

Figure 4: Fate and Transport of Oil when chemical dispersants are used

5 Summary and Conclusion

A one-dimensional model describing the vertical transport of oil subsequent to a surface spill was described. The model accounts for the influences of emulsification, dissolution, and biodegradation of the oil in the water column. The force balance on an individual oil droplet includes gravity, buoyancy and the drag forces.

The model provides a description of the fraction of oil present in each phase or region of the model: on the surface, at the seafloor, or dissolved or suspended in the water column. The release of droplets from the sea surface into the water column is modeled stochastically and is assumed to be time-dependent to indirectly account for surface dispersion and evaporation. Once introduced into the water column, individual droplets may change density and/or size due to emulsification, dissolution, and biodegradation. Droplets may also collide with suspended sediments and eventually get transported to the seafloor. The rate of collision of an oil droplet with a sediment is assumed to be stochastic process. On the other hand, because their density is generally lower than that of seawater, oil droplets could also travel back to the sea surface due to buoyancy.

Two hypothetical case studies are presented, differing only in that one assumes the employment of a chemical dispersant. For the conditions considered in these two examples, the fraction of oil reaching the seafloor is small in either case, although the inclusion of the dispersant increases this amount by a factor of about 50 (2% vs. 0.044%). Of course these values are dependent on assumed values for each of the parameters influencing the model.

The one-dimensional model described here can easily be refined should site-specific descriptions of physical and chemical processes affecting the modeled oil droplets become available. The simple one-dimensional approach allows inspection of the influence of the various processes on the fraction of oil reaching the seafloor. Extension to two- or three-dimensions is also feasible, introducing the processes of advection and dispersion. These additions could make the model more suitable for real-life application in coastal areas with complex velocity fields.

References

[1]   Alabdali, F., Maasoud, M.S., and Alghadban, A.N. (1996). "Bottom sediments of the Arabian Gulf. 3. Trace-metal contents as indicators of pollution and implications for the effect and fate of the Kuwait oil-slick," *Environmental Pollution*, 93(3), 285-301.

[2]   Almuzaini, S. and Jacob, P.G. (1996). "An assessment of toxic metals content in the marine sediments of the Shuaiba industrial area, Kuwait, after the oil spill during the Gulf War," *Water Science and Technology*, 34(7-8), 203-210.

[3]   Al-Rabeh, A.H., Çekirge, H.M. and Günay, N. (1992). "Modeling the fate and transport of Al-Ahmadi oil spill," *Water, Air, and Soil Pollution*, 65, 257-279.

[4]   Barakat, M.A.K., Shimy, T.M., and Soliman, M. (1997). "Morphology of mediterranean coastal sediments and its relation to oil spill pollution," *Energy Sources*, 19(2), 183-195.

[5]   Bedient, P.B., Rifai, H.S., and Newell, C.J., (1999). Ground Water Contamination Transport and Remediation, Second Edition, Prentice Hall, Inc., Upper Saddle River NJ.

[6]   Bobra M., Fingas, M. and Tennyson E. (1992). When oil spills emulsify. *Chemtech 22*, 236-241

[7]   Bruheim, P., Bredholt, H., and Eimhjellen, K. (1997). "Bacterial degradation of emulsified crude oil and the effect of various surfactants," *Canadian Journal of Microbiology*, 43(1), 17-22.

[8]   Fingas, M.F., Fieldhouse B., Gamble, L., Mullin, J. (1995) Studies of water-in-oil emulsions: stability classes and measurements. Proc. 18 AMOC, 21-42.

[9]   Hinze (1955). Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes. *A.I.Ch.E.* Journal 1, 289-295

[10]   Ivanov, I.B., Danov, K.D., and Kralchevsky, P.A. (1999). "Flocculation and coalescence of micron-size emulsion droplets," *Colloids and Surfaces – A: Physicochemical and Engineering Aspects*, 152, 161-182.

[11]   Johnston, C.S. (1992). "The short- and long-term effects of oil spills on marine ecosystems. Use and misuse of the seafloor," *Report of the Dahlem Workshop*, Wiley, New York, 357 pages.

[12]   Kazezyılmaz, M.C., Güleç, B. and Otay, E.N. (1998). "A case study of contaminant transport modelling: Tuzla oil spill" *Proc. Of 1st Int. Conference on Oil Spills in the Mediterranean and Black Sea Regions*. K 01, 1-9.

[13]   Li, M. and Garrett, C. (1998). "The relationship between oil droplet size and upper ocean turbulence," *Marine Pollution Bulletin*, 36(12), 961-970.

[14]   Maasoud, M.S., Alabdali, F., Alghadban, A.N., and Alsarawi, M. (1996). "Bottom sediments of the Arabian Gulf .2. Tph and Toc contents as indicators of pollution and implications for the effect and fate of the Kuwait oil-slick," *Environmental Pollution*, 93(3), 271-284.

[15]   Sobey, R.J., and Barker, C.H. (1997). "Wave-driven transport of surface oil," *J. Coastal Research*," 13(2), 490-496.

[16]   Thorpe, S.A. (1995). "Vertical dispersion of oil droplets in strong winds; the Braer oil spill," *Marine Pollution Bulletin*, 30(11), 756-758.

[17]   Turrel, W.R. (1995). "Modelling the Braer oil spill – a comment on Proctor et al. (1994)," M*arine Pollution Bulletin*, 30(1), 92-93.

[18]   Turrel, W.R. (1994). "Modelling the Braer oil spill – a retrospective view," M*arine Pollution Bulletin*, 28(4), 211-218.