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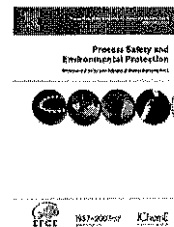
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Multimedia fate of oil spills in a marine environment—An integrated modelling approach

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ABSTRACT

A fugacity-based methodology is presented to predict the fate of spilled oil in the marine environment. In the proposed methodology, oil weathering processes are coupled with a level IV (dynamic) fugacity-based model. A two-compartment system, comprised of water and sediment, is used to explore the fate of oil in a marine environment.

During a spill, oil is entrained into the water column due to natural dispersion, which is considered as the primary input source to the water compartment. The direct input to the sediment compartment is assumed negligible. However, the water column acts as a source to the sediment compartment. Unlike the conventional multimedia modelling approach, the impact area is not predefined. Instead, the oil slick spreading process determines the contaminated area growth. Naphthalene is used as a representative oil compound (an indicator) to demonstrate the application of the methodology.

The current study suggests that the water compartment response to the chemical input is faster than the sediment compartment. The major fate processes identified are advection in water and volume growth in the sediment.

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1. Introduction

Development of coastal oil spill contingency plans requires prediction of the fate/transport of oil in the marine environment. A marine system is a complex multimedia environment that can be divided into three main (henceforth referred to as bulk) compartments, namely air, water, and sediments. These bulk compartments contain sub-compartments such as suspended solids and biota in the water column, and solids and water in the sediment compartment.

The transformation of oil, which is also known as weathering, is associated with a wide variety of physiochemical and biological processes. Mackay et al. (1980) developed semi-empirical equations to describe the weathering processes. These equations were subsequently incorporated into the fate sub-model of a natural resource damage assessment modelling system for marine and coastal areas (Reed, 1989). The sub-model was designed to estimate the distribution of a

contaminant on the sea surface, and to predict water column and sediment concentrations. Sebastiao and Soares (1995) transformed the time dependent weathering algorithms of Mackay et al. (1980) and Reed (1989) into a system of differential equations. They solved a system of model equations numerically to describe spreading (area growth), evaporation, volume balance (accounts for the volume lost by evaporation and by natural dispersion into the water column), water incorporation, and viscosity increase with time. However, the work was limited to modelling the fate of surface oil and did not include the dispersion of oil in the water column or sedimentation to the sea floor. Huda et al. (1999) combined sub-modules for oil slick dynamics at the water surface, 3D transport of the oil phase in the water column using the conventional advection–diffusion equation and oil sedimentation at the seabed.

During the last two decades, a fugacity-based approach in modelling the distribution of contaminants in a multimedia

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environment for complex ecological systems has been studied by various researchers (e.g., Mackay et al., 1983; Mackay, 1991; Mackay et al., 1992; Sadiq, 2001; Sweetman et al., 2002). Sadiq (2001) used fugacity- and equivalence-based approaches for determining the fate of drilling waste discharges in the water column and pore water of sediments in the marine environment. Sweetman et al. (2002) determined the fate of PCBs in the multimedia, also using a fugacity-based approach.

A fugacity-based approach is an effective means to study the behavior of organic chemicals in a multimedia environment because of its capability to handle an enormous amount of details on environmental transport processes and dispersed phases (sub-compartments) within a bulk compartment. However, the fugacity approach is based on low chemical concentrations in the media (Mackay, 1991). Oil spills usually have high concentrations of chemicals and thus the validity of the fugacity-based methodology can be questioned. Of note, however, is the fact that we employed the fugacity approach to model the low-concentration oil fractions which enter into the water column due to the natural dispersion weathering process. The fate and transport of the high-concentration surface oil slick is modelled using existing weathering algorithms.

The current paper proposes a new methodology, which combines the aforementioned weathering algorithms with a level IV fugacity model, to predict the multimedia fate and transport of oil for a batch spill scenario on the water surface. The application of the proposed methodology is also presented.

2. Model formulation

The current study has drawn upon the work of Sebastiao and Soares (1995) in modelling the oil slick physiochemical weathering processes, namely spreading, evaporation, natural dispersion and emulsification. Here, however, the multimedia oil fate in a marine environment is predicted by employing a level IV fugacity-based model.

A marine system is considered as an evaluative environment consisting of two bulk compartments – water and sediment. It is assumed that the water compartment contains homogenous dispersed phases (sub-compartments) of suspended solids and biota, and the sediment contains solids and pore water. In a conventional fate modelling approach, the dimensions of the evaluative environment are predefined (Mackay et al., 1983; Sadiq, 2001; Sweetman et al., 2002). The contribution of the proposed methodology is that it allows the growth of the water compartment to account for an oil spreading mechanism. The proposed methodology also takes into consideration the various environmental transport processes within the control volume (such as transport due to currents and degrading reactions).

The oil weathering processes and the level IV model are discussed in the subsequent sections.

2.1. Oil slick weathering modelling

API (1999) lists 10 weathering processes for the fate and transport of a surface oil slick. These include: (1) spreading, (2) advection, (3) evaporation, (4) dissolution, (5) natural dispersion, (6) emulsification, (7) photo-oxidation, (8) sedimentation, (9) shoreline stranding, and (10) biodegradation. API (1999) also presents the concept of a generic timeline for the weathering

processes. Among these weathering processes, on the basis of the order of a few days and under calm sea conditions, four are considered to be of particular importance (Sebastiao and Soares, 1995): spreading, evaporation, natural dispersion, and emulsification. In this section, the existing algorithms to model the weathering processes are presented.

2.1.1. Surface spreading and advection

The rate of change of surface area of the oil slick is based on the gravity-viscous formulation earlier proposed by Fay (1969) and Hoult (1972) and later modified by Mackay et al. (1980). The rate of spreading is calculated as:

$$\frac{dA_s}{dt} = K_1 A_s^{2/3} \left[\frac{V_m}{A_s} \right]^{4/3} \quad (1)$$

where A_s = area of slick (m^2), V_m = volume of spilled oil (m^3), K_1 = constant with default value of $150 s^{-1}$ (Mackay et al., 1980).

Allowance is usually made for the loss of volume in the spreading rate expression as a result of evaporation, dissolution, and dispersion. A prerequisite for spreading of a crude oil is that its pour point should be lower than the ambient water temperature. The spreading process is generally ceased at the terminal thickness of 0.01 cm for heavy crude oils and 0.001 cm for lesser viscous substances such as gasoline, kerosene and light diesel fuel (Reed, 1989). The model assumes circular slicks of uniform thickness h , which can be calculated as:

$$h = \frac{V_m}{A_s} \quad (2)$$

Advection is the movement of the oil due to the influence of overlying winds and/or underlying currents (NRC, 1985). The advection or drift velocity $\vec{V}$ can be calculated from the following expression (Hoult, 1972):

$$\vec{V} = \alpha_w \vec{V}_w + \alpha_c \vec{V}_c \quad (3)$$

where α_w = wind drift factor (~ 0.03), $\vec{V}_w$ = wind velocity at 10 m above the mean water surface level, α_c = current drift factor (~ 1.1), $\vec{V}_c$ = depth-averaged current velocity

In open seas the wind elongates the slick in the direction of prevailing winds and oil thickness varies within the slick. However, the total slick area can be approximated as that of a circular slick. Spreading and advection do not affect the chemical composition of oil (API, 1999).

2.1.2. Evaporation

The preferential transfer of light- and medium-weight components of the oil from the liquid phase to the vapor phase is known as evaporation (Exxon Corporation, 1985). Evaporation is considered to be the primary process resulting in loss of mass during the first few hours of an oil spill (Buchanan and Hurford, 1988; Sebastiao and Soares, 1995). Two methods are typically used to compute evaporation rate: (i) the pseudo-component approach (Yang and Wang, 1977; Sebastiao and Soares, 1998) and (ii) the analytical approach (Mackay et al., 1980; Stiver and Mackay, 1984).

In the pseudo-component approach, oil is characterized by a set of fractions grouped by molecular weight and boiling point; this results in different evaporation rates for different fractions. In the analytical approach, vapor pressure is

expressed as a function of fraction evaporated. The oil's evaporation curve is predicted from its distillation curve. Sebastiao and Soares (1998) showed that the pseudo-component approach provides better results for a light crude oil. Another study carried out by ASCE (1996) recommended the use of the analytical approach for heavy and mixed oils. This suggests that the improvements obtained with either of the methods cannot be applicable to all situations. In the current work, we have adopted the analytical method proposed by Stiver and Mackay (1984) because it uses a simple algorithm and the required parameters are readily available from distillation data (Sebastiao and Soares, 1995). The expression for the volume fraction evaporated is:

$$F_E = \ln \left[1 + B \left(\frac{T_G}{T} \right)^\theta \exp \left(A - B \frac{T_O}{T} \right) \right] \left[\frac{T}{BT_G} \right] \quad (4)$$

where

$$\theta = \frac{K_2 A_s t}{V_O}$$

$$K_2 = 2.5 \times 10^{-3} W^{0.78}$$

F_E = volume fraction evaporated, K_2 = mass transfer coefficient for evaporation (m/s), W = wind speed (m/s), V_O = initial volume of spilled oil (m³), T_O = initial boiling point at F_E of zero (K), T_G = gradient of the boiling point, T_B , and F_E line (K), T = environmental temperature (K), A , B = constants derived from distillation data.

Stiver and Mackay (1984) calculated the magnitude of the constants A and B as 6.3 and 10.3, respectively, using linear regression of distillation data for five different types of crude oils.

2.1.3. Natural dispersion

Small droplets (diameter < 0.1 mm) of oil are incorporated in the water column during the natural dispersion process. The process occurs due to mixing of oil into the water column, which is mainly attributed to breaking waves. In general, oil-in-water emulsions are not stable and larger oil droplets (diameter > 0.1 mm) may coalesce and return to the surface under calm sea conditions. Natural dispersion is not a well-understood process (Mackay and MacAuliffe, 1989).

Reed (1989) computed the dispersion rate per hour by employing the entrainment formulation of Mackay et al. (1980), which is expressed as:

$$D = D_a \times D_b = [0.11(W + 1)^2] \times [(1 + 50\mu^{1/2}h_s t)^{-1}] \quad (5)$$

where D_a = the fraction of sea surface dispersed per hour, D_b = the fraction of the dispersed oil not returning to the slick, W = wind speed (m/s), μ = viscosity (cp), h = slick thickness (m), s_t = oil-water interfacial tension (dyne/m).

The viscosity of oil is allowed to increase due to the incorporation of water into oil (emulsification), which is discussed in the following section.

2.1.4. Emulsification

The emulsification process involves the mixing of water droplets into the oil medium. According to CONCAWE (1983), a crude oil with relatively low asphaltene content is expected to be less likely to form a stable emulsion. The

result of emulsification is not only a large increase in volume but also a large increase in viscosity (Sebastiao and Soares, 1995).

Mackay et al. (1980) proposed the following expression for the rate of incorporation of water into an oil slick:

$$\frac{dY}{dt} = 2 \times 10^{-6} (W + 1)^2 \left(1 - \frac{Y}{C_3} \right) \quad (6)$$

where Y = fraction of water in oil, C_3 = final fraction water content (0.7 for crude oils and heavy fuel oil, and 0.25 for home heating oil).

An increase in viscosity due to mousse formation is computed by the following equation (Mooney, 1951):

$$\mu = \mu_O \exp \left[\frac{2.5Y}{1 - C_3 Y} \right] \quad (7)$$

where μ_O = parent oil viscosity, which can be calculated with the percentage asphaltene content A_C as: $\mu_O = 224A_C^{1/2}$.

Evaporation also causes a viscosity increase, which can be modelled as:

$$\mu = \mu_O \exp(C_4 F_E) \quad (8)$$

where C_4 = a constant between 1 and 10, where 1 is for light substances such as gasoline, and 10 is for crude oils.

2.1.5. Governing equations of the weathering processes

Different weathering processes occur concurrently and depend on one another. Sebastiao and Soares (1995) modelled the fate of surface oil only and did not consider environmental compartmentation (water column and sediment). Their model assumed calm sea conditions, and advection of the slick was not considered. The current study follows the same algorithm to model the weathering processes. However, the formulations of the weathering processes are coupled with an oil multimedia fate and transport model (which is described in Section 2.2).

The governing equations used to model the weathering processes are as follows (Sebastiao and Soares, 1995):

$$\frac{dF_E}{dt} = \frac{K_2 A_s}{V_O} \exp \left(A - \frac{B}{T} (T_O + T_G F_E) \right) \quad (9a)$$

$$\frac{dV}{dt} = -V_O \frac{dF_E}{dt} - DV \quad (9b)$$

$$\frac{dY}{dt} = 2 \times 10^{-6} (W + 1)^2 \left(1 - \frac{Y}{C_3} \right) \quad (9c)$$

$$\frac{dA_s}{dt} = K_1 A_s^{-1} V^{4/3} \quad (9d)$$

$$\frac{d\mu}{dt} = C_4 \mu \frac{dF_E}{dt} + \frac{2.5\mu}{(1 - C_3 Y)^2} \frac{dY}{dt} \quad (9e)$$

The volume rate of oil entrained into the water column can be calculated as:

$$\frac{dV_{ent}}{dt} = DV \quad (9f)$$

where V is the volume of oil at a given time and other parameters are defined elsewhere in this section.

2.2. Fugacity-based multimedia fate and transport models: an overview

This section presents an overview of fugacity-based multimedia models; Mackay (1991) has given a comprehensive analysis of the fugacity-based modelling approach. Based on the level of complexity of the problem, Mackay (1991) recommended four systems: level I, level II, level III, and level IV.

In level I, all of the bulk compartments/phases are assumed to be at equilibrium. A chemical compound is considered as conserved in that it is neither destroyed by reactions nor conveyed out of the evaluative environment by flows. The model is written in a fugacity format in which fugacity acts as a surrogate for concentration, and Z values (also known as fugacity capacities) establish equilibrium partitioning for a chemical in each phase. The level II scenario requires equilibrium among all phases (i.e., common fugacity). However, transport processes such as reaction and advection are included in the model in terms of D values. At level III,

equilibrium is assumed between dispersed phases/sub-compartments but not between bulk phases. The inter-media transport process between two bulk phases is accounted for by inter-media D values. The model presumes steady state conditions that can be obtained after prolonged exposure of the system to constant input conditions. Similar to the level II calculations, level III modelling allows reaction and advective transport of chemicals out of the bulk phase. Mackay et al. (1983) developed the QWASI model using level III formulations. They applied the model to predict the fate of PCBs and heavy metals in a lake environment. Sadiq (2001) used the QWASI model in a probabilistic mode to simulate the fate of drilling waste discharges in a marine environment.

The level IV approach is an extension of level III, but accounts for unsteady state conditions. Sweetman et al. (2002) implemented the level IV modelling approach to predict the fate of PCBs in multimedia over a 60-year period. The current study applies the level IV model in describing the fate of an oil spill in a marine environment.

Table 1 – Description of parameters used in level IV model (Mackay, 1991)

Parameters and equations	Description
Z (mol/m³ Pa), fugacity capacity calculations:	
• Water	Z_{B2} is bulk fugacity capacity for water phase
$Z_{B2} = v_2 Z_2 + v_5 Z_5 + v_6 Z_6$	Z_2 , Z_5 , and Z_6 are fugacity capacities for water, suspended solids, and biota, respectively
$Z_2 = 1/H$	v_2 , v_5 , and v_6 are volume fractions of water, suspended solid, and biota in the water compartment, respectively. The magnitude of v_2 is usually negligibly different from unity
$Z_5 = Z_2 \rho_5 \phi_5 K_{OC}$	ρ_5 and ρ_6 (kg/L) are densities of suspended solid, and biota in the water compartment, respectively
$Z_6 = Z_2 \rho_6 \phi_6 K_{OC}$	ϕ_5 and ϕ_6 are organic fractions of suspended solid and biota
• Sediment	Z_{B4} is bulk fugacity capacity for sediment
$Z_{B4} = v_7 Z_2 + v_8 Z_4$	v_7 and v_8 are volume fractions of solids, and pore water in the sediment compartment, respectively
$Z_4 = Z_2 \rho_4 \phi_4 K_{OC}$	ρ_4 is density of solids in the sediment compartment
	K_{OC} (L/kg) is organic carbon-water coefficient: $K_{OC} = 0.41 K_{OW}$, K_{OW} is octanol–water partition coefficient
D-value (mol/Pa h) calculations	
• Water	D_{R2} and D_{A2} represent transport processes due to reaction and advection, respectively, within the water compartment
$D_{R2} = Z_{B2} V_2 k_2$, $D_{A2} = Z_{B2} G_2$	$V_2 \approx V_{B2}$
$D_{G2} = Z_{B2} \frac{dV_{B2}}{dt} = Z_{B2} h_W \frac{dA_2}{dt}$	k_2 (h ⁻¹) is reaction rate constant in water
$D_{24} = D_{Dif} + D_{DS}$	G_2 (m ³ /s) is volumetric flow rate, which can be calculated by current velocity (U) with the cross-sectional area perpendicular to the flow direction, i.e., $2Rh_W$
Serial Configuration	R is radius and h_W is depth of the water compartment
$\frac{1}{D_{Dif}} = \frac{1}{k_{24} A_2 Z_2} + \frac{1}{B_{WX} A_2 Z_2}$	D_{G2} is a pseudo- D value, which accounts for the 'growth' within the water compartment
$D_{DS} = A_2 U_{DS} Z_5$	dA_2/dt is given by Eq. (1)
	D_{24} is an inter-media D value and represents the transport process from water to sediment. This is equal to an algebraic sum of two other transport processes occurring in parallel, i.e., D_{Dif} and D_{DS}
• Sediment	D_{Dif} denotes the diffusive process and its reciprocal is an algebraic sum of the reciprocal D values on water side diffusion and effective diffusivity within sediment. Usually, the error introduced by neglecting water side mass transfer coefficient (k_{24}) term is considered negligible
$D_{R4} = Z_{B4} V_4 k_4$	D_{DS} is deposition process associated with the suspended solid
$D_{Bur} = A_2 U_{Bur} Z_4$	U_{DS} (m/h) is suspended solid deposition rate
$D_{G4} = Z_{B4} \frac{dV_{B4}}{dt} = Z_{B4} h_S \frac{dA_4}{dt}$	k_{24} (m/h) is water side mass transfer coefficient
$D_{42} = D_{Dif} + D_{RS}$	B_{WX} (m ² /h) is effective diffusivity
$D_{RS} = A_2 U_{RS} Z_4$	Δ_5 (m) is diffusion path length in sediment; h_S (m) is sediment depth
	D_{R4} and D_{Bur} represent transport processes due to reaction and sediment burial, respectively
	k_4 (h ⁻¹) is reaction rate constant in sediment
	U_{Bur} (m/h) is sediment solids' burial rate
	D_{G4} is a pseudo- D value, which accounts for the 'growth dilution' within the sediment compartment
	D_{RS} is sediment re-suspension process
	U_{RS} (m/h) sediment re-suspension rate

2.2.1. Two-compartment level IV modelling approach

Two bulk compartments (i.e., water and sediment) are used for level IV modelling, where each bulk compartment consists of sub-compartments such as suspended solids and biota (fish) in the water column, and solids and pore water in the sediments. A system of differential mass balance equations for the two-compartment model is given as follows:

For water

$$\frac{d}{dt}(V_{B2}Z_{B2}f_2) = I_2 + D_{42}f_4 - (D_{R2} + D_{A2} + D_{24})f_2 \quad (10)$$

For sediment

$$\frac{d}{dt}(V_{B4}Z_{B4}f_4) = I_4 + D_{24}f_2 - (D_{R4} + D_{Bur} + D_{42})f_4 \quad (11)$$

The subscripts 2 and 4 represent water and sediment, respectively (adopted from Mackay, 1991), and B represents the bulk phase. The input rate of a chemical compound is denoted by I_i (mol/s). A description and the related equations for the parameters Z and D are presented in Table 1. The compartment volumes are a function of time so as to account for the growth of the oil slick due to spreading. However, the bulk Z values are considered constant. This results in the following system of differential equations:

For water,

$$Z_{B2}V_{B2}\frac{df_2}{dt} = I_2 + D_{42}f_4 - (D_{R2} + D_{A2} + D_{24} + D_{G2})f_2 \quad (12)$$

For sediment,

$$Z_{B4}V_{B4}\frac{df_4}{dt} = I_4 + D_{24}f_2 - (D_{R4} + D_{Bur} + D_{42} + D_{G4})f_4 \quad (13)$$

where

$$D_{G2} = Z_{B2}\frac{dV_{B2}}{dt} \quad (14)$$

$$D_{G4} = Z_{B4}\frac{dV_{B4}}{dt} \quad (15)$$

Eqs. (12) and (13) are combined with a system of differential equations for the weathering processes and the solution can be obtained by employing the fourth-order Runge-Kutta method.

The concentration in any medium can be calculated by multiplying the fugacity of the medium with its fugacity capacity; i.e., the Z -value (for example, $C_{Fish} = f_2 \times Z_6$ calculates the concentration in fish).

3. A case study

To demonstrate the application of the proposed methodology, a case study is now presented in which a spill of Statfjord crude oil of 100 tonne ($\sim 120 \text{ m}^3$) in a marine environment is simulated. Sebastiao and Soares (1995) simulated the weathering processes for this spill and validated their results with previously published experimental data. The physical characteristics of the Statfjord crude oil used in the current simulation are presented in Table 2.

The initial oil slick thickness of 0.02 m is fixed arbitrarily as recommended by Mackay et al., 1980. The subsequent area calculations are not sensitive to this initial thickness assumption. Use of Eq. (2) leads to the initial area spread of 6000 m^2 .

Table 2 – Statfjord crude oil characteristics used in the modelling of weathering processes

Oil characteristics	Values
Density (kg/m^3)	832
Wind speed (m/s)	4.17
Viscosity @ 40 °C (cp)	3.03
T_0 – initial boiling point at zero evaporation (K)	301
T_G – gradient of the boiling point and fraction evaporation line (K)	500
Oil–water interfacial tension (dyne/m)	2000
Water temperature (K)	288

The affected area of the water and the sediment phases is assumed equal to the area of the surface oil slick, and the area growth is a function of time. The volume of both compartments is determined by multiplying the average well-mixed depth with the surface area at a particular time.

The initial values for both the fraction evaporated and the fraction of water content in the slick are considered to be zero. Allowance is made for the loss of oil volume as a result of evaporation and natural dispersion. The oil volume entrained into the water column due to the natural dispersion process is used to calculate the oil volumetric flow rate. The emission rate $I_2(t)$, is obtained by multiplying the oil volumetric flow rate (Q_{ent}) with the molar concentration C_i (mol/ m^3) of a compound constituting the oil, i.e.,

$$I_2(t) = Q_{ent} \times C_i \quad (16)$$

Because concentration C_i is actually a function of the weathering process, the use of a constant concentration in Eq. (16) represents a simplifying assumption in the current work.

Oil is a complex mixture of thousands of various compounds (API, 1999); naphthalene is used as a representative compound in the present study, with the physiochemical properties given in Table 3. It is assumed that the oil droplets remain in the water column and deposit to the sediment only after attaching to the suspended solids within the water phase. Thus, in the open sea, the direct naphthalene input to the sediment phase is assumed to be negligible.

The environmental multimedia parameters used for the level IV fugacity-based model are provided in Table 4. These parameter values are taken as crisp estimates, and uncertainties that may be associated with the parameters are not considered in the analysis. To demonstrate the application of the proposed methodology, a deterministic analysis using point estimates is justified. However, we strongly recommend the use of probabilistic/fuzzy-based methods as described elsewhere (Sadiq, 2001; MacLeod et al., 2002) to account for variability and uncertainty in multimedia models.

4. Results and discussion

The multimedia model output includes time-dependent fugacity profiles for both bulk compartments (water and sediment), and concentration profiles for the water column and fish. Such profiles are conventionally used in calculating the exposure in ecological and human health risk analyses.

The surface oil slick area growth is shown in Fig. 1(a). This area prescribes the dimensions of both evaluative compartments at a given time. The slick growth ceases as its thickness

Table 3 – Physiochemical properties of naphthalene used in the simulation

Parameter	Notation	Value	Units
Molecular weight	MW	128.2	g/mol
Solubility @ 25 °C	C ^s	31.7	g/m ³
Vapor pressure @ 25 °C	P ^s	10.4	Pa
Logarithmic value – octanol-water partitioning coefficient	log K _{ow}	3.35	–
Reaction rate constant water	k ₂	2.89 × 10 ^{−3}	h ^{−1}
Reaction rate constant sediment	k ₄	1.93 × 10 ^{−4}	h ^{−1}
Sediment-water phase effective diffusivity	B _{wx}	1.91 × 10 ^{−6}	m ² /h
Naphthalene concentration	C _i	8 (~1000)	mol/m ³ (ppm)

decreases to 0.01 cm, resulting in a final area of $1.52 \times 10^5 \text{ m}^2$ at 225 h. The oil volume curve is also shown in Fig. 1(a), with volume decreasing by the processes of evaporation and dispersion. The dispersion-emulsification formulation (as discussed in Section 2.1) eventually drives the residual oil (oil not evaporated) into the water column, thus giving the surface slick a finite lifetime. In the current example, the calculated surface slick lifetime is 435 h (~18 d).

The emission rate of naphthalene into the water column is presented as a function of time along with the water fugacity curve in Fig. 1(b). The chemical input to the water column becomes zero at 435 h, which corresponds to the surface slick lifetime. The shape of the emission rate curve depends on natural dispersion rate and oil slick volume (see Eq. (9f)). Oil slick volume decreases with time due to the evaporation and natural dispersion weathering processes. Assuming constant wind speed and oil-water interfacial tension, the variation of the product term $(\mu^{1/2}h)^{-1}$ in Eq. (5) governs an increase or decrease of dispersion rate with time in the current simulations. After reaching its peak, approximately at 1 h (see Fig. 1b), the emission curve starts decreasing. At an elapsed time of 16 h a small increase in the emission rate curve is observed due to the higher dispersion rates.

The water and sediment fugacity curves are shown in Fig. 1(c). A peak in the water fugacity occurs at approximately 3 h (which is very close to the input curve peak), whereas the sediment fugacity curve peaks at an elapsed time of 447 h. The

water compartment shows a rapid decrease of its burden after the chemical input is stopped, but the sediment is slower to respond. Fig. 1(c) thus indicates that the water compartment response is faster than that of the sediment compartment. This behavior stems from the fact that the water compartment has relatively high advection (D_{A2}) and reaction (D_{R2}) processes.

The group VZ/D provides valuable insight into the residence time associated with a transport process; the shorter the residence time, the more significant the process. The water-to-sediment transfer time for depletion of water through the D_{24} process can be calculated as:

$$t_{\text{res}24} = \frac{V_{B2}Z_2}{D_{24}} = \frac{h_W Z_2}{[(B_{WX}Z_2/\Delta_S) + U_{DS}Z_2]} = 53.3 \text{ years} \quad (17)$$

The advection process residence time can be calculated as:

$$t_{\text{res}A2} = \frac{V_{B2}Z_{B2}}{D_{A2}} = \frac{\sqrt{\pi} \sqrt{A_2(t)}}{2 U_A} \quad (18)$$

The above expression shows that the advection residence time is implicitly a function of time during the slick area growth, and it increases with the square root of area. The advection residence time, averaged over the analysis period of 500 h, is calculated as 5 h. The reaction process residence time ($t_{\text{res}R2} = 1/k_2$) is 346 h or ~14.4 days.

Table 4 – Environmental multimedia parameters used in level IV fugacity-based model

Parameters	Notation	Value	Unit
Depth water	h_W	100	m
Volume fraction suspended solids in water	v_5	5×10^{-6a}	–
Volume fraction biota in water	v_6	1×10^{-6a}	–
Organic fraction suspended solid	ϕ_5	0.2 ^b	–
Organic fraction biota	ϕ_6	0.05 ^c	–
Density suspended solids	ρ_5	1500 ^b	kg/m ³
Density fish	ρ_6	1000 ^d	kg/m ³
Advection rate water	U_A	0.018 ^d	m/s
Deposition rate suspended solids	U_{DS}	5×10^{-7b}	m/h
Depth sediment	h_S	0.05	m
Diffusion path length in sediment	$\Delta_S = 0.5h_S^d$	0.025	m
Density sediment	ρ_4	2500 ^d	kg/m ³
Volume fraction sediment solids	v_7	0.37 ^c	–
Volume fraction pore water	v_8	0.63 ^c	–
Organic fraction sediment	ϕ_4	0.04 ^b	–
Re-suspension rate sediment	U_{RS}	$2 \times 10^{-7b,d}$	m/h
Burial rate sediment	U_{Bur}	$3.4 \times 10^{-8c,d}$	m/h

^a Sweetman et al. (2002).

^b Mackay et al. (1992).

^c Mackay (1991).

^d Sadiq (2001).

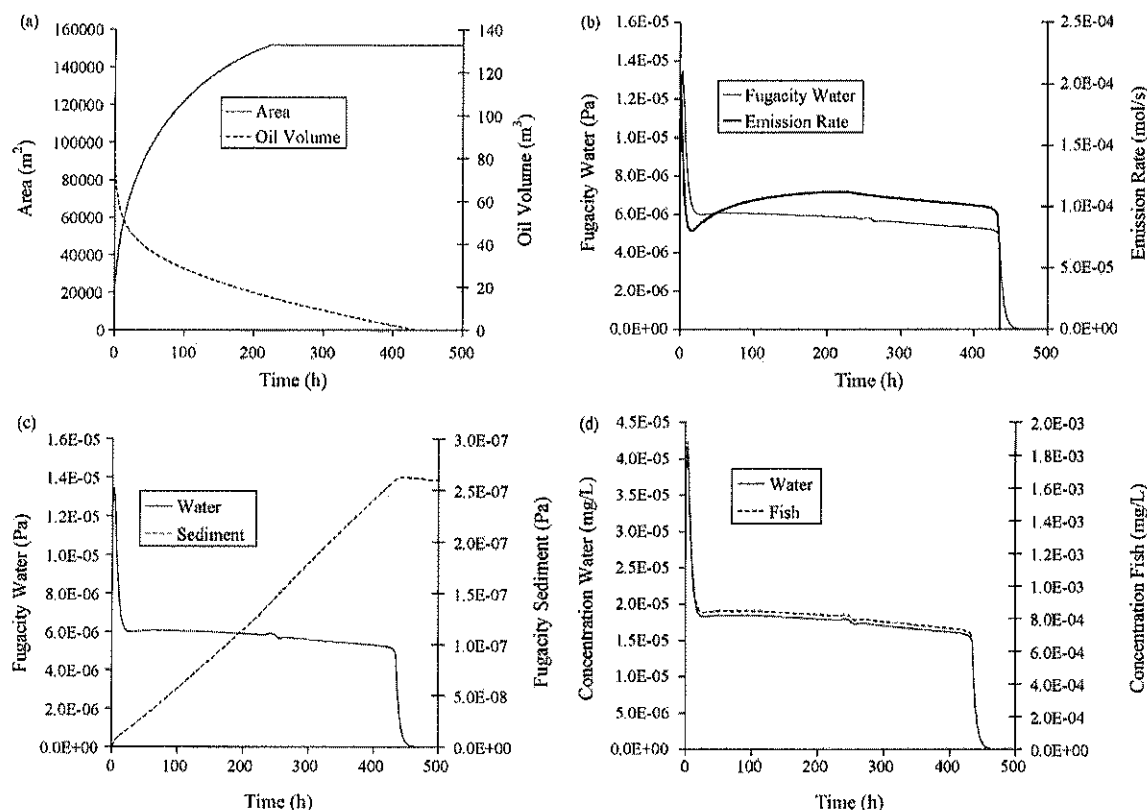


Fig. 1 – Multimedia fate of Statfjord crude oil in the marine environment.

The last process associated with the water compartment is the growth process. The residence time for this pseudo transport process can be calculated as:

$$t_{\text{resG2}} = \frac{V_{B2}Z_{B2}}{D_{G2}} = A_2 \left[\frac{dA_2}{dt} \right]^{-1} = \frac{A_2^2}{K_1 V^{4/3}} \quad (19)$$

With respect to the time at which the slick growth ceases, i.e., $[dA_2/dt] \rightarrow 0$, Eq. (19) shows that $t_{\text{resG2}} \rightarrow \infty$. This suggests that the growth transport process is only important during the area growth regime, and should not be included in model Eqs. (12) and (13) outside the growth regime. In the current example, at an elapsed time of 2 h, the growth residence time has the same value as that of the averaged advection residence time. Further, the growth process residence time increases and at an elapsed time of 106 h its magnitude becomes equal to the value of the reaction process residence time. Once the slick growth is ceased (at ~225 h), however, the growth process is no longer included in the fate modelling calculations.

The analysis suggests that the advection process has the lowest residence time. Hence, advection is the most important transport process in the water compartment.

In the case of sediment-to-water inter-media processes, the residence time is:

$$t_{\text{res42}} = \frac{V_{B4}Z_4}{D_{42}} = \frac{h_s Z_4}{[B_{WX}Z_2/\Delta_s + U_{RS}Z_4]} = 5.5 \text{ years} \quad (20)$$

The reaction residence time ($t_{\text{resR2}} = 1/k_4$) is approximately 5200 h. The residence time for the sediment growth process is the same as that for the water compartment growth residence

time. The last transport process is the sediment burial and the associated residence time is:

$$t_{\text{resBur}} = \frac{h_s}{U_{\text{Bur}}} = 168 \text{ years} \quad (21)$$

The analysis shows that during the growth regime (up to 225 h), the growth process is the most important transport process in the sediment compartment.

Another important parameter is Z , which distributes the concentration between phases. A phase of high Z value (such as fish) absorbs a greater quantity of solute (organic chemical), resulting in higher concentrations while retaining a low fugacity. The converse is true for a phase having a low Z value. The Z value for fish (Z_6) is approximately $1.091 \text{ mol/m}^3 \text{ Pa}$; for water, the value (Z_2) is $0.024 \text{ mol/m}^3 \text{ Pa}$. This leads to fish concentrations which are Z_6/Z_2 times higher than the water column concentrations. Fig. 1(d) provides a comparison of fish and water column concentration profiles for the case study.

The predictive concentration profiles presented here are based on existing, validated oil weathering algorithms, and the multimedia fugacity-based model developed in the current work. It should be noted that further validation of the results would require laboratory/field dynamic concentration measurements in coastal environmental media such as fish and ambient water.

5. Conclusion

The predicted trends of oil spill fate in a multimedia marine environment are in agreement with the theory of the fugacity

modelling approach (e.g., the higher concentration trends in fish than in water are because of the higher Z value for fish). The study shows that the water compartment response to the chemical input is faster than the sediment compartment; this is expected because the advection process is present only in the water column. Further, the analysis shows that the advection process displays the lowest residence time. We therefore conclude that the proposed methodology effectively applies existing oil weathering algorithms, and the level IV fugacity model, to predict the fate of an oil spill in a marine environment. Extensions to the current work would include further model validation by means of laboratory/field environmental data and the inclusion of data uncertainty analysis.

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