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Oil spill forecasting (prediction)

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ABSTRACT

Oil spills in the ocean are a matter of concern due to the damaging effect they can have on coastal and offshore resources. This work presents a review of present-day modeling techniques used in the mitigation of oil spills by booms, skimmers, chemical dispersants, and other equipment and the importance of the controlling parameters of these techniques. Three basic questions need to be addressed by oil spill models: (1) where the spill will move, (2) when will the spill get to the modeled endpoints, and (3) what will be its state when it arrives. The first two questions are relatively urgent, as far as response measures are concerned, and depend closely on the use of accurate data on winds, sea currents, and wave action as oil spill accidents evolve. Obtaining a reasonable answer to the third question lies in the use of reliable fate algorithms. Oil spill models can be divided in two types: Eulerian and Langragian. Adding to information regarding the oil type and its initial location, all oil spill models require data for the wind fields, sea state, sea-surface temperature, and currents, as well as other environmental parameters, if available. Such reliable data suit the needs of oil spill modeling predictions and are available daily at global, regional, and coastal scales within the broader scope of operational oceanography. Advanced oil spill models available at present use satellite synthetic aperture radar (SAR) images/data to detect possible oil slicks and assimilate slick and drifter observations to correct slick predictions. The emphasis of research and governmental institutions has been on improving 4D predictions obtained through simulation of oil spills backward in time to track the slicks back to their source. Such backward simulations, when integrated with ships’ Automatic Identification Systems (AIS), will be used to locate the sources of oil slicks around the world’s oceans and seas.

Keywords: Oil spills, modeling, fate algorithms, shoreline susceptibility, operational use of oil spills models

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1. Introduction

Oil spills in the ocean and in exclusive economic zones are a matter of concern due to the damaging effect they can have on various coastal and offshore resources. Fisheries, recreational infrastructure, industrial facilities, marine and coastal vegetation, and wildlife in general are particularly vulnerable to oil spill accidents. Yet, the movement of oil spills is notoriously difficult to predict in the open sea, where ever-changing met-ocean conditions can quickly alter the physical processes acting on spilled oil.

Examples of the influence of changing met-ocean conditions on oil spills have been witnessed during the M/V Exxon Valdez (1989) and M/V Prestige (2002) accidents. Both accidents recorded the scattering and beaching of oil by strong currents and winds through vast areas (Pettersen et al. 2003; González et al. 2006). In addition, recirculation and scattering of oil by natural processes were crucial phenomena contributing to the movement of oil during the Deepwater Horizon spill of 2010 (Atlas and Hazen 2011; Thibodeaux et al. 2011; Mariano, Kourafalou, Srinivasana, Kang, Halliwell, Ryan, and Roffer 2011). Anionic surfactants such as dioctyl sodium sulfosuccinate (DOSS) included in chemical dispersants were found to be sequestered in deepwater hydrocarbon plumes at 1,000–1,200 m water depth, persisting up to 300 km from the Deepwater Horizon platform some 64 days after dispersant applications ceased (Kujawinski et al. 2011). In the Baltic and western Mediterranean Seas, statistical analyses of oil spill trajectories identified areas where the impact of spilled oil is potentially more significant (Lu et al. 2012; Olita et al. 2012; Soomere et al. 2014). The understanding of small variations in circulation models was recognized by the latter authors as being paramount in the management of civil protection teams, often with limited resources and equipment, during the mitigation of large oil spill accidents.

In order to mitigate the impacts of oil spills as much as possible, it is common to fight them by deploying a variety of equipment such as booms and skimmers. In addition, alternative methods comprise the burning of spilled oil or the local use of chemical dispersants. For optimal use of equipment and dispersants within the framework of national or regional contingency plans, international protocols, response agencies, and organizations on oil pollution (e.g., Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea [REMPEC], European Maritime Safety Agency [EMSA], Baltic Marine Environment Protection Commission - Helsinki Commission [HELCOM], Consortium for Advanced Research on Transport of Hydrocarbon in the Environment [CARTHE], Australian Maritime Safety Authority [AMSA], Commonwealth Scientific and Industrial Research Organization [CSIRO], United Nations Environmental Program, Barcelona Convention [UNEP], etc.), it is necessary to employ numerical models to predict where the spill will most likely move, which resources are threatened, and how soon they will be threatened. Numerical models must also predict the expected state of the oil when it arrives on the shore, i.e., how much oil has been evaporated, the degree of emulsification of remaining oil, how much oil remains at the surface, how much oil was (and will be) dispersed as fine droplets through the water column, and how much oil will get to a particular location.
The particles of oil in a slick are transported by the sea water in which (or on which) they are located. The prediction of such advective movement depends critically on the availability of reliable met-ocean forecasts. In addition, the particles of oil can be transported by two other mechanisms associated with the water mass per se. First, a thick oil slick initially spreads over the water surface under the action of gravity. This mechanism becomes less important after the first few hours, as the thickness of the slick decreases and its viscosity increases, when a much more significant mechanism takes over: diffusion caused by seawater currents. Diffusion mechanisms cause the slick to spread over a large area and, often, to break up.

In addition to data regarding the oil type and volume, duration, and location of the spill, the oil spill models require wind and wave field data. Sea-surface temperature and currents and, sometimes, other environmental parameters such as water density, in the case of a subsurface oil spill source, are also crucial. For operational oil spill predictions, all these data should be available in near real time (Sepp Neves, Pinardi, and Martins 2016).

Owing to the development of operational oceanographic forecasting systems such as Copernicus Marine Environmental Monitoring Service (CMEMS; http://marine.copernicus.eu/), National Oceanic and Atmospheric Administration (NOAA; http://nomads.ncep.noaa.gov:9090/), and, elsewhere in the world under the broader initiatives of the Global Ocean Observing System (GOOS), reliable data suiting the needs of oil spill modeling predictions are now available daily at global, regional, and coastal scales (e.g., Alves et al. 2015, 2016). Therefore, to give reliable support to response agencies during major oil spill incidents and provide a sound basis for any user-designed application aiming to manage either the exploitation or the protection of the marine environment from oil spill accidents, it is necessary to have access to an efficient and quality-controlled operational estimate of wind and marine-state variables such as those provided by the aforementioned operational forecasting systems.

At present, advanced oil spill models allow for the use of satellite-derived synthetic aperture radar (SAR) imagery (Fig. 1) able to detect possible oil slicks (Klemas 2010; Liu et al. 2011a, b; Zodiatis et al. 2012). As they track the motion of observed slicks, advanced oil-spill models are able to switch from coarse to high-resolution ocean data when the oil slick passes from a coarse to a higher-resolution forecast domain. These advanced models allow the incorporation of observations from slicks and drifters to correct slick predictions and, if needed, can also assist backward simulations (in time) to track oil slicks back to their source(s). These options, combined with the integration of modeling data with ships’ Automatic Identification System (AIS), can help locate the source(s) of specific oil slicks.

This Chapter presents a summary of the physical processes parameterized in oil spill models and their effect(s) on the forward modeling of spill accidents and oil slick movement. The aim of this chapter is to provide the readers with a complete understanding of the physical processes controlling oil spill movement and scattering in offshore regions at a time when exploration drilling is equated, or has occurred in the near past, on multiple
continental margins in the world. In summary, this chapter is focused on the following questions:

1. What are the physical processes affecting (and controlling) the movement of oil spills straight after their inception and until biodegradation is capable of reassimilating this same volume of spilled oil in nature?
2. What basic equations are used in the oil spill models most commonly used by civil protection authorities and mitigation agencies?
3. What institutions in the world can, at this point in time, be considered as examples of good practice? What good practice do they implement in their approach to oil spill mitigation and prevention?
State-of-the-art oil spill models are complex, and a complete understanding of the modeled processes is beyond the scope of this Chapter. Basic equations included in the majority of Lagrangian oil spill models will be described instead. In Section 2, the drifting of oil slicks and the basic concepts behind oil spill modeling will be provided. Section 3 will focus on advection and diffusion processes. Section 4 will explain the fate–weathering processes. Section 5 will provide examples of the operational use of oil spill models. Section 6 will provide a summary of items required to further improve oil spill models with emphasis on the modeling processes of dissolution and photooxidation of oil spills.

2. Drifting of oil spills

The transport of substances (such as oil) in the sea is referred to as “drift.” In the context of ocean forecasting, drift closely depends on the physical conditions of the sea, i.e., winds, currents, and waves. Because oil is a fluid, it will spread and change its properties once it is spilled. The source of the oil may be on the surface (a ship or offshore or coastal platform) or in the subsurface (an offshore well-head blowout or a ruptured pipeline).

When oil is spilled offshore it records a number of physical and chemical changes, some of which result in its removal from the sea surface. Other changes cause oil to persist at the surface or in shallow coastal areas. Although oil can be (and often is) completely assimilated by the marine environment, the time involved in this assimilation depends on factors such as the amount of oil spilled, its initial physical and chemical characteristics, and the prevailing met-ocean conditions in which the oil remains at sea or is washed up on the coast.

Understanding how physical and chemical processes interact to alter the composition and behavior of oil with time is important to all aspects of oil spill response. For example, it may be possible to predict with confidence that oil will not reach vulnerable resources, rendering a clean-up response unnecessary. When an active response is required, the type of oil and its probable behavior and fate will determine what response options are likely to be effective.

a. Oil spill models

Two distinct approaches are usually applied to the modeling of drift trajectories: the Lagrangian or Eulerian approaches. The equations in the Eulerian approach are based on the mass- and momentum-conservation equations applied to the oil slick or, instead, on a convection–diffusion equation. In this latter, the diffusive part of the equation represents the spreading of oil and the convective terms represent advection of oil by sea currents and winds, commonly named as the advection–dispersion equation (1)

\[
\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial y} + D_y \frac{\partial^2 C}{\partial y^2} - w \frac{\partial C}{\partial z} + D_z \frac{\partial^2 C}{\partial z^2}
\]  

(1)

where \(\frac{\partial C}{\partial t}\) is the time rate of concentration change, \(\frac{\partial C}{\partial x}\), \(\frac{\partial C}{\partial y}\), and \(\frac{\partial C}{\partial z}\) are the change of concentration at \(x\), \(y\), and \(z\) axis, \(u\), \(v\), and \(w\) are the sea current field components, and \(D\) is the diffusive displacement, which parameterizes the turbulent effects.
Figure 2. Schematic representation of the transport and weathering processes acting on offshore oil spills.

The Lagrangian models represent oil slicks in the form of a large number of particles advected by the combined effect of winds, currents, waves, and diffusion (Fig. 2). Lagrangian models have proved to be more suitable for swift simulations during oil spill emergencies, being simpler, more efficient, and computationally less costly than Eulerian models (Fig. 3). The accuracy of the particle position will rely on the accuracy of the initial position, on the ability of the met-ocean models to provide accurate predictions, and on the inclusion of the proper physical mechanisms acting on the tracked particles.

A large number of numerical Lagrangian oil spill models have been developed since the early 1980s: from two-dimensional point source particle-tracking models and complex oil-slick polygon representations to three-dimensional advection–diffusion models. Some of the most well-known Lagrangian models, both in the two- and three-dimensional space, are as follows: SINTEF OSCAR2000 (Reed, Aamo, and Daling 1995), OILMAP (Spaulding et al. 1994; Applied Science Associates 1997), GULFSPILL (Al-Rabeh, Lardner, and Gunay 2000), ADIOS (Lehr et al. 2002), MOHY (Daniel et al. 2003), MOHID (Carracedo et al. 2006), POSEIDON OSM (Pollani et al. 2001), OD3D (Hackett, Breivik, and Wettre 2006; Hackett, Comerma, Daniel, and Ichikawa 2009), PISCES (Delgato, Kumzerova, and Martynov 2006), SEATRACK (Ambjörn 2007), MEDSLIK (Lardner et al. 1998, 2006; Zodiatis et al. 2008, 2012; Lardner and Zodiatis 2016, 2017), GNOME (Zelenke et al. 2012), OILTRANS (Berry, Dabrowski, and Lyons 2012), OSERIT (Legrand and Dulière 2012), and MEDSLIK-II (De Dominicis et al. 2013a,b). Three-dimensional oil spill models are able to calculate the distribution of oil hydrocarbons in the water column and oil sedimentation.
Figure 3. Schematic diagram representing the computational modules for an advanced oil spill model that first reads the environmental data and the initial oil spill conditions, then calculates the fate–weathering processes (evaporation, emulsification, dispersion, spreading, viscosity changes), computes the thickness of the thick and thin oil, and estimates the oil particle positions, and then the beaching, sedimentation, and oil state (surface, dispersed, beached, sedimented) and oil concentration.

The majority of existing Lagrangian oil spill models include the processes of spreading, advection, and diffusion of oil together with a standard set of transformation (“fate” or “weathering”) processes. They use the same, or similar (with small variations), semiempirical relationships obtained from laboratory and field experiments (Reed et al. 1999). As a general rule, most oil spill models do not consider processes such as dissolution, photooxidation, or chemical and biological decomposition of hydrocarbons. However, an attempt to include these processes has recently been carried out by Spanoudaki (Spanoudaki 2016) using a modified version of MEDSLIK-II model.

In addition to the advection of oil due to the effect of wind, currents, Stokes drift, and diffusive displacements, oil spills experience time-dependent changes that are linked to distinct physical processes. In the first hours after an accident, slicks spread over the sea surface under the action of gravitational forces, with discrete oil parcels recording complex spreading displacements. The lighter fractions of oil evaporate, significantly reducing the volume of oil in the sea, whereas the remaining fractions begin to absorb water and emulsify. These changes are reflected as variations in the properties of the spilled oil, namely density, viscosity, and volume of surface slicks. Part of the oil is driven below the water surface by
Table 1. Main oil spill model inputs and outputs for specific met-ocean variables.

<table>
<thead>
<tr>
<th>Met-ocean variables</th>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D or 3D sea currents Speed and direction</td>
<td>Type of oil pollution (single, multiple, polygons)</td>
<td>Oil spill location</td>
</tr>
<tr>
<td>Winds Speed and direction (10 m)</td>
<td>Initial location</td>
<td>Oil at surface (concentration)</td>
</tr>
<tr>
<td>Sea-surface temperature</td>
<td>Surface or spill depth</td>
<td>Dispersed oil (concentration)</td>
</tr>
<tr>
<td>Waves (significant height, wave direction and period)</td>
<td>Start time and date</td>
<td>Beached oil (concentration)</td>
</tr>
<tr>
<td>Water density or temperature and salinity profiles</td>
<td>Volume released</td>
<td>Slick thickness</td>
</tr>
<tr>
<td></td>
<td>Spill rate and duration of spill</td>
<td>Slick concentration</td>
</tr>
<tr>
<td></td>
<td>Total volume</td>
<td>Fate parameters</td>
</tr>
<tr>
<td></td>
<td>Oil type</td>
<td>Oil plume</td>
</tr>
</tbody>
</table>

the action of waves and is thus dispersed. In the water column, the movement of discrete oil parcels is followed using subsurface current data.

To compute the fate processes affecting the oil, computer models for oil spill simulation augment time in discrete steps, which, except for an instantaneous spill, divide the spill into several sub-spills, one occurring in each time step. The fate processes are considered independently for each sub-spill. Most oil spill models use modified versions of Mackay’s fate algorithms for evaporation, emulsification, and dispersion (Mackay, Paterson, and Trudel 1980). Mackay’s algorithms divide slicks into a thick part near the center and a thin part, usually called a “sheen,” that forms the edges of the slick. The sheen is very thin, generally of the order of 10 microns, whereas the thick slick may, in the case of a large spill, be initially several centimetres thick. Flow of oil from the thicker core feeds the thinner parts. Evaporation and dispersion both occur much more rapidly from the thin sheen than from the thick areas and these processes are modelled differently for the two components of the slick.

b. Input data used in oil spill models

To use any oil spill model, input information about the oil spill and the met-ocean conditions is needed (Table 1).

Lagrangian oil models split the active tracer equation into two component equations:

\[
\frac{\partial C}{\partial t} = -U \nabla C_1 + \nabla (K \nabla C_1) + \sum_{j=1}^{M} r_j(C_1)
\]  

(2)

In equation (2), \(\frac{\partial C}{\partial t}\) is the time rate of oil concentration change, \(U\) is the sea current with components \((u, v, w)\), \(K\) is the diffusivity tensor that parameterizes the turbulent effects,
and \( r_j \) are the \( M \) transformation rates of the oil concentration due to physical and chemical processes. The two component equations split by Lagrangian oil spill models are as follows:

1. The advection–diffusion equation (equation 3)

\[
\frac{\partial C}{\partial t} = -U \nabla C_1 + \nabla \left( K \nabla C_1 \right)
\]

(3)

where the oil slick is discretized by a large number of particles transported by water currents, winds, waves, and diffusion processes. Generally, the wind dominates the advection of the surface slicks, whereas the sea currents are important in periods with weak winds and for subsurface spills. The action of waves/Stokes drift becomes important in shallow waters, especially during storm-weather conditions.

2. Fate–Weathering transformation equation (4)

\[
\frac{\partial C_1}{\partial t} = \sum_{j=1}^{M} r_j (C_1)
\]

(4)

where \( C_1 \) is the oil concentration due to the weathering processes, i.e., evaporation, emulsification, dispersion in the water column, and viscosity changes.

3. Deterministic component of the oil spill model: Currents, winds, and waves

The three larger effects on oil spills are imposed by water-current movement, by the frictional forces of the wind, and by the action of the waves, which initially cause the slick to skid over the water surface. Moreover, the wind’s intensity predominates the evaporation, whereas the sinking of the oil particles at the upper-subsurface mixed layer is caused by the action of the waves. The success of response to oil spill incidents depends also on the availability of operational met-ocean data for use by oil spill models to predict the movement of the oil slicks and to forecast how soon it will get at vulnerable areas.

a. Deterministic component of the oil spill model: Wind and currents

Wind is one factor in driving the currents in the water body, but it also acts directly on oil slicks to move them relative to the sea surface and so must also be considered as an independent variable in obtaining a satisfactory prediction of the behavior of an oil spill on the sea surface. The common modeling technique employed by nearly all oil spill simulation models is to use a “wind factor” approach, i.e., the effect of wind will move oil at a certain fraction of the wind speed and at a certain angle to the wind direction. This angle will be to the right of the wind direction in the Northern Hemisphere and to the left of the wind direction in the Southern Hemisphere.
There is considerable dispute among oil spill modelers as to what are the best choices for the values of the drift factor and angle. Most oil spill models use values of around 3% for the former, and between 0 and 30 degrees for the latter. However, there is a known caveat to this approach, as wind also drives water currents and their effect on the oil slick is, to some extent, considered twice in some models: first, when calculating water-current flow and, second, when calculating the drift component affecting the oil spill.

Despite their complexity, oil spill models are flexible enough to allow a range of options to alleviate the problem of estimating wind-related drift. The first option is to select current velocity at an average depth of the mixed water layer, i.e., at depths at which the effects of wind on the drift component are significantly reduced. In shallow areas, an ocean forecasting model may be sufficiently fine to resolve the vertical structure of the current flow so that the motion of the surface layer is computed accurately. In such a case, the best option is to set the drift factor to zero and to use the computed surface-water flow to predict slick motion. Alternatively, one can reduce the drift factor in shallow water, rather than set it to zero, giving preference to surface current data. A third option is to reduce the effective wind data used to compute drift by an amount equal to the wind values used to compute sea-current flow. In this case, the most reasonable current velocity is that taken from surface waters. Examples of the sensitivity of current depth in oil spill modeling are provided by De Dominicis et al. (2013b).

The most straightforward option for modelers is to use current data computed using only buoyancy forces, ignoring the wind forces. A drift factor for the slick motion relative to the water will completely avoid any double counting. However, this option cannot be used when forecast currents are used, as forecast data based on buoyancy forcing alone are not available.

In addition to sea currents, the wind acts on oil slicks forcing them to move with a certain fraction of wind speed “α” and at a certain angle “β” to the right of the wind direction (see the following equations). Sea-surface wind–induced currents can be parameterized as a function of wind intensity and of the angle between winds and currents by using the following equations:

\[
U_w = \alpha (W_x \cos \beta + W_y \sin \beta)
\]

\[
V_w = \alpha (-W_x \sin \beta + W_y \cos \beta)
\]

where \(W_x\) and \(W_y\) are the wind velocity components, \(\alpha\) is the percentage of the wind to be added to the sea-current velocity, and \(\beta\) is the deviation angle between sea currents and wind.

\[5\]

b. Deterministic component of the oil spill model: Wave induced currents

Stokes drift velocity takes into account the effect of wave-induced sea currents, at each Lagrangian parcel, that add up to the local sea currents. It results from the fact that oil particles move faster forward when they are at the top of the waves’ circular motion, and
are moved backwards when they are at the bottom of a wave. Stokes drift velocity \((S)\) is calculated from the significant wave height \((H_s)\), the wave zero crossing period \((T_z)\), and the water depth \((z)\) according to the equation

\[
(S_x, S_y) = \frac{1}{8} H^2 k \omega d
\]

where \(H\) is the significant wave height, \(k\) is the wave number, \(\omega\) is the waves’ angular frequency, and \(d\) is the vector wave direction.

Generally, both the surface currents and the Stokes drift increase with wind speed, as does, of course, the wind drift itself. It is not feasible to provide a general comparison of these effects on oil spills because the currents and the sea state (waves) are dependent on the bathymetry and the coastal topography, even to the extent of being on occasion opposite in direction to the wind. In open water with a depth over 200 meters, the three drifts are usually in the same direction, the Stokes drift being 10% to 20% of the wind drift.

c. Spreading

Spreading takes into account the movement of the thick part of the oil slick as a light fluid on top of a more dense fluid (water) under the force of gravity. Except for a short period in the earliest stages of a spill, when the inertia of the oil plays a role in resisting the tendency to spread, for most of the time oil viscosity provides the dominant resistance to spreading under gravitational forces. The theory of gravitational spreading against viscous resistance was first developed by Fay (1971). Equation (7) provides an expression for the change in area of the thick slick on any time step, and the second term in is based on Fay’s theory of gravity–viscous spreading. The first term in this equation represents the change in area of the thick slick caused by loss of oil into the sheen

\[
\Delta A_{tk}^{(s)} = - \frac{\Delta V_{tn}^{(s)}}{T_{tk}} + C_2^{(s)} A_{tk}^{1/3} T_{tk}^{4/3} dt
\]

where \(C_2^{(s)}\) is a constant and \(\Delta V_{tn}^{(s)}\) is the volume increment flowing from thick to thin slicks, \(T_{tk}\) is the surface thickness of the thick part of the surface oil slick volume, \(A_{tk}\) is the surface area of the thick part of the surface oil slick volume, and \(dt\) is the time step.

The volume is related to the increment in area of the thin slick, \(\Delta A_{tn}^{(s)}\) such as

\[
\Delta V_{tn}^{(s)} = \Delta A_{tn}^{(s)} T_{tn}
\]

once we have a value for \(\Delta A_{tn}^{(s)}\), we can update the area \(A_{tk}^{(s)}\) of the thick slicks taking into account \(T_{tn}\), the surface thickness of the thin part of the surface oil slick volume.

Spreading is considered to occur for a period of 48 hours after the release of each sub-spill, or until the thickness of the thick part of the slick becomes equal to that of the thin slick. If this occurs, the model terminates all further spreading, transfers all the remaining
oil in the thick slick (and in the droplet clouds beneath it) onto the thin slick. From that point onwards, the model will also ignore evaporation and dispersion from the thick slick. The movement (or transport) of oil is, from this point, dominated by advective forces such as currents, wind, waves, and associated water turbulence.

The increment in area of the thin slick \( \Delta A_{in}^{(s)} \) is approximated by a formula similar to Fay’s (Fay 1971), i.e., proportional to the 3rd-root of the area multiplied by the time-step and by an exponential function of the thickness of the thick slick. This latter exponential function reflects the tendency of the oil slicks to stop spreading when they become very thin:

\[
\Delta A_{in}^{(s)} = C_1 A_{in}^{1/3} \exp \left( -\frac{C_3}{T_{lk} + 0.0001} \right)
\]

where \( C_1 \) and \( C_3 \) are the model’s parameters, \( T_{lk} \) is the surface thickness of the thick part of the surface oil slick volume, and \( dt \) is the time step.

d. Stochastic component of the oil spill model: Diffusion

Diffusion causes oil slicks to spread widely and to break up. The stochastic transport that results from diffusion (Ahlstrom 1975; Hunter 1987) is written as

\[
\begin{align*}
dx'(t) &= Z_1 \sqrt{2K_x} dt = [2n - 1] \sqrt{6K_h} dt \\
dy'(t) &= Z_2 \sqrt{2K_y} dt = [2n - 1] \sqrt{6K_h} dt \\
dz'(t) &= Z_3 \sqrt{2K_z} dt = [2n - 1] \sqrt{6K_v} dt
\end{align*}
\]

where \( K_h, K_v \) are the horizontal and vertical diffusivities, \( d \) is the particle mean path, \( n \) is a random real number between 0 and 1, \( Z_1, Z_2, \) and \( Z_3 \) are random vector amplitudes, and \( dt \) is the time step.

The horizontal diffusivity is considered to be isotropic and the values used are within the range of 1 to 100 m\(^2\) s\(^{-1}\), consistent with estimates of Lagrangian diffusivity carried out by De Dominicis et al. (2012). In some oil spill models, the horizontal diffusivity is estimated using the sea-surface current speed and the Smagorinsky (1963) horizontal diffusion equation. The vertical diffusion at the upper surface (or mixed layer) is considered to be 0.01 m\(^2\) s\(^{-1}\), whereas below the upper surface it is 0.0001 m\(^2\) s\(^{-1}\).

4. Fate–Weathering processes of the oil spill model

The oil spills are modeled using a Monte Carlo method, in which the spill is divided into a large number of Lagrangian parcels of equal size. At each time step, each parcel is given an advection and a diffusive displacement. In addition, parcels experience changes linked to fate processes. The lighter components of the oil evaporate at a rate that depends on wind speed and sea-surface temperatures. The remaining fraction of oil will absorb water, i.e., emulsify. Evaporation and emulsification change the intrinsic properties of the oil, i.e., density, viscosity, and volume.
Figure 4. Schematic diagram showing expected volume transfers between thin and thick slicks based on Mackay’s concepts of weathering processes. The changes in surface-oil volumes of the thin $\Delta V_{tn}$ and thick $\Delta V_{tk}$ parts of a slick result from evaporation (e), dispersion (d) and spreading (s).

a. Volume changes

The volume of oil particles is changed after the fate processes act on the slick. The oil released on each time step is considered as consisting of a thin (sheen) and thick parts. In each part, the oil properties change by evaporation, emulsification, spreading, and dispersion (Fig. 4).

These processes lead to changes in the volumes of oil in each constituting part (Fay 1971; Mackay and Leinonen 1977; Mackay et al. 1979; Mackay, Paterson, and Nadeau 1980; Mackay, Paterson, and Trudel 1980)

$$V'_{tk} = V_{tk} - \Delta V^{(e)}_{tk} - \Delta V^{(d)}_{tk} - \Delta V^{(s)}_{tn}$$

$$V'_{tn} = V_{tn} - \Delta V^{(e)}_{tn} - \Delta V^{(d)}_{tn} + \Delta V^{(s)}_{tn} \quad (11)$$

where $\Delta V^{(e)}_{tk}$ and $\Delta V^{(e)}_{tn}$ is the volume lost by evaporation, and $\Delta V^{(d)}_{tk}$ and $\Delta V^{(d)}_{tn}$ are the volume lost by dispersion. In addition, $\Delta V^{(s)}_{tn}$ is the amount of oil flowing from the thick to the thin parts of the slick.

b. Evaporation

Evaporation changes the volume of the thin and thick parts of the slick and is the main transformation process recorded by the spilled oil after its initial release. Evaporation removes a significant portion of the total mass of the slick within a short time, usually the portion high in volatile fractions, whereas heavy fuel oils lose relatively little volume to evaporation. Algorithms computing the evaporation depend on the wind speed, sea-surface temperature, thickness of the slick, vapor pressure of the oil (which depends on the oil type), and the period of exposure of the oil at the sea surface.

The volume of oil lost by evaporation is computed using Mackay’s algorithm for evaporation (Mackay, Paterson, and Nadeau 1980). In this algorithm, each oil spill parcel consists
of a light evaporative component and a heavy nonevaporative component. The initial fraction of the evaporative component is set according to the type of oil. At each time step, the fraction of the light component remaining in each oil spill parcel is reduced. For the thin slick, it is assumed that all the remaining evaporative component will be evaporated during the next time step so that the volume of oil evaporated from thin slicks in each time step equals the total content of the light component in the thin slick

$$\Delta V_{tn}^{(e)} = V_{tn} (f_{\text{max}} - f_{tn})/(1 - f_{tn})$$

(12)

where $f_{tn}$ is the fraction of the oil in the thin slick that has already evaporated at the beginning of the step, and $f_{\text{max}}$ is the initial fraction of the evaporative component, which represents the maximum value that $f_{in}$ can attain.

In case of spills with heavy oil, the estimates of the fate parameters such as evaporation are in general less than those of very light oil, whereas the opposite stands in the case of beaching and viscosity (Figs. 5 and 6).

For thick slicks, the increment in the fraction $f_{tk}$ of evaporated oil is expressed as the product between the vapor pressure $P_{oil}$ and the change in “evaporative exposure” $\Delta E_{tk}$:

$$\Delta f_{tk} = P_{oil} \Delta E_{tk} \text{ where } P_{oil} = P_0 \exp (-c f_{tk})$$

(13)
In this equation, \( P_0 \) is the initial vapor pressure and \( c \) is a constant that measures the rate of decrease of vapor pressure with the fraction already evaporated. The increment in exposure is expressed as the product between a mass transfer coefficient \((K_m)\), time step \((dt)\), the slick area \(A_{tk}\), and the molar volume of the oil spilled \(V_{mol}\). This numerator is then divided by the gas constant \((R = 8.2 \times 10^{-5} \text{ barm}^3 \text{ mol}^{-1} \text{ K})\), the water temperature \(T\) in \(^\circ\text{K}\) and the initial volume of the sub-spill \(V^{(0)}\), to give us

\[
\Delta E_{tk} = \frac{K_m V_{mol} A_{tk} dt}{RT V^{(0)}} = \frac{K_m V_{mol} A_{tk} (1 - f_{tk}) dt}{RT V_{tk}}
\]

where \(K_m = C^{(e)} \left(W_{kph}\right)^{\gamma}\).

In these two equations, \(W_{kph}\) represents the wind speed and \(V_{tk}\) is the current volume of oil in the thick slick(s), which is equal to \(V^{(0)}(1 - f_{tk})\).

The volume of oil lost by evaporation, per time step, is equal to the increment in evaporated fraction multiplied by the original volume

\[
\Delta V_{tk}^{(e)} = \Delta f_{tk} V^{(0)} = \Delta f_{tk} V_{tk} / (1 - f_{tk})
\]

The evaporative component in thin slicks is often assumed to disappear immediately, but thin slicks are effectively fed by oil from thick slicks that have not fully evaporated. This
leads to the formula

\[ f_{ln} = f_{\text{max}} - \Delta V_{ln}^{(s)} \left( f_{\text{max}} - f_{lk} \right) / V_{ln}' \]  

meaning, in effect, that evaporation leads to an increase in the viscosity of spilled oil.

c. Emulsification

Emulsification is the process responsible for the formation of a water-in-oil emulsion. It comprises the process by which water becomes mixed with oil in the slick. Emulsification does not start until a certain amount of oil has been evaporated; however, for Mackay’s model of mousse formation the emulsification starts the moment the oil is spilled.

The Mackay model for the change in the fraction \( f_w \) of water in an oil-water mousse, per time step (Mackay et al. 1979), is given for calm water by

\[ \Delta f_w = C_2^{(m)} \left( 1 - C_3^{(m)} f_w \right) dt \]  

The presence of wind creates waves, which greatly enhance the rate of emulsification, and the previous model for \( \Delta f_w \) is multiplied by the factor \((W + 1)^2\) where \(W\) is the wind speed (in m/s), \(C_2^{(m)}\) and \(C_3^{(m)}\) are constants, with the water-in-oil fraction having the upper limit \(C_3^{(m)}\), and \(dt\) is the time step.

The principal effect of emulsification is to create an emulsion of greatly increased viscosity when compared with the oil initially spilled. This has serious implications for certain methods of treatment of the slick. For example, the spraying of surfactants, whose effect is to reduce the surface tension of the oil and hence enable the slick to be readily dispersed in the water body, ceases to be effective when the oil viscosity becomes too high. Burning, another method used to remove oil slicks, also becomes ineffective when the water content is high. Another negative effect of emulsification is that it increases the volume of the slick; in certain cases, the volume of oil becomes three to four times larger than the initial volume of oil released, despite recorded evaporated volumes of nearly half the original oil released. This means that the cleanup costs, whether by skimmers or directly from the beaches, are often greatly increased.

d. Dispersion

Dispersion is the uptake into the water column of oil droplets of diminishing size, until they are no longer part of the slick in any practical sense. Wave action breaks the oil slicks in droplets of various sizes and drives them into the water column, forming a cloud of droplets beneath the spill. The droplets are classified as one of the following: (1) large droplets \(X_L\) that rapidly rise and coalesce again with the spill or (2) small droplets \(X_s\) that rise slowly and may be immersed long enough to diffuse into the lower layers of the water column (Fig. 7). In this latter case, oil droplets are lost from the surface spill and considered to be permanently dispersed in the water column. In shallow waters, some of this dispersed oil may become sedimented on the seabed (see Section 4g).
Figure 7. Schematic representation of the modes of dispersion in large and small oil droplets below the surface spill. The model of dispersion of oil into the water column is based on the work of Buist (1979) and Mackay et al. (1979), in which $R_L$ and $R_S$ are the downward volume fluxes of oil per unit area of the slick entering the water as large ($X_L$) and small ($X_s$) droplets respectively.

The diagnostic parameter distinguishing small droplets from their larger counterparts is their rising velocity, which is comparable with their diffusive velocity. In contrast, the rising velocity of large droplets is much larger than their diffusive velocity.

The rate of dispersion is largely dependent upon the type of oil spilled and the sea conditions, developing rapidly with low-viscosity oils in the presence of breaking waves. Conversely, dispersion is significantly reduced with the formation of oil–water emulsions (Buist 1979; Mackay et al. 1979), with the fraction of the slick dispersed in each time step being given by

$$\Delta f_d = C_3^{(d)} (W_{m/s} + 1)^2 \, dt$$

where $W_{m/s}$ is the wind speed in m/s.

Mackay proposed the following expression as a model for the fraction of small droplets in the dispersed oil:

$$f_s = \left\{ 1 + C_4^{(d)} \left( \eta_{em} / 10 \right)^{1/2} \left( T_{rk} / 0.001 \right) (\sigma / 24) \right\}^{-1}$$

where $\sigma$ is the interfacial surface tension between the oil and sea water and $C_4$ a constant.

The volume loss from thin slicks is given by the following equation:

$$\Delta V_{tn}^{(d)} = f_s \Delta f_d V_{tn}^{(d)}$$

e. Density and viscosity changes in spilled oil

Oil density depends on the type of oil spilled, which is classified using American Petroleum Institute gravity (API) units. API units are a measure of the oil weight relative to water. From API gravity values it is possible to calculate oil density. The conversion from API to density requires the calculation of specific gravity as follows:

$$SG = \frac{141.5}{(API + 131.5)}$$
The specific gravity can subsequently be converted to density using the equation

$$\rho = SG \rho W$$

(22)

where $\rho W$ is the water density.

Changes in oil viscosity are computed according to the amounts of emulsification and evaporation recorded in time and space. Evaporation leads to an increase in viscosity, and the formula used to represent viscosity changes in spilled oil is

$$\eta_{oil} = \eta_0 \exp\left(K^{(e)} f_{tk}\right)$$

(23)

where $\eta_0$ is the initial viscosity and $K^{(e)}$ is a constant that determines the time-dependent increase in viscosity with evaporation.

Oil viscosity is of importance in determining the viability of dispersant spraying on a spill. As viscosity increases through evaporation and emulsification, dispersant spraying becomes less effective.

The viscosity $\eta_{em}$ of the oil-water “mousse” is given by

$$\eta_{em} = \eta_{oil} \exp\left\{2.5 f_w \left/ \left(1 - C_{1(m)} f_w\right)\right.\right\}$$

(24)

f. Beaching

It may happen that the horizontal displacement of an oil slick moves part of it onto the coast, a process known as “beaching.” The beaching of a particle of oil is not permanent, however, and in subsequent time steps there are significant chances if the particle is washed back into the water. Nevertheless, a fraction of the oil becomes permanently beached by seeping into the sand or becoming adsorbed onto rocks. Oil on the beach, therefore, consists of two categories: oil that may later be washed back into the water column and oil that may not be washed back (Figs. 8, 9, and 10).

The rate of adsorption, as well as the probability of being washed off the coast, depends on the type of coastline. For example, oil on an exposed headland is more likely to be washed back into the water than oil deposited in an enclosed bay. Or, to take another example, oil deposited on a sandy beach will be absorbed much quicker than oil on a cliff face. Models that take beaching into account allow for the classification of coasts into defined categories such as sandy with small or large pebbles, rocky with exposed headlands, and so on.

The change in the status of an oil particle due to adhesion to the coast is taken into account by checking whether the parcel intersects any of the coastline segments ($L_i$). If the particle crosses the coastline, it is placed at the position of intersection of its path with this same coastline segment, and its status changes from “on surface” to “beached.” Usually, in oil spill modeling the status change of the oil particle is achieved by changing the status index of the parcel from 1 or 2 for parcels on the surface to a value equal to the negative of the index of the particular segment of the coastline the oil particle hits.

$$x_{k(t)}, y_{k(t)} \in L_i \Rightarrow \sigma(n_{k(t)}) = -L_i$$

(25)

where $\sigma(n_{k(t)})$ is the particle status index and $\varepsilon$ is the thickness offset.
g. Sedimentation

In shallow waters, the action of sea currents and, even more importantly, of the surface wind–driven waves can cause particles of sand or other seabed material to be stirred up...
so that they form a cloud in the water. If a parcel of dispersed oil enters such a cloud, it may adsorb particles of bottom matter with the result that its density increases, perhaps to a level where it will sink to the bottom. This process is called sedimentation of dispersed oil and results in the oil being more or less permanently fixed on the seabed. Its removal will usually depend on some slow biological process of degradation.

Modeling this sedimentation process is not only complex but also depends on data that are not usually available such as the thickness, density, and particle size distribution of the bottom sediment. For this reason, most current oil spill models take a very simplistic view of the process. For example, if any parcel of oil approached within 0.2 m of the seabed then there is a certain probability of its becoming sedimented. The sedimentation is accomplished by changing the parcels status from “dispersed” to “sedimented,” after which its position remains fixed, no longer transported by currents or by diffusion.

The requirement that a parcel must approach close to the bottom guarantees that this process will almost certainly be limited to shallow waters because the vertical diffusion below the thermocline is always relatively small, and the dispersed oil from a surface slick hardly ever reaches depths over 100 meters below the surface.
5. Operational use of oil spill modelling

The response agencies for oil pollution incidents need reliable operational-level information about the movement and evolution of any spilled oil at local and regional scales. At present, met-ocean data provided from the operational forecasting services, such as the Copernicus marine (CMEMS, NOAA, etc.) and atmospheric services (ECMWF, NCEP, etc.), have been proven important in operationally assisting (1) the agencies responsible for marine safety and (2) the response agencies responsible for mitigating any impacts on the marine environment that may arise from major oil pollution incidents.

The initial response in an oil spill accident is to identify as soon as possible the exact location of the spill, so that one can predict where the slick will move and which resources it will affect. Therefore, remote satellite observations have become one of the most important tools for detecting oil slicks in the open sea (Klemas 2010; Liu et al. 2011a, b, c; De Dominicis et al. 2013a, b; Zodiatis et al. 2012). SAR imagery provided by RADARSAT, ESA ENVISAT, and the more recent SENTINEL are useful instruments in oil spill detection owing to its large coverage, light-independent sensing, and all-weather capability (there are limitations in case of too strong/too weak winds). In 2007, the EMSA established a dedicated service, named CleanSeaNet (CSN), to provide the Member States’ response agencies real-time alerts and processed online data from the satellite-data providers previously mentioned.
Moreover, the EMSA-CSN data has been coupled with several well-established operational oil spill models running in the Mediterranean Sea, Black Sea, Baltic Sea, North Sea, and Northeast Atlantic Ocean.

In the U.S., Academia are directly involved in the monitoring of the impact of oil spills to marine habitats and their species. After a first assessment from the U.S. Department of Interior (McNutt et al. 2011), universities such as Stanford and Miami are effectively involved in the monitoring of maritime species and in understanding the impact of oil in coastal communities (see http://news.stanford.edu and EPA regulatory reference https://www.epa.gov/sites/production/files/2014-04/documents/b_40cfr110.pdf).

The Universities of Miami and South Florida have extensive Ocean Circulation research programs that aim to understand the circulation (and fate) of pollutants in the Gulf of Mexico (e.g., http://ocgweb.marine.usf.edu/). In addition, software such as GODAE’s Oceanview and GNOME (NOAA) are used to assist the monitoring (and prediction) of ocean conditions and pollutant spreading in U.S. waters.

In the U.S. Gulf of Mexico, CARTHE has recently been established to understand (and model) oil spills associated with drilling and maritime activities (CARTHE 2017). High-resolution coastal modeling was conducted during the Hurricane Isaac period and predictions of storm surge were quantified. High-resolution simulations of the near-field plume, as well as multi-phase modeling near the air–sea interface, are well in progress. In addition, Lagrangian coherent structures (LCSs) are used as a model performance metric. LCSs are the skeletons of patterns formed by passive tracers. Hence, when information on such patterns is available, models can be calibrated in such a way that the LCSs they sustain are correctly located relative to these patterns. LCSs can also be used as a prediction tool as they can sustain highly attracting cores that enable forecasting changes in the shape of a passive tracer pattern by indicating directions of sustained stretching. As early as 2012, CARTHE have modeled the dispersion of marine pollutants on coastal areas of the Gulf of Mexico using LCSs in their algorithms. This approach has had the advantage of acknowledging (and resolving) the dispersion of pollutants at oceanic submesoscales. In fact, Schroeder et al. (2012) have found that tightly spaced clusters of drifters constitute an efficient and inexpensive observational technique that should be used to understand the relative dispersion statistics from rapidly evolving submesoscale flows. The authors found, on the basis of both $D^2(t)$ (particle mean square separation as a function of time) and $\lambda(\delta)$ (scale-dependent finite-size Lyapunov exponent), that time scales of $t < 15$ hours and space scales of $\delta < 1$ km (characteristic of submesoscale phenomena) exhibit enhanced relative dispersion compared with larger scales of motion. For the studied area in Schroeder et al. (2012), values obtained reached $\lambda \approx 20$ days$^{-1}$ for $\delta < 100$ m, which is an order of magnitude greater than those obtained for the offshore mesoscale flows.

As a result of these latter experiments, Schroeder et al. (2012) suggested that computations with realistically configured 1/60° resolution of the Regional Ocean Modeling System (ROMS) model were unable to capture the enhanced dispersion regime imposed by submesoscale phenomena. These results indicated the need for subgrid-scale models for submesoscale transport to be incorporated in the daily prediction of oil spill transport.
In Australia, the AMSA has the responsibility of leading a National Plan for Maritime Environmental Emergencies. It trains, plans, and coordinates the response of mitigation teams at national, local, and industry level. At the same time, it collates a database of oil spills and other pollution events from the Australian Exclusive Economic Zone, therefore acquiring knowledge from real-time data on maritime and drilling accidents (AMSA 2017). The innovative part of their remit, which includes the modeling of oil spill movement 24/7, is the collaborative nature of their work. In fact, they collaborate across a wide spectrum of institutions and countries to include partners such as (1) Commonwealth, State, and Northern Territory governments; (2) shipping, ports, oil, salvage; (3) exploration and chemical industries; and (4) emergency services across Australia’s coastal waters, offshore islands, and territories. AMSA publishes a series of oil spill modeling results on https://www.amsa.gov.au/forms-and-publications/environment while requesting that exploration companies such as BP develop and test their own models. In Australia, between 1910 and 1961, there was an average of 1.23 ± 0.43 incidents per year, spilling an average of 114,062 ± 352,512 tons of oil per year. These averages increased to 3.83 ± 2.65 events with 123,277 ± 166,735 tons of oil spilled per year from 1962 to 1990, and again, from 1991 to 2012 to 6.50 ± 5.17 events with 164,299 ± 290,655 tons of oil spilled per year (e.g., Morgan et al. 2014). Offshore platform and tanker spills have accounted for 37% and 27% of this total, respectively, highlighting the need to develop real-time spill models to assess the impact of accidents on the wildlife and coastal communities.

The AMSA is responsible for mitigating oil spills using a large range of data, whereas CSIRO is responsible for monitoring the coast and marine habitats after oil spill accidents occur (www.amsa.gov.au and http://www.publish.csiro.au/book/7585/). The two institutions use a range of models and datasets, from local oceanographic data to satellite imagery, to follow national legislation where oil-spill mitigation and monitoring are concerned. As stated on the AMSA’s website, “AMSA and CSIRO collaborate to guarantee the use of the most up-to-date monitoring science, methods and advice. CSIRO is an independent, trusted science adviser to the National Plan.” Similar protocols, although not yet fully developed, are being considered by China (Yu et al. 2016), as the Bohai strait witnesses frequent oil spills of moderate dimension, and also by South Korea (Loh et al. 2017) and Brazil, the latter through the REMO network (Marta-Almeida et al. 2013).

In order to strengthen the marine safety in the Mediterranean sea, a multi-model oil spill prediction system was implemented within the framework of the Mediterranean Decision Support System for Marine Safety (MEDESS4MS) (MEDESS4MS 2017; Zodiatis et al. 2016), where four well-established oil spill models developed for the region (MEDSLIK, MOTHY, POSEIDON OSM, MEDSLIK-II) are coupled with 14 hydrodynamic, 7 atmospheric, and 7 sea-state forecasting systems via a user interface and a network data repository (NDR). An NDR was prepared and harmonized for the MEDESS-4MS support system, with different input/outputs from all the 28 different operational forecasting systems and the four oil spill models indicated previously.
Accurate wind and sea currents data, with high frequency (e.g., hourly) and high spatial resolution, are required to obtain any successful oil spill prediction. In order to evaluate the performance of the MEDSLIK-II oil spill model, the trajectories of seven surface buoys were intercompared for a period of 180 hours in October 2007, during a Lagrangian experiment in the Liguria Sea using the MyOcean MFS ocean forecasts (De Dominicis et al. 2013a). The results from this experiment show that a maximum spatial error between the observed and simulated paths of the trajectories of the order of three times the horizontal resolution of the hydrodynamical model is acceptable, with a predictability skill between 1 and 2.5 days, depending on the variability of the sea currents.

Like the previous experiment, in order to evaluate the performance of the Aegean Levantine Eddy Resolving Model (ALERMO) hydrodynamical forecasting system, oil spill predictions were carried out in the northern Aegean Sea using an oil spill dispersion model (http://diavlos.oc.phys.uoa.gr) and 25 drifting buoys and dedicated oil spill drifting instruments deployed in October 2012 (Hernandez et al. 2015). The trajectories from this Lagrangian experiment were compared with the oil spill drift predictions. The experiment showed that, over the first 20 hours, forecasts are more efficient than persistence data for the center of mass of oil spills (Fig. 11). Furthermore, in areas of strong and varying dynamical features (fronts, eddies), forecast errors grow significantly, emphasizing the need for more advanced prediction systems such as ensemble forecasts.

6. Further improvements on oil spill modelling

It was mentioned in the previous sections that the most common numerical formulation is the representation of the oil mass as a cloud of discrete particles, each one representing
a volume of oil that is subject to weathering and motion induced by physical met-ocean forces. The representation of particles and the formulation of oil fate processes may vary considerably among oil models, but all are critically dependent on met-ocean (physical) forcing to determine the oil spill fate and, especially, its motion. Currents, waves, and winds are the most important factors, although the state-of-the-art oil-drift models are able to make use of external data sets for currents, surface wave energy, wave-induced drift (Stokes drift), air temperature, water temperature and salinity, and turbulent kinetic energy obtained from numerical models for weather, ocean circulation, and waves. However, the way(s) these data are used varies considerably depending on the parameterizations introduced by the particular oil spill model. Ocean circulation data, primarily sea currents and, to a lesser degree, water temperature and salinity, are the forcing components that must be further improved, chiefly because ocean forecasting is less skilful and mature than weather and wave forecasting. At present, ocean models simulate some components of the current field better than others: tides, wind drift, and coastal currents are well reproduced, whereas eddies and meanders are often poorly simulated. It is therefore evident that the quality of oil spill forecasts depends on which current components are dominant in a particular area and the weight given to the ocean current data by the oil spill model. The hydrodynamic forecasting systems that are based on the assimilation of available ocean observations usually offer better forecast accuracy; thus, the use of the velocity fields from this kind of system provides more realistic fields for oil spill dispersion.

Oil spill forecasting is typically carried out using a numerical model of the fate and motion of the oil in the sea. Oil fate (or weathering) includes evaporation, emulsification, natural dispersion, and other oil-specific processes and is determined by the chemical properties of the particular oil type under the influence of ambient environmental conditions. However, an incomplete understanding of fate processes and of turbulent mixing introduces the need for subgrid-scale parameterizations in all oil spill models. These parameterizations require the estimation of empirical coefficients that depend on both the type and age of oil, and on environmental factors such as wind speed, temperature, wave height, and salinity. Uncertainties in parameterizations used in these models, initial conditions, and environmental data all lead to uncertainties in estimates of oil locations and state. More detailed descriptions of the different phases of the weathering process in oil spill modeling are clear from the recent literature, although most of them require further research in the laboratory and in the field.

Oil spill models typically do not include a realistic description of dissolution and degradation, although these weathering processes are significant for estimating the impact of an oil spill to marine ecosystems and for risk assessment for the mid and long term. Oil can dissolve in the water column from the surface slick or from dispersed oil droplets. Dissolution and evaporation are competitive processes. Dissolution can be significant from dispersed oil droplets due to the lack of atmospheric exposure and the higher available oil surface area per unit of volume. The algorithm developed by Mackay and Leinonen (1977) is usually applied in oil spill modeling, which treats dissolution as a mass flux related to
solubility and temperature. The lower molecular–weight aromatic and aliphatic hydrocarbons are both more volatile and more soluble than those of higher molecular weight. These lower molecular–weight aromatic compounds (monoaromatic and polynuclear aromatic hydrocarbons [MAHs and PAHs]) are the most toxic components of oil to aquatic organisms. Therefore, it is important to track their fate in the water column and sediments to predict the impact of oil spills on marine ecosystems. Degradation on the other hand may occur as the result of photooxidation, which is a chemical process energized by ultraviolet light from the sun acting on the surface slick, and by biological (bacterial) breakdown of dissolved oil and oil droplets dispersed in the water column, termed biodegradation. Oil biodegradation by native bacteria is one of the most important natural processes that can attenuate the environmental impacts of marine oil spills. However, very few numerical oil spill models include biodegradation kinetics of spilled oil. Furthermore, in oil spill models where biodegradation is simulated, it is mostly represented as a first order decay process neglecting the effect of several important parameters that control biodegradation rate, such as oil composition (easily biodegradable chemicals such as alkanes and small aromatic molecules with one or two rings will be depleted first, leaving the recalcitrant components in the water column), microbial population, dispersed oil droplets–water interface, and availability of dissolved oxygen and nutrients. Generally, there is a need for a more realistic description of biodegradation kinetics in oil spill models, allowing for a more accurate prediction of natural oil biodegradation, evaluation of possible bioremediation strategies, and risk assessment in the mid and long term.

Based on the previous considerations, it is evident that it is important to differentiate between different chemical groups in oil spill modeling based on their physical, chemical, and toxicological characteristics and track their fate separately to allow for more accurate prediction of oil weathering processes. To this end, the pseudo-component (PC) approach (Jones 1997; Lehr et al. 2000) has been adopted in several oil spill models for simulating certain weathering processes such as dissolution and degradation (e.g., French-McCay 2004; Spanoudaki 2016). Under this approach, the large number of chemical compounds that constitute the oil are grouped into a relatively small number of discrete noninteracting components (PCs), based on physical–chemical properties (volatility, solubility, biodegradability). The resulting PCs behave as if they were single substances with characteristics typical of the chemical group. The fate of each component is thus tracked separately. In a modified version of MESLIK-II (Spanoudaki 2016), biodegradation of the different PCs in oil droplets and dissolved oil is modeled by Monod kinetics. The kinetics of oil particle size reduction due to the microbe-mediated degradation at water–oil particle interface is represented by the shrinking core model. This allows for a more accurate estimation of the total fate of different groups of chemical compounds present in oil spills. However, further research is required in the laboratory and in the field to assess the impact (exposure and injury) of oil to ecosystems, describe the effect of different parameters on biodegradation kinetics, assess the impact of microbial communities, and evaluate various bioremediation strategies. Generally, the movement of oil through the water column and on the water surface
is very complex as chemical and biological changes in the oil affect its physical properties, which, in turn, affects the fate of spilled oil in the marine environment.

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