ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

NUMERICAL MODELING OF OIL SPILL OVER THE SEA SURFACE

M.Sc. Thesis by

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Department : Ocean Engineering

Programme: Ocean Engineering

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DENİZ YÜZEYİNDE PETROL YAYILIMININ SAYISAL OLARAK MODELLENMESİ

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LIST OF SYMBOLS

$\mathbf{A, A_0}$	:	Area of the oil slick
API	:	American Petroleum Institute gravity
C	:	Constant determined by experiments
D	:	Transformation matrix
$\mathbf{D_h}$	:	Horizontal diffusion coefficient
$\mathbf{E_T}$	:	Turbulent diffusivity
$\mathbf{F_e}$	:	Evaporative loss fraction
$\mathbf{F_v}$	:	Volume fraction of oil evaporated
g	:	Gravitational accelaration
h	:	Water depth
$\mathbf{h_f}$	:	Initial film thickness
K	:	Surface mass transfer coefficient
$\mathbf{K_d}$	:	Dissolution mass transfer coefficient
$\mathbf{K_E}$	:	
$\mathbf{K_M}$	:	Mass transfer coefficient
$\mathbf{L_x, L_y}$	:	Displacements of each point in the x and y directions
$\mathbf{M_{di}}$	:	The amount of oil component i lost by dissolution
$\mathbf{P_0}$	:	Vapor pressure in atmosphere at the temprature T_E
R	:	Gas constant
$\mathbf{R_n}$, $[R]_0^1$	:	Random number in the 0-1 interval
S	:	Oil solubility in water
$\mathbf{S_0}$	:	Solubility for fresh oil
$\mathbf{S_d}$	:	Total dissolution rate of the oil slick
$\mathbf{S_i}$	:	Solubility of the particular component i
ΔS	:	Distance that any element travels by horizontal diffusion
t	:	Time
T	:	Water temprature
$\mathbf{T_0}$	:	Initial boiling point
$\mathbf{T_E}$	:	Ambient air temprature
$\mathbf{T_G}$	:	Distillation curve gradient
$\mathbf{T_i}$	:	Initial temprature
$\mathbf{T_o}$	:	Surface temprature of the oil
$\mathbf{T_p}$	:	Product temprature
δt	:	Time step
$\mathbf{U_A}$,$\mathbf{U_{wind}}$	:	Wind speed at 10 m above the water surface
$\mathbf{U_{dx}, U_{dy}}$	:	Advective velocities in the x and y directions
$\mathbf{U_{sw}}$	:	Surface wind-induced currents
$\mathbf{U_{sww}}$	:	Surface wave-induced currents
V	:	Total volume of the oil slick
$\vec{\mathbf{V}}$	:	Mean drift velocity
$\vec{\mathbf{V}}'$	:	Fluctuation velocity component

$\mathbf{V_0}$: Initial spill volume
$\mathbf{V_c}$: Surface water current velocity
$\mathbf{V_i}$:
$\mathbf{V_i^B}$: Buoyancy-driven component
$\mathbf{V_i^c}$: Large scale component
$\mathbf{V_i^d}$: Wind-induced component
$\mathbf{V_i^T}$: Tidal component
$\mathbf{V_i^{wad}}$: Velocity due to wave drift component
$\mathbf{V_i^{wid}}$: Velocity due to wind drift component
$\mathbf{V_M}$: Molar volume
$\mathbf{V_s}$: Drift velocity of the surface oil
$\vec{\mathbf{V}}_\mathbf{t}$: Drift velocity of an oil particle
$\vec{\mathbf{V}}'_\mathbf{t}$: Turbulent fluctuation of the drift velocity
$\mathbf{V_w}$: Wind speed at 10 m above the water surface
$\mathbf{X_i}$:

$\boldsymbol{\alpha}$: Decay constant
$\boldsymbol{\alpha_c}$: Surface water current factor
$\boldsymbol{\alpha_w}$: Wind drift factor
$\boldsymbol{\mu}$: Dynamic viscosity
$\boldsymbol{\nu}$: Kinematic viscosity of the water
$\boldsymbol{\nu_s}$: Kinematic viscosity of water
$\boldsymbol{\rho_o}$: Density of oil
$\boldsymbol{\rho_w}$: Density of water
$\boldsymbol{\sigma}$: Surface tension
$\boldsymbol{\tau}$: Evaporative exposure parameter
$\boldsymbol{\theta}$: Deflection angle
$\boldsymbol{\theta'}$: Uniformly distributed random angle in the interval 0-π

NUMERICAL MODELING OF OIL SPILL ON THE SEA SURFACE

SUMMARY

Rapid growth in world population and continuous economic developments have led to a significant increase in world energy need and world's primary energy source is oil. Because of this, there is a serious oil trade movement in the world; cargo ships and pipelines submerged in the marine environment, carry large amounts of petroleum across open and coastal seas. Such activities raise the oil spill risk. As a consequence of accidents, critical amounts of oil spill spread on the surface of the sea and threaten natural life. Especially, after large oil tanker accidents, thousands of tones of crude oil spill.When an oil spill occurs, it is important to act as quickly as possible in order to minimize damages that can affect people and natural life. Thus, for the necessary operations to be done on time following an accident, oil spill modeling is an essential tool. The scope of this thesis is to develop a two dimensional numerical model for oil spill/oil slick trajectory predictions. In this approach, oil spill spreading on sea surface is modeled using empirical formulae and this model is combined with the surface flow model. Afterwards, oil spill scenarios are created and spreading of an oil slick, whose density and initial position are known, is examined, and using MATLAB, flow simulations are made and results are discussed.

DENİZ YÜZEYİNDE PETROL YAYILIMIN SAYISAL OLARAK MODELLENMESİ

ÖZET

Sürekli gelişen teknoloji ve artan dünya nüfusu dünya enerji ihtiyacını önemli şekilde artırmaktadır ve ana enerji kaynağı petroldür. Bu yüzden dünyada ciddi bir petrol alışveriş hareketi bulunmaktadır; tankerler ve deniz dibi boruları büyük miktarlarda petrol taşımaktadırlar. Bu gibi aktiviteler de petrol kirliliği riskini artırmaktadır. Meydana gelen kazalar neticesinde önemli miktarlarda petrol suya yayılmakta ve canlı ortamını tehdit etmektedir. Özellikle büyük petrol tankerlerinin kazaları sonucunda binlerce ton ham petrol denize dökülmektedir. Bir petrol kirliliği meydana geldiğinde, insanlara ve doğal kaynaklara gelebilecek zararı en aza indirmek için kirliliğe en kısa zamanda müdahale etmek gerekmektedir. Bu yüzden, kaza sonrası denize dökülen petrolün yayılımının modellenmesi oluşan kirliliğe gerekli müdahaleyi zamanında yapabilmek açısından önemlidir. Bu tezin amacı petrol yayılımının iki-boyutlu nümerik modelini oluşturmaktır. Bu amaç doğrultusunda deniz yüzeyinde petrol yayılımı ampirik formüller yardımıyla ile modellendi ve bu model yüzey akıntısı modeli ile birleştirildi. Daha sonra olası petrol dökülme senaryoları yaratılarak viskozitesi ve başlangıç konumu bilinen bir yağ tabakasının deniz yüzeyindeki yayılımı incelendi, MATLAB programı yardımı ile simülasyonlar yapıldı ve sonuçlar değerlendirildi.

1. INTRODUCTION

Rapid growth in world population and continuous economic developments have led to a significant increase in world energy need and world's primary energy source is oil. Because of this, there is a serious oil trade movement in the world; cargo ships and pipelines are submerged in the marine environment, carry large amounts of petroleum across open and coastal seas. Such activities raise the oil spill risk. Hence, a significant amount of oil is spilled into seas from operational discharges of ships as well as from accidental tanker collisions and groundings (Wang et al., 2005). Spilled oil threatens surface resources and a wide range of subsurface aquatic organisms linked in a complex food chain (EPA, 2005). Furthermore, oil spills may foul the harbour facilities and vessels (Chao et al., 2001). Hence, in response to accidents, government agencies usually prepare oil spill contingency plans. An important component of these plans is the use of mathematical models to predict the oil slick motion and distribution of oil particle concentration in the coastal waters (Chao et al., 2001). Therefore, it is crucial to forecast oil spill transport and fate using such models in order to determine response and clean-up operations (Wang et al., 2005).

After an oil spill, transport and fate of spilled oil are affected by various physical, chemical and biological processes. Spreading, advection, evaporation, dissolution, emulsification, photo- and auto-oxidation, sedimentation and biodegradation are among these processes. While spilled oil is governed by spreading and advection as soon as it is spilled, it generally takes a long time for the chemical and biological effects to be effective. Spilled oil forms a thin film called oil slick. Due to the current, waves and wind action, oil slick moves on the sea surface. The slick spreads over the water surface due to a balance between gravitational, viscous and surface tension forces, while composition of the oil changes from the initial time of the spill (Wang et al., 2005). Light fractions evaporate, watersoluble components dissolve in the water column, and immiscible components become emulsified and dispersed in the water column as small droplets (Wang et al., 2005).

The specific behaviour processes that occur after an oil spill determine how the oil should be cleaned up and its effect on the environment. For example, if an oil evaporates rapidly, cleanup is less intense, but the hydrocarbons in the oil enter the atmosphere and cause air pollution. An oil slick could be carried by surface currents or winds to a bird colony or to a shore where seals or sea lions are breeding and severely affect the wildlife and their habitat. On the other hand, a slick could be carried out to sea where it disperses naturally and has little direct effect on the environment (Fingas, 2000).

Oil spill modeling is a very complex task where a large number of interacting factors participate. The trajectory of a particular spill is of fundamental importance since it determines the impact of oil on coastal areas and on other sensitive ecosystems (Martinez & Tovar, 1999). Moreover, to take appropriate response actions, forecasting oil slick movement can be very helpful. Thus, mathematical modeling of oil spill is essential to predict the fate and transport of spilled oil under different conditions. Such information can be used not only in environmental impact assessment studies, but also in forecasting oil slick trajectory which is the key for early warning and contingency planning.

The aim of this thesis is to develop a two dimensional numerical model for oil spill oil slick trajectory predictions. For this reason understanding the nature of oil is essential. Oil spill is analyzed in Chapter 2; types of oil and its properties which effective in the fate of oil are presented. Risk of oil spill is examined and statistical data is given.

In Chapter 3, evolments in the numerical modeling of oil spill from past to present are presented. A large number of oil spill models is in use today. These range in capability from simple trajectory, or particle tracking models, to three-dimensional trajectory and fate models that may include simulation of response actions and estimation of biological effects on the marine ecosystem. There are also commercially available oil spill models, such as COZOIL, NOAA, OILMAP and WOSM that track oil movement and the distribution of oil particles in the water column. In view of the limited understanding of the oil spill weathering processes, the accuracy of the simulations must be viewed with some reservation. Two models purporting to contain same algorithms may give quite different results from the same input data. Implementation is critical to algorithm performance. Morover,

performance of one algorithm (module) inside a model will be affected by the performance of other algorithms in the model (Papadimitrakis et al., 2004) .

In Chapter 4, development of the mathematical model used in this study is explained step by step. Lagrangian particle-tracking technique is used to simulate the transport of oil slick. In this technique, the oil slick is considered as the sum of large number of small particles and each particle is followed and its location is recorded as a function of time. To predict surface currents caused by wind and tides a 2-D vertically averaged finite-element code is used. The hydrodynamic data obtained from this FORTRAN code is used in the oil spill tracjectory program.

In Chapter 5, firstly, model application to a rectangular pool is performed. Transport of the oil slick is simulated. Then, results are compared with the results from other studies. After that, the model is applied to Bosphorus Strait as a case study. Oil spill scenarios are created and simulation of the oil slick transport in Bosphorus Strait is examined.

2. OIL SPILL ANALYSIS

2.1 Introduction

In all industrial societies oil is a necessity. It is the main energy source and according to National Research Council (2003) this is not going to change much in the future. According to NRC (2003), to meet the increased demand, an increase in world oil supply of roughly 45 mb/d (6.4 mt/d) is projected for the next two decades. Clearly, due to this increased demand, oil transportation by vessel will increase as well. In addition, refineries will have to increase capacity, and more coastal petroleum handling facilities will be needed. However, these have the potential to increase the input of hydrocarbons into the oceans (NRC, 2003).

The impact of an accidental oil spill is primarily perceived as a major environmental problem, but associated socio-economic effects also play an important role (Burgherr, 2006). Burgherr (2006) also pointed out that the extent of these impacts is likely to be determined by a diverse set of factors: (1) the amount, rate and type of oil spilled; (2) the location that comprises geographical position as well as political and legal issues; (3) the vicinity to sensitive resources; (4) the choice and effectiveness of cleanup strategies.

Papadimitrakis et. al (2006) indicated that the transport and fate of oil spills in the marine environment are influenced by some factors such as the initial volume and the physico-chemical characteristics of the spilled oil, the characteristics of the spill region, the water composition and circulation under and around oil spill, the wind field above the spill area, and several physico-chemical and biological processes.

2.2 Types of Oil and Their Properties

Oil is a general term that describes a wide variety of natural substances of plant, animal, or mineral origin, as well as a range of synthetic compounds (Fingas, 2000). There are hundreds of major compounds and thousands of minor ones in composition

of different types of oil. As their composition varies, each type of oil or petroleum product has certain unique characteristics or properties (Fingas, 2000). The main physical properties which affect the behaviour and the persistence of an oil spilled at sea are specific gravity, distillation characteristics, viscosity and pour point. All are dependent on chemical composition (e.g. the amount of asphaltenes, resins and waxes which the oil contains) (ITOPF, 2002).

Behaviour and the effects of the oil in the environment is determined by these properties. Furthermore, these properties also influence the efficiency of cleanup operations (Fingas, 2000).

Understanding the nature and distribution of sources and their inputs, as well as the behaviour of petroleum in the environment, is the key for understanding the petroleum effect on the marine environment (NRC, 2003).

2.2.1 Composition of oil

Crude oils are composed of hydrocarbon compounds (compounds containing only hydrogen and carbon) ranging from smaller, volatile compounds to very large, non-volatile compounds (Fingas, 2000). In fact, the elements hydrogen and carbon together constitute about 97 % of most oil, while the minor elements nitrogen, sulfur, and oxygen make up the remaining 3 % (NRC, 2003). Crude oil can also comprise mineral salts as well as trace metals such as nickel, vanadium, and chromium. This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil (Fingas, 2000). Fingas (2000) exemplified that, crude oils that consist primarily of large compounds are viscous and dense while petroleum products such as gasoline or diesel fuel are mixtures of fewer compounds and thus their properties are more specific and less variable.

In general, the hydrocarbons found in oils are characterized by their structure. The hydrocarbon structures found in oil are the saturates, olefins, aromatics, and polar compounds, some examples of which are shown in Figure 2.1 (Fingas, 2000).

The main sub-group of the saturates is alkanes. Alkanes are composed of hydrogen and carbon compound with the maximum number of hydrogen atoms around each carbon. Hence, this group is named as “saturates” since the carbons are saturated with carbons. Boiling point and density of alkanes increase with increasing number

of carbon atoms. The saturate group also includes cyclo-alkanes, which are compounds made up of the same carbon and hydrogen constituents, but with the carbon atoms bonded to each other in rings or circles (Fingas, 2000). Moreover, waxes are the larger saturate compounds.

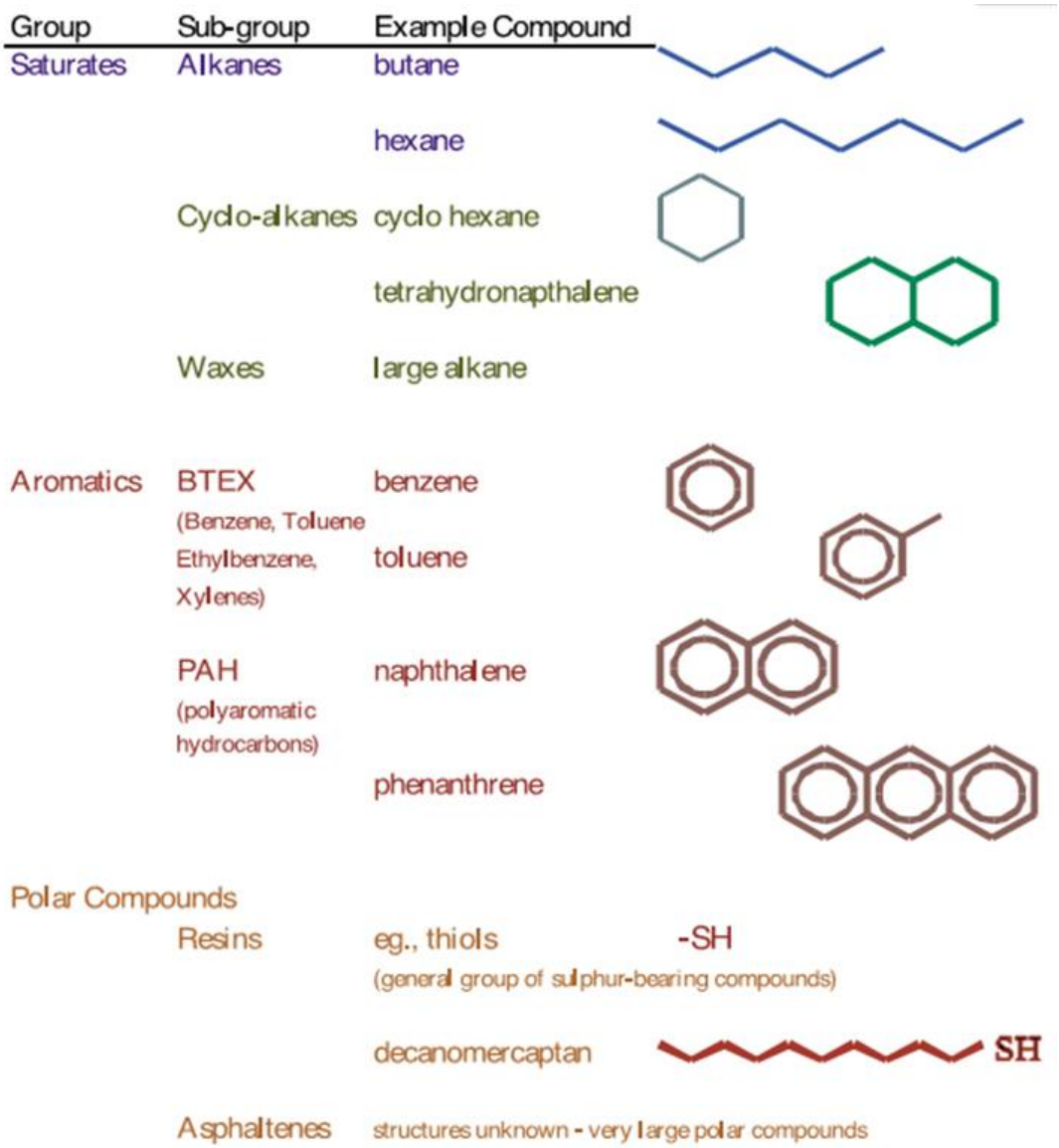

Figure 2.1 : Chemical compunds in oils (Fingas, 2000)

The olefins, or unsaturated compounds, are another group of compounds that contain fewer hydrogen atoms than the maximum possible. Fingas (2000) stated that olefins have at least one double carbon-to-carbon bond that displaces two hydrogen atoms. Significant amounts of olefins are found only in refined products.

The aromatic compounds include at least one benzene ring of six carbons which are very stable and therefore persistent in the environment. Fingas (2000) highlighted that three double carbon-to-carbon bonds float around the ring and add stability.

The most common smaller and more volatile compounds found in oil are often referred to as BTEX, or benzene, toluene, ethyl-benzene, and xylenes. Polyaromatic hydrocarbons, or PAHs, are compounds consisting of at least two benzene rings (Fingas, 2000). A typical crude oil may contain 0.2 percent to more than 7 percent total PAH (NRC, 2003).

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents. These compounds can be point source pollutants (e.g. oil spill) or non-point source (e.g. atmospheric deposition) and are one of the most widespread organic pollutants. Some of them are known or suspected carcinogens, and are linked to other health problems. They are primarily formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, or tobacco. Tar also contains PAHs.

Of the hydrocarbon compounds common in petroleum, PAH appear to pose the greatest toxicity to the environment. Most of the PAH compounds in petroleum are not as toxic as those produced by certain combustion processes, but most groups are significant components of runoff from paved surfaces (NRC, 2003).

Polar compounds are those that have a significant molecular charge as a result of bonding with compounds such as sulphur, nitrogen, or oxygen. The “polarity” or charge that the molecule carries results in behaviour that, under some circumstances, is different from that of unpolarized compounds. In the petroleum industry, the smallest polar compounds are called “ resins,” which are largely responsible for oil adhesion. The larger polar compounds are called “ asphaltenes” because they often make up the largest percentage of the asphalt commonly used for road construction. Asphaltenes often have very large molecules and, if in abundance in an oil, they have a significant effect on oil behaviour.

2.2.2 Properties of Oil

In this section, oil properties such as viscosity, density, specific gravity, solubility, flash point, pour point, distillation fractions, interfacial tension, and vapour pressure are discussed.

Viscosity is the resistance to flow in a liquid. As the viscosity of a liquid decreases, it will flow promptly. For example, water has a low viscosity and flows readily, whereas honey, with a high viscosity, flows poorly. The viscosity of the oil is largely determined by the amount of lighter and heavier fractions that it has. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity (Fingas, 2000). Highly viscous oils tend to weather more slowly because they do not spread into thin slicks (NRC, 2003). Instead, they form tarballs, which can be transported long distances and accumulate in thick deposits on shorelines that can persist for decades (NRC, 2003).

As with other physical properties, viscosity is affected by temperature, with a lower temperature giving a higher viscosity (Fingas, 2000). For most oils, the viscosity varies as the logarithm of the temperature, which is a very significant variation (Fingas, 2000). Oils that flow readily at high temperatures can become a slow-moving, viscous mass at low temperatures (Fingas, 2000). Since sea temperatures are often lower than cargo or bunker temperatures on board of a vessel, viscosity-dependent clean-up operations such as skimming and pumping generally become more difficult as the spilled oil cools (ITOPF, 2002).

Density is the mass (weight) of a given volume of oil and is typically expressed in grams per cubic centimetre (g/cm^3) (Fingas, 2000). It is the property used by the petroleum industry to define light or heavy crude oils (Fingas, 2000). Density is also important because it indicates whether a particular oil will float or sink in water (Fingas, 2000). As the density of water is 1.0 g/cm^3 at 15°C and the density of most oils ranges from 0.7 to 0.99 g/cm^3, most oils will float on water (Fingas, 2000). As the density of seawater is 1.03 g/cm^3, even heavier oils will usually float on it (Fingas, 2000). Light oils contain petroleum hydrocarbons that are readily lost via evaporation and microbial degradation (NRC, 2003). Heavy oils contain a greater percentage of the higher-molecular-weight petroleum hydrocarbons that are more resistant to weathering (NRC, 2003).

Another measure of density is *specific gravity*, which is an oil's relative density compared with that of water at 15°C. It is the same value as density at the same temperature. Another gravity scale is that of the American Petroleum Institute (API. The API gravity is based on the density of pure water, which has an arbitrarily assigned API gravity value of 10° (10 degrees). Oils with progressively lower specific gravities have higher API gravities (Fingas, 2000).

The following is the formula for calculating API gravity:

API gravity = [141.5 ÷ (density at 15.5°C)] – 131.5 **(2.1)**

Oils with high densities have low API gravities and vice versa (Fingas, 2000).

Solubility in water is the measure of how much of an oil will dissolve in the water column on a molecular basis (Fingas, 2000). Solubility is important in that the soluble fractions of the oil are sometimes toxic to aquatic life, especially at higher concentrations (Fingas, 2000). As the amount of oil lost to solubility is always small, this is not as great a loss mechanism as evaporation (Fingas, 2000). In fact, the solubility of oil in water is so low (generally less than 100 parts per million) that it would be the equivalent of approximately one grain of sugar dissolving in a cup of water (Fingas, 2000). However, solubility is an important process because the water-soluble fractions of the oil are sometimes toxic to aquatic life (NRC, 2003). Thus, although solubilization represents a minor loss process, the concentration of toxic compounds dissolved in water from oil may be sufficient to have impacts on marine organisms (NRC, 2003).

The *flash point* of an oil is the temperature at which the liquid gives off sufficient vapours to ignite upon exposure to an open flame. A liquid is considered to be flammable if its flash point is less than 60°C. There is a broad range of flash points for oils and petroleum products, many of which are considered flammable, especially when fresh. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils have an abundance of volatile components and may be flammable for as long as 1 day until the more volatile components have evaporated. On the other hand, Bunker C and heavy crude oils generally are not flammable when spilled (Fingas, 2000).

Pour point is the temperature below which an oil will not flow (ITOPF, 2002). As oils are made up of hundreds of compounds, some of which may still be liquid at the

pour point, the pour point is not the temperature at which the oil will no longer pour (Fingas, 2000). The pour point represents a consistent temperature at which an oil will pour very slowly and therefore has limited use as an indicator of the state of the oil (Fingas, 2000). In fact, pour point has been used too much in the past to predict how oils will behave in the environment (Fingas, 2000). The pour point is a function of the wax and asphaltene content of the oil (ITOPF, 2002). For example, waxy oils can have very low pour points, but may continue to spread slowly at that temperature and can evaporate to a significant degree (Fingas, 2000).

Distillation characteristics of an oil describe its volatility (ITOPF, 2002). As the temperature of an oil is raised, different components reach their boiling point one after another and evaporate, i.e. are distilled (ITOPF, 2002). This data is obtained on most crude oils so that oil companies can adjust parameters in their refineries to handle the oil (Fingas, 2000). This data also provides environmentalists with useful insights into the chemical composition of oils (Fingas, 2000). For example, while 70% of gasoline will boil off at 100°C, only about 5% of a crude oil will boil off at that temperature and an even smaller amount of a typical Bunker C (Fingas, 2000). The distillation fractions correlate strongly to the composition as well as to other physical properties of the oil (Fingas, 2000).

The oil/water interfacial tension, sometimes called *surface tension*, is the force of attraction or repulsion between the surface molecules of oil and water. Together with viscosity, surface tension is an indication of how rapidly and to what extent an oil will spread on water. The lower the interfacial tension with water, the greater the extent of spreading. In actual practice, the interfacial tension must be considered along with the viscosity because it has been found that interfacial tension alone does not account for spreading behaviour (Fingas, 2000).

The *vapour pressure* of an oil is a measure of how the oil partitions between the liquid and gas phases, or how much vapour is in the space above a given amount of liquid oil at a fixed temperature. Because oils are a mixture of many compounds, the vapour pressure changes as the oil weathers. Vapour pressure is difficult to measure and is not frequently used to assess oil spills (Fingas, 2000).

2.3 Oil Spill Risk

Pollution by oil spills of the marine environment , and particularly of coastal waters and adjacent shoreline areas, has received growing attention by scientists and governments, over the past few decades, as a consequence of a number of serious accidents involving the release of large amounts of oil in the sea waters (Papadimitrikis, 2004). However, oil and its products are fundamental to the lives of most of the world's population. It is a critical element in world economy. The demand for oil is huge not only as a fuel for cars, ships and aircraft but also in the manufacture of plastics, road surfacing, cosmetics and thousands of other products. Some everyday products manufactured from oil or petroleum products include: rulers, crayons, contact lenses, cosmetics, deodorants, paint, CDs, videos and roofing tiles.

In fact, the production and consumption of oil and petroleum products are increasing worldwide and the threat of oil pollution is increasing accordingly. The movement of petroleum from the oil fields to the consumer involves as many as 10 to 15 transfers between many different modes of transportation including tankers, pipelines, railcars, and tank trucks . Oil is stored at transfer points and at terminals and refineries along the route. Accidents can happen during any of these transportation steps or storage times (Fingas, 2000).

Obviously, an important part of protecting the environment is ensuring that there are as few spills as possible . Both government and industry are working to reduce the risk of oil spills, with the introduction of strict new legislation and stringent operating codes (Fingas, 2000).

2.3.1 Accident Definition and Damage Thresholds

Different databases include various damage types and distinct minimum thresholds for each damage type to decide if an accident is considered or not (Burgherr, 2006). Based on PSI's severe accident definition for ENSAD, an oil spill is considered severe if at least 10000t of hydrocarbons is released (Burgherr, 2006).

Since 1974, ITOPF has maintained a database of oil spills from tankers, combined carriers and barges. This covers all accidental spillages except those resulting from acts of war. The database contains information on both the spill itself (amount and

type of oil spilt, cause and location) and the vessel involved. For historical reasons, spills are generally categorised by size (<7 tonnes, 7-700 tonnes and >700 tonnes) although the actual amount spilt is also recorded. Information is now held on nearly 10,000 incidents, the vast majority of which (84%) fall into the smallest category i.e. <7 tonnes.

ETC uses a minimum level of 1000 barrels (136t), and ERC includes spills of at least 10000 gal (34t).

2.3.2 Tanker Spills

During the period from 1980 to 1999, the size of the tanker fleet has been relatively stable, with the number of tankers increasing from 7112 to 7270, and the deadweight of the tanker fleet decreasing from 340 million tonnes to 299 million tonnes. Due to the phase-out schedule of OPA 90 and MARPOL Regulation 13G, the fleet is becoming younger, such that in 1999 more than 50 percent of the tanker fleet was less than 15 years of age. In recognition of the fundamental changes that took place after the *Exxon Valdez* accident, spill data from 1990 onward were used as the basis for estimating the amount of oil spilled from tankers (tank ships and tank barges) (NRC, 2003).

International spill data were obtained from the *Environmental Research Consulting* database and includes information gleaned from the International Maritime Organization, ITOPF, and other national and regional agencies. These international data are not consistently collected and do not include spills under 10,000 gallons (34 tonnes) in size, and are therefore regarded as underestimates. The international spill quantities were increased by 25 percent to obtain the minimum estimate, by an additional 10 percent to obtain the best estimate, and further increased by 25 percent to obtain the maximum estimate. The international and North American figures were then combined to produce the worldwide estimates of spillage from tankers. The best estimate is 100,000 tonnes; the minimum and maximum estimates are 93,000 tonnes and 130,000 tonnes, respectively (NRC, 2003).

Although tanker spills only account for about 15% of the annual total amount of oil entering the sea, they receive much attention for several reasons. Almost 60% of the oil consumed in the world is transported by tankers. Despite numerous efforts resulting in identifiable improvements, oil spills from tankers are still a major threat

because many traffic routes cross the boundaries of the “Large Marine Ecosystems” and of marine biodiversity hotspots.Very large spills are viewed as the most visible and dramatic causes of marine and coastal pollution as can be seen from their often exceptional media presence. However, previous studies in many cases focused on particular aspects of oil spills such as the amount spilled and distributional trends, ecological consequences, economic costs of pollution, cleanup techniques or examined specific geographical areas (Burgherr, 2006).

Analyses of tanker spills can be assigned to four topical areas:

1. Temporal trends in annual number and volume of spills.

2. Distribution of spill volume, i.e. contribution of larger spills to total volume and vice versa.

3. Geographic distribution of spills and identification of regional hot spots.

4. Trends in spill numbers and volumes of key factors (i.e.,flag state, hull type, tanker age, accident cause and sensitivity of location).

2.3.3 Statistical Analysis

2.3.3.1 Number of Oil Spills

The incidence of large spills is relatively low and detailed statistical analysis is rarely possible, consequently emphasis is placed on identifying trends. Thus, it is apparent from the Figure 2.2 below that the number of large spills (>700 tonnes) has decreased significantly during the last thirty years. The average number of large spills per year during the 1990s was less than a third of that witnessed during the 1970s (ITOPF, 2006).

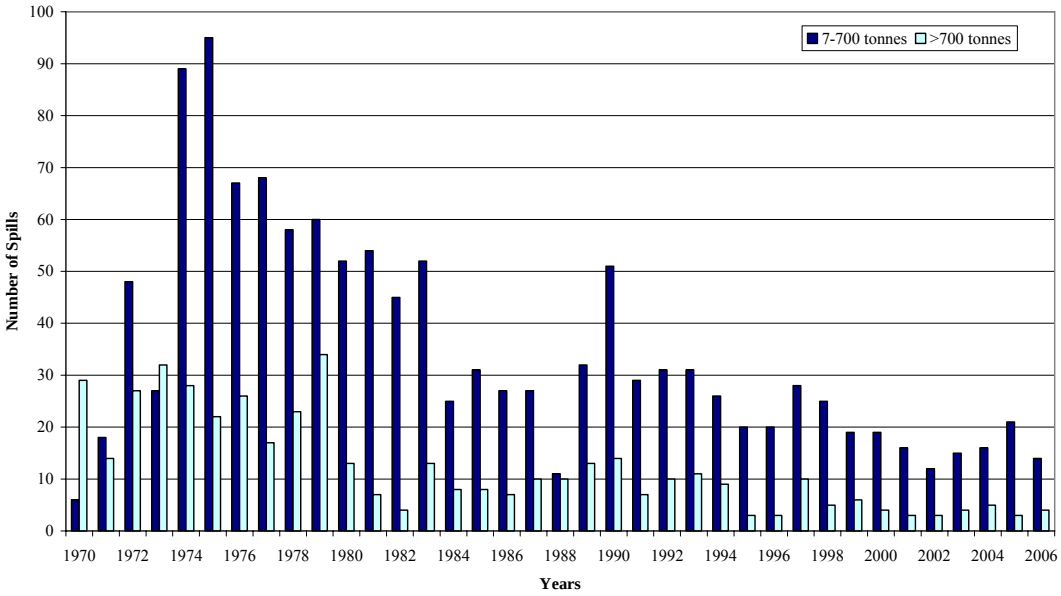

Figure 2.2 : Number of spills over 7 tonnes (ITOPF, 2006)

2.3.3.2 Quantities of Oil Spilt

The vast majority of spills are small (i.e. less than 7 tonnes) and data on numbers and amounts is incomplete. However in most years it is probable that they make a relatively small contribution to the total quantity of oil spilled into the marine environment as a result of tanker accidents.

Reliable data on spills 7 tonnes and above is held and the amounts of oil spilt during these incidents have been added to give a series of annual estimates of the total quantity spilled for the years 1970-2006.

It is notable that a few very large spills are responsible for a high percentage of the oil spilt. For example, in the ten-year period 1990-1999 there were 358 spills over 7 tonnes, totalling 1,138 thousand tonnes, but 830 thousand tonnes (73%) were spilt in just 10 incidents (just under 3%). The figures for a particular year may therefore be severely distorted by a single large incident. This is clearly illustrated by 1979 (Atlantic Empress - 287,000 tonnes), 1983 (Castillo de Bellver - 252,000 tonnes) and 1991 (ABT Summer - 260,000 tonnes).

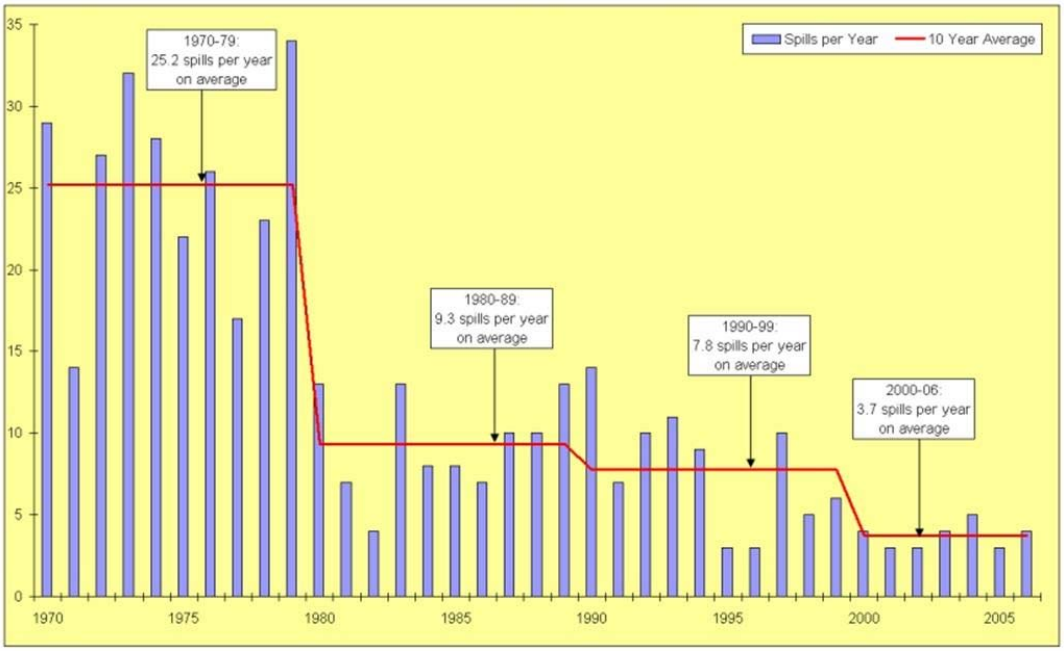

Figure 2.3 : Number of spills over 700 tonnes (ITOPF, 2006)

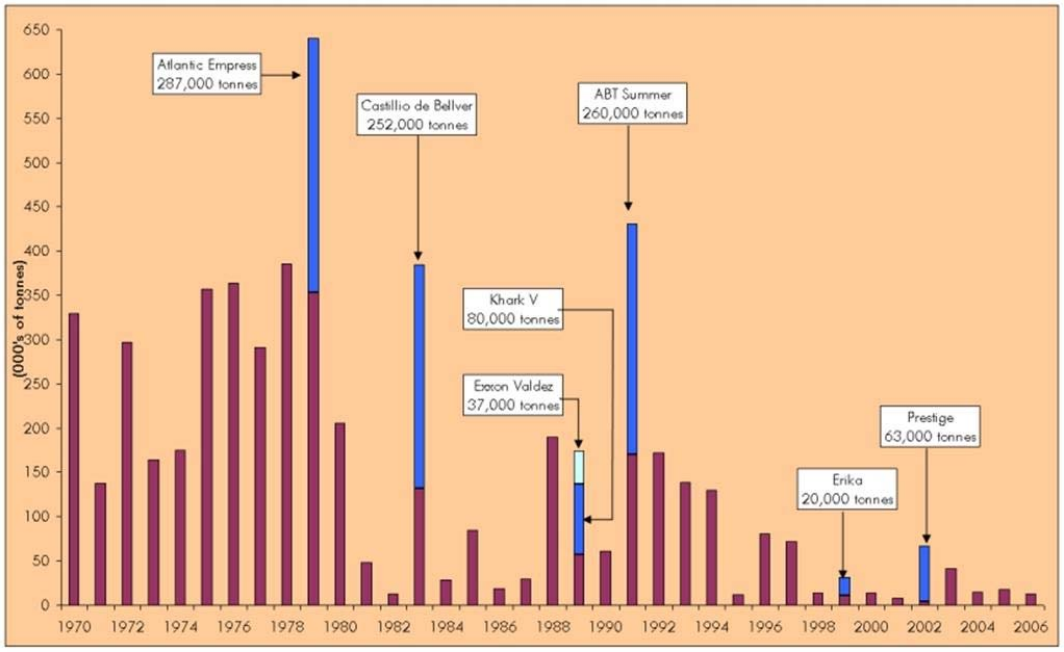

Figure 2.4 : Quantities of oil spilt (ITOPF, 2006)

2.3.3.3 Causes of Spills

Most incidents are the result of a combination of actions and circumstances, all of which contribute in varying degrees to the final outcome. The following analysis explores the incidence of spills of different sizes in terms of the primary event or operation in progress at the time of the spill. These "causes" have been grouped into "Operations" and "Accidents". Spills for which the relevant information is not

available or where the cause was not one of those given are listed under "Other/unknown".

It is apparent from the Table 2.1 that:

- most spills from tankers result from routine operations such as loading, discharging and bunkering which normally occur in ports or at oil terminals;
- the majority of these operational spills are small, with some 91% involving quantities of less than 7 tonnes;
- accidental causes such as collisions and groundings generally give rise to much larger spills, with at least 84% of incidents involving quantities in excess of 700 tonnes being attributed to such factors.

Table 2.1 : Incidence of spills by cause, 1974-2006 (ITOPF, 2006)

	< 7 tonnes	**7-700 tonnes**	**> 700 tonnes**	**Total**
OPERATIONS				
Loading/discharging	2821	332	30	3183
Bunkering	548	26	0	574
Other operations	1178	56	1	1235
ACCIDENTS				
Collisions	173	296	97	566
Groundings	235	222	118	575
Hull failures	576	90	43	709
Fires & explosions	88	15	30	133
Other/Unknown	2181	148	24	2353
TOTAL	7800	1185	343	9328

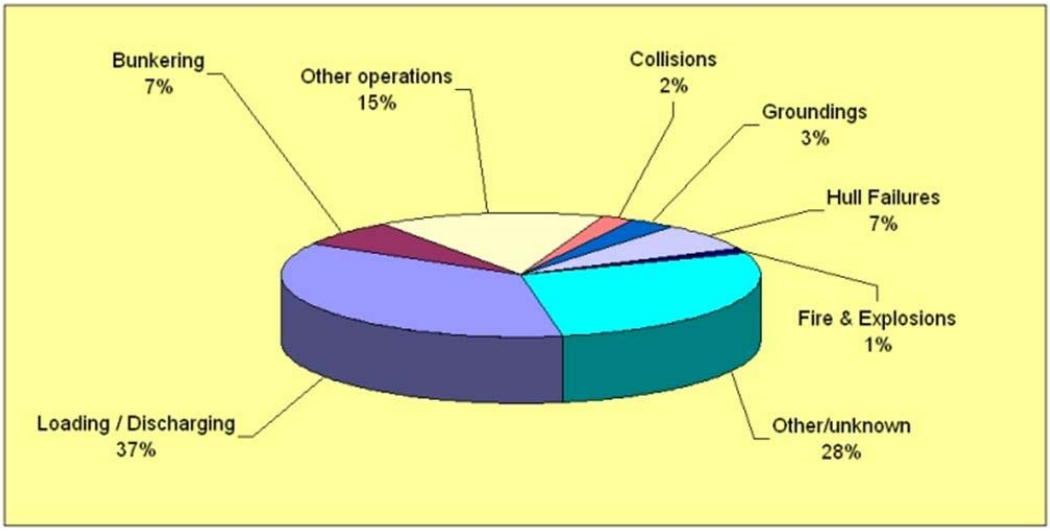

Figure 2.5 : Incidence of spills < 7 tonnes by cause,1974-2006 (ITOPF, 2006)

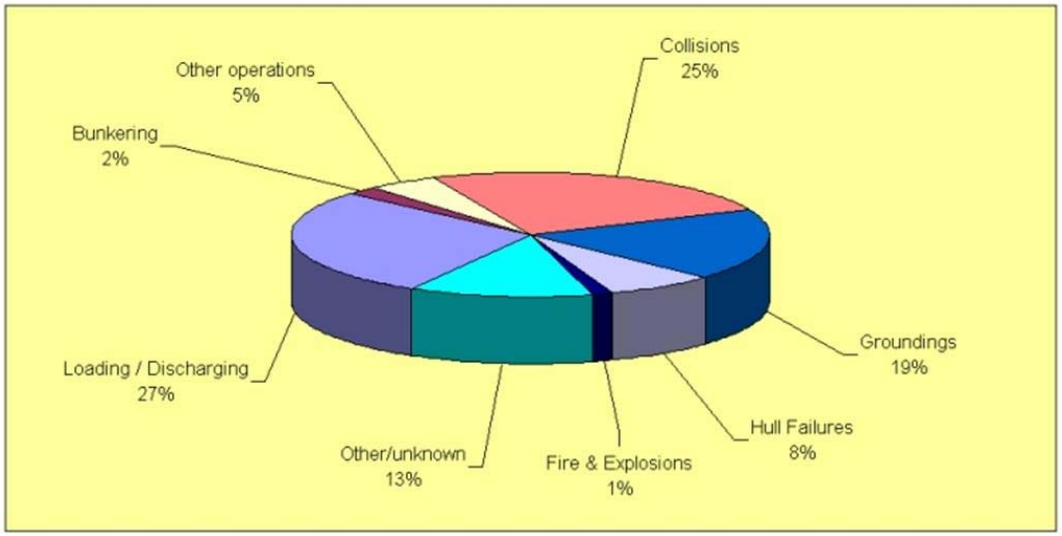

Figure 2.6 : Incidence of spills 7-700 tonnes by cause,1974-2006 (ITOPF, 2006)

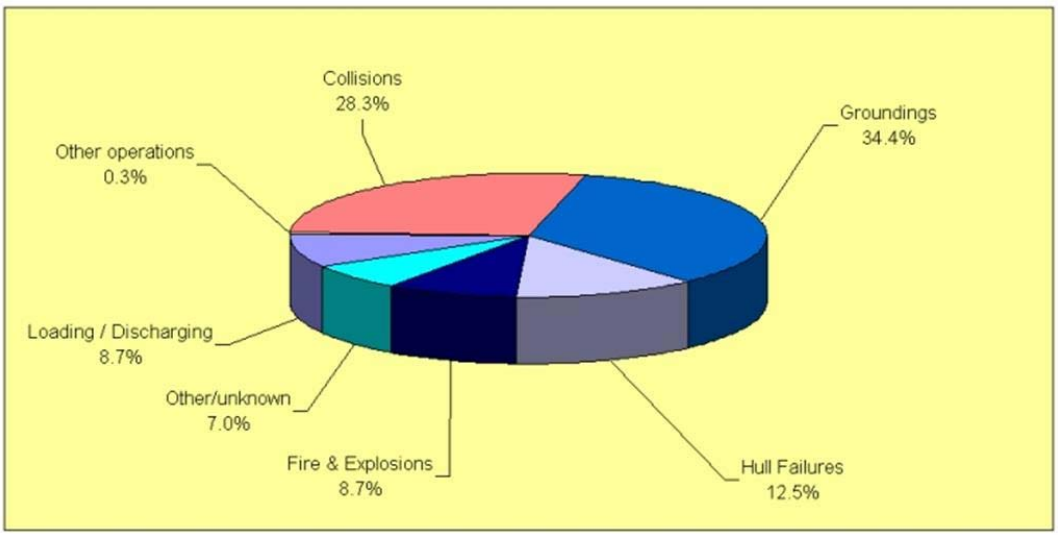

Figure 2.7 : Incidence of spills >700 tonnes by cause,1974-2006 (ITOPF, 2006)

3. HISTORICAL BACKGROUND

3.1 Introduction

In this chapter an overview of different approaches used in numerical models for behavior and fate of oil spilled in the marine environment is presented.

Over the past three decades simplified empirical formulae contributed greatly in a rapid evaluation of the oil slick spreading and drifting (Tkalich, 2004). Modern oil spill models can utilise more accurate and physically relevant mathematical formulations (Tkalich, 2004). Moreover, with the widespread use of computers over the past two decades has come the development of mathematical models and accompanying computer programs to attempt to simulate the behaviour of spilled oil (Lehr & Beatty, 2000). The success of these models has been mixed (Lehr & Beatty, 2000). As emergency events, oil spills do not provide ideal conditions for experimentantation and hypothesis testing (Lehr & Beatty, 2000). Clean-up personnel are properly more interested in mediating the environmental damage from the oil than in providing resources and data to on-scene scientists (Lehr & Beatty, 2000). This means that oil spill modeling is a data-starved field, where measurements performed in laboratories or on small experimental spills that are orders of magnitude smaller than real accidental spills are used as substitutes for measurements on the real thing (Lehr & Beatty, 2000). As a consequence, many of the algorithms used in oil spill models are often quite simple and attempt to capture only the gross behaviour of the oil slick, ignoring finer scale processes (Lehr & Beatty, 2000).

The fate and transport of oil spilled in water are governed by complex, interrelated, physicochemical processes that depend on oil properties, hydrodynamic conditions, and environmental conditions (Mackay and McAuliffe 1988). Oil in a water body, regardless of whether it originated as a surface or subsurface spill, consists of a floating surface slick and oil mixed as suspended oil droplets in the water column.

Continuous exchange occurs between the surface and suspended oil (ASCE, 1996). The transport and fate of spilled oil is governed by: the advection due to current and wind; horizontal spreading of the surface slick due to both turbulent diffusion, and gravitational, inertial, viscous, and surface tension forces; emulsification; mass transfer and change in pysicochemical properties of oil due to weathering processes such as evaporation, entrainment (dispersion), and dissolution; and the interaction of oil with the shoreline and ice (ASCE, 1996).

Spill models are normally constructed by linking mathematical formulations or algorithms to represent oil transport and fate processes. Fate processes of primary interest include spreading, evaporation, entrainment, or dispersion (oil dispersed into the water column), dissolution, emulsification (incorporation of water into the surface oil), oil-shoreline and oil-ice interactions and sedimentation (ASCE, 1996).

3.2 Advection

Advection is a physical process that involves the drifting of the surface oil slick and the subsurface oil. It is the main mechanism governing the location of oil following its discharge. The advection of surface oil is caused by the effects of surface current and wind drag on oil. Surface current is also significantly affected by wind conditions. The advection of suspended oil is the movement of oil droplets entrained in the water column due to the water current.

Given that most oils are initially buoyant and float on the sea surface, their transport is dominated by the surface current, winds, and wave fields. The structure of water currents is complex and three-dimensional, given the interaction between wind, waves, and currents and the generation of turbulent kinetic energy by shear and breaking wave activity (ASCE, 1996).

The majority of spill models use a simplified linear superposition technique to approximate spill motion. In this strategy the transport rate for a slick is represented by employing a vector sum of the transports induced by the mean flow, tides, wind, waves and turbulent dispersion. Information on the mean flow and tidal currents is determined from observations or hydrodynamic models for the region of interest. The currents induced by winds and waves are normally lumped together and represented by an empirically based drift factor and deflection angle dependent on

the local wind speed and direction (Stolzenbach et al. 1977; Huang and Monastero 1982). The drift speed typically varies from 2.5% to 4.4% of the wind speed, with a mean value of 3-3.5%. The deflection angles vary between 0 and 25° to the righ/left of the wind direction (northern/southern hemisphere) with a mean value of about 15° (ASCE, 1996).

Oil moves horizontally in the marine environment under forcing from wind, waves, and currents. Being itself a fluid with a density only slightly less than that of water, oil is also transported vertically in the water column in the form of droplets of various sizes. Both vertical and horizontal current shears are therefore important factors in the net motion of oil at sea (Reed et al., 1999).

Early oil spill models were typically two-dimensional surface models, using constant or variable parameters to link wind and current velocities to the velocity of the surface oil slick (Reed et al., 1999). Reed et al. (1994a) suggests that, in light winds without breaking waves, 3.5% of the wind speed in the direction of the wind gives a good simulation of oil slick drift in offshore areas. As wind speed increases, oil will be dispersed into the water column, and current shears become more important (Reed et al., 1999).

Advective currents in oil spill simulations may be derived from current atlases or other static approximations. Direct or indirect linkages to hydrodynamic models are becoming much more common, as the latter have become more widely used and easily applied. Direct coupling between oil spill and hydrodynamic forecast models is common in operational oil spill response systems. Input of surface currents from real-time radar measurements is also possible, but set-up times for such systems tend to limit their usefulness. Surface drifting buoys represent yet another source of real-time surface current data. Transport on scales of 10 to 100 m is important in determining the spreading of oil.

In some models, individual lots of oil or "spillets" are used to represent the slick, particularly for spills that are released over an extended period of time or are distributed spatially. In other models, the oil slick is represented by an ensemble of parcels regardless of the size or type of oil slick. The number of parcels increases or decreases with time, due to effects from other oil spill processes. The oil transport vectors are calculated individually for each oil spillet or parcel (ASCE, 1996).

With the increasing availability of high-powered computational facilities, researchers are employing sophisticated 3D hydrodynamic models to specify the current field for input to oil spill models. In this approach the mean, tidal, and wind-induced currents are predicted simultaneously using a hydrodynamic model. The advantages of this approach are that interaction between the various flow components are correctly represented and that conservation laws are strictly enforced. These models also have the ability to accurately represent the spatial and temporal structure of the flow field (ASCE, 1996).

3.3 Spreading

Spreading is the horizontal expansion of an oil slick due to mechanical forces such as gravity, inertia, viscous, and interfacial tension. The physics of this process are different from the expansion of oil slicks due to turbulent diffusion. Spreading of the oil slick is an important process in the early stages of oil slick transformation. Spreading is also affected by the weathering processes, which tend to change the mass and physicochemical properties of the slick. In free surface conditions the oil slick area has a strong influence on weathering processes such as evaporation and dissolution (ASCE, 1996).

Slick thickness and area are key variables in oil weathering and transport models. Oil slick area (or film thickness) is used in the computation of evaporation, which determines changes in oil composition and properties with time. Oil film thickness is used by many models in the computation of the rate of natural dispersion, which determines the persistence (lifetime) of the oil on the sea surface. In addition, estimates of film thickness and slick area are required for evaluation of the potential efficiency of different oil spill combat methods, and for assessments of environmental impacts (Reed et al., 1999).

The earliest spreading formulas idealized spreading processes by using a floating, insoluble chemical, such as oil, on calm water (Lehr & Beatty, 2000). The most used models for spreading are based on the work by Fay. Fay suggested that spreading is best described in three phases - inertial, viscous, and surface tension. The inertial phase is dominated by gravity forces, the viscous phase by gravity and viscosity forces, and the surface tension phase by surface tension spreading. The Fay model has been subject to criticism for several reasons (NRC, 2003). First the viscosity of

the water, not the oil, is used as a primary driving mechanism (NRC, 2003). Second, the model generally underpredicts spreading when tested (NRC, 2003). This observation may be explained in part as a consequence of horizontal diffusion resulting from shear diffusion of waves (Elliott, 1986).

Several tests of the Fay spreading model have been conducted (NRC, 2003). Flores et al, (1998) found that the Fay model underpredicted the spread of oil under quiescent conditions. Lehr et al. (1984) studied spreading using a series of test spills in the Arabian Gulf. They also found that the Fay model grossly under-predicted and proposed amendments to the model, suggesting that the sheen and thicker portions of the spill be modeled separately (NRC, 2003). No new formulations of the Fay spreading model have found wide acceptance; however, the formulation is often adjusted in models to account for the underpredictions shown in tests (NRC, 2003).

Mackay et al. (1980a,b) proposed a `thick-thin' variant of the gravity-viscous equation developed by Fay and Hoult, with the thick portion feeding oil to the thin layer. However, the term representing the effect of the density difference between water and oil in the original Fay equation was included in a general spreading constant. The resulting spreading rate is therefore independent of the initial oil density and insensitive to subsequent changes in density caused by evaporation and emulsification. The recognition of a link between the thick and thin portions of an oil slick represented an advance, but the model lacked any physics-based relationship between the two phases of the slick (Reed et al., 1999).

Lehr et al. (1984b) proposed a revised model to account for the observed non-symmetrical spreading of oil slicks. The extension of the slick in the wind direction was presumed to increase with time in proportion to the wind speed, while the lateral spreading of the slick was represented by the original Fay equation for gravity spreading. On this basis, the slick was represented in terms of an elongated ellipse, rather than the circular disk predicted by the Fay equation. The spreading rate in the direction of the wind was represented by an empirical wind factor obtained from observations. This model did not account for variability in thickness within the slick (Reed et al., 1999).

Johansen (1985) used a particles-based approach to model the oil spreading due to gravitational and interfacial forces. In this model, Johansen (1985) used the

unidirectional spreading equations developed by Fay to model the lateral extension of the slick. Spreading was treated as a diffusion process and was simulated using the random walk method. The diffusion coefficient was computed from Fay's equations (ASCE, 1996).

NOAA (1994) has incorporated a corresponding spreading model in the ADIOS model, with the slick represented as an ellipse, elongated in the direction of the wind. The initial area of the slick is computed according to the area at the time of transition between Fay's gravity-inertial spreading and gravity-viscous spreading regime. Fay's surface tension regime is not used in the model, but instead the slick is presumed to stop spreading when it reaches a terminal thickness of e.g. 0.1 mm. This approach produces a slick with homogeneous thickness, contrary to the observations from full-scale experiments and accidental spills. Johansen (1984) and Elliot et al. (1986) developed the concept of shear spreading, caused by natural dispersion and subsequent resurfacing of oil droplets. More recent experimental work in the laboratory (Delvigne and Sweeney, 1988) and in the field (Reed et al., 1994a) strongly supports this approach, which is generally accepted as the correct explanation of the physics behind the spreading phenomenon, once gravity spreading has ceased.

Experimental studies have demonstrated that viscous oils spread more slowly than less viscous oils (Reed et al., 1999). This effect is not accounted for in the original Fay equations, but several attempts have been made to include this parameter in Fay-type spreading models (Reed et al., 1999). Based on experiments within a limited viscosity range, Buist and Twardus (1984) proposed to reduce the spreading rate predicted by the Fay equations by a factor depending on the viscosity ratio between oil and water. In a subsequent paper, Buist et al. (1989) performed a series of tests with waxy crude oils, and proposed a terminal thickness function incorporating the difference between the pour point of the oil and the ambient water temperature.

Under natural conditions, oil spreading will not stop when the terminal thickness is reached (Reed et al., 1999). At this point, the oil slick will tend to break up into patches and small fragments due to wave action and current shears, and these patches or fragments will be spread due to oceanic turbulence (Reed et al., 1999). This is one of the reasons for the somewhat pessimistic attitude expressed by Lehr (1996) towards attempts to improve Fay-type spreading models: `it is doubtful that any of

these approaches will accurately predict the slick area over any extended time period because of the neglect of outside environmental factors'. The factors neglected in these approaches are mainly wave action and spreading induced by shear currents and oceanic turbulence, which are presumed to be the dominant longterm spreading processes (Reed et al., 1999).

Lehr (1996) also points out that most spreading algorithms assume instantaneous release of oil in open water conditions, while real spill incidents may involve leaks which continue at a varying rate for hours or days. Methods used to predict spreading of instantaneous spills are questionable for cases with continuous spills (Reed et al., 1999). This is mainly due to the fact that as oil leaks from continuous spills, the oil will be moved away from the source with wind and currents (Reed et al., 1999). In such cases, at some distance from the source, lateral spreading forces will dominate, while spreading forces along the slick axis will be negligible (Reed et al., 1999). As pointed out earlier by Waldman et al. (1972), this implies that the oil will spread more in the manner of spreading in a channel (i.e. one-dimensional spreading, symmetric about the slick axis). In such cases, the slick cannot be considered as a homogenous entity (as in the Fay (1969, 1971), Mackay et al. (1980), and Lehr et al. (1984) models). Obviously, with a continuous release, the thickness and the properties of the oil in the slick will vary not only with time, but also with the distance from the source (Reed et al., 1999).

3.4 Evaporation

In many oil spills, evaporation is the most important process in terms of mass balance. Within a few days following a spill, light crude oils can lose up to 75 percent of their initial volume and medium crudes up to 40 percent. In contrast, heavy or residual oils will lose no more than 10 percent of their volume in the first few days following a spill. Most oil spill behavior models include evaporation as a process and as a factor in the output of the model.

The basis for most of the evaporative work is the extensive study on the evaporation of water. In fact, the currently used equations still employ empirical portions of these equations. Several fundamental differences exist between the evaporation of a pure liquid such as water and a multicomponent system such as crude oil. First the evaporation rate for a single liquid such as water is a constant with respect to time.

Evaporative loss (by total weight or volume) is logarithmic with respect to time for multicomponent mixtures. This logarithmic variation is due to the depletion of the more volatile components, which occurs exponentially with time. The second major difference between water and oil evaporation is the effect of atmospheric conditions. Water evaporation is strongly dependent on wind speed and relative humidity. Air can only hold a certain water mass. Furthermore, air normally does not contain a high level of benzene and other components, and the saturation level of these in air is often well above concentrations that can be achieved from an evaporating slick. Additionally in oil, the slick temperature is important because of temperature-dependent partial pressure (ASCE, 1996).

Blokker (1964) was the first to develop separate equations for oil evaporation at sea, based on the assumption that fuel was a one-component liquid. The ASTM distillation data with the average boiling points of successive fractions were used as the data source, and a weathering curve was calculated. Mackay and Matsugu (1973) approached the problem by adopting the classical water evaporation work of Sutton (1934), supplemented by additional experimental data (e.g. Thibodeaux 1979). Their equations for mass transfer are used equation with third-party data and found that the equations yielded results that were close to the experimental data. The most frequently used work in spill modeling is that of Stiver and Mackay (1984). In their formulation, the rate of evaporation is related to vapor pressure, spill area, a mass transfer coefficient that depends on wind speed, environmental temperature, and oil type.

Bobra (1992) conducted laboratory studies on the evaporation of several crude oils and petroleum products. The comparison of his data with Stiver and Mackay (1984) equations shows that the equations predict the evaporation of most oils relatively well, slightly underpredicting in the initial phase (the underpredicting is not a serious concern). However, after time exceeds 8 hours, the equations overpredict evaporation. The "overshoot" can be as much as 5% of oil mass, at the 24-h mark. This overprediction is especially true for very light oils.

Evaporation of previously dissolved oil components could take place directly from the water phase. This process is relatively important for the alkanes, cycloalkanes, and light aromatics (Mackay et al. 1983b; McDonald et al. 1984). Hamoda et al. (1989) developed a model to describe the volatilization of the dissolved components

from the bulk of the solution. Mass transfer coefficients were experimentally determined for some specific conditions.

Fallah and Stark (1976) proposed a random model to predict the evaporation of oil at sea. Mackay et al. (1980a) developed an extensive oil spill model incorporating a number of process equations including evaporation. The earlier work of Leinonen and Mackay (1975) was used with a modification by Yang and Wang (1977). The process is essentially that of dividing the oil into a number of different fractions and analyzing the loss of each fraction by evaporation. The mass transfer function used is the familiar one proposed by Mackay and Matsugu (1973).

Two different types of methods are used for evaporation calculations: pseudo-component and analytical methods. In the pseudo-component approach, the fraction evaporated is computed as a funtion of time and temprature alone. Analytical method is based on several simplifications, including the questionable assumption of a linear relationship between the boiling point of the liquid phase and the fraction lost by evaporation. This linear relation is specified in terms of an initial liquid phase boiling point temperature and the gradient of this boiling point temperature versus the fraction evaporated (Reed et al., 1999).

Payne et al. (1984) and Payne and McNabb (1984) developed an oil spill model using the pseudocomponent approach. Given the boiling point and American Petroleum Institute (API) gravity of each cut (or pseudocomponent), the vapor pressure of the cut as a function of temperature can be calculated. Ross and Dickens (1987) used some empirical data to model the evaporation of oil under snow. Lunel (1991) combined the mass transfer rates of evaporation and dissolution to deal with these competing processes simultaneously. Lehr et al. (1992) developed an oil spill weathering model (ADIOS) using the evaporative algorithm developed by Stiver and Mackay (1984). The oil spill weathering model described by Aamo et al. (1993) uses the distillation cut approach to model evaporation, and couples this calculation to the weathering processes of water uptake, emulsification, stabilization, and dispersion via reference to laboratory and field weathering data.

Jones (1997) has modified this method by introducing an empirical relation between molar volumes and boiling point, based on data for n-alkanes. In this way, the pseudo-component model may be used in spite of the common lack of data on

specific gravity of the boiling point cuts. The same author has also introduced an empirical equation for determination of the vapor pressure as a function of boiling point and oil temperature. This equation is said to produce more realistic pressure values, particularly at high boiling points, than the Clausius-Clapeyron equation and Trouton's rule used in Payne et al. (1987).

A similar pseudo-component concept is used in the SINTEF weathering model (Daling et al., 1997). However, the mass transfer coefficient in this model is based on formulations commonly used for computations of surface of fluxes of momentum, heat and moisture in open sea (Smith, 1988). This implies that the mass transfer coefficient is proportional to the wind speed, with the air-sea drag coefficient used as the factor of proportionality. However, as shown by Amorocho and DeVries (1980) and Blake (1991), the drag coefficient depends on the wind speed due to changes in the surface roughness of the sea with the sea-state. The drag coefficient for near-neutral conditions appears to increase from a constant value of about 1×10^{-3} at wind speeds under 6 or 7 m/s, where white caps start to form, to about twice that value at 20 m/s (Amorocho and DeVries, 1980).

Due to the large data requirements and computational complexity of the pseudo-component concept, simpler methods have been proposed, such as the so called analytical method developed by Stiver and Mackay (1984). This method is used presently in many oil drift models, as well as by NOAA (1994) in the ADIOS model.

When Jones (1997) made his comparisons between the extended analytical model and the pseudo-component method, he found that the extended analytical method in general predicted significantly larger evaporative losses than his own pseudo-component model. He presumed that the difference could be explained by the use of different algorithms for calculating vapor pressures in the two models. The high evaporative losses predicted by the analytical model may also in part be explained by the postulated linear approximation of the boiling point curve (Reed et al., 1999).

In the derivation of the analytical method, Stiver and Mackay (1984) also introduce the evaporative exposure parameter τ. They show that the relation between the evaporative loss and this parameter is thermodynamic in nature and does not depend on how the exposure is achieved. Hence, the relation is only a function of the initial

oil composition and the oil temperature. For constant wind speed, the evaporative exposure parameter may be expressed as

$$\tau = Kt/h_f \quad \textbf{(3.1)}$$

where K is the surface mass transfer coefficient, h_f is the initial film thickness and t is the exposure time. This implies that if the evaporative loss is computed as a function of time for one combination of wind speed and initial film thickness, the results may be used for any another combinations of wind speed and film thickness by a simple time scaling. The same applies to cases with variable wind, where the exposure is obtained from the integral

$$\tau = \int (K/h_f)\, dt \quad \textbf{(3.2)}$$

Johansen and Skognes (1988) applied this concept in a statistical trajectory model in order to reduce the computational requirements of the evaporation calculations. In this model, the evaporative loss is computed as a function of time for a selection of crude oils at a chosen reference condition (defined in terms of a fixed initial oil film thickness and a constant wind speed). These results are tabulated in a file, which is later read during the start-up of the trajectory model. During the trajectory simulations, the evaporative loss is determined by simple interpolation, on the basis of the integrated evaporative exposure along each trajectory (Reed et al., 1999)

Fingas (1997) has conducted such experiments for a variety of crude oils and oil products, and derived simple empirical relations for prediction of the evaporative loss as a function of time, based on commonly available distillation data for oils (i.e. per cent by weight distilled at 180°C). However, Fingas (1999) also concluded from these experiments that wind speed and exposed surface area do not significantly influence the evaporation rate. For this reason, he advocated that his correlations should be used with no corrections for film thickness on wind speed, but with a minor correction for temperature. These conclusions are not at present generally accepted in the field of oil spill modeling, and run counter to most prior work in this area (Reed et al., 1999)

Jones (1997) compared predictions with his pseudo-component model at different wind speeds and oil film thicknesses with the predictions based on the empirical equations proposed by Fingas, and concluded that the empirical correlations in general produced signifcantly smaller evaporative losses than the pseudocomponent

method. However, as Jones (1997) points out, Fingas used low wind speeds and relatively thick oil to establish the parameters in his model. When examining the results under such conditions, Jones found that the models were in good agreement. If the evaporative exposure relevant for the laboratory conditions could be established, adjustments of the empirical predictions for other conditions (wind speed, film thickness) could be made. However, further tests at other wind speeds and comparisons with calculations based on the pseudo-component concept should be made before such adjustments can be recommended for general use (Reed et al., 1999)

3.5 Dissolution

Dissolution is the chemical stabilization of oil components in water. Dissolution is not considered in all numerical models because the effect on the mass balance of oil is small. Usually much less than 1% of the oil spilled on the water surface will dissolve. The dissolution can, however, be of great importance from a toxicological point of view. The most soluble oil components are usually the most toxic. Even low concentrations of these toxic components could lead to serious effects on biological systems (ASCE, 1996).

Dissolution is an important process from the point of view of possible biological harm, although it accounts for a negligible fraction of the mass balance of oil. Hydrocarbons which are likely to dissolve in the water are likely to evaporate. Dissolution, which tends to occur in the first few hours of a spill, thus has to compete with evaporation. Although solubility values for various hydrocarbon components are avaible, these values are difficult to utilize correctly for modeling purposes, since they are often inconsistent for the same compounds (Shen et al., 1987).

Brookman et al. (1985) reviewed the solubility of oil and oil components in water. Most solubility data were obtained for distilled water at 25 °C, using various schemes. The solubility of oil components in water varies widely depending on composition. Solubility decreases very rapidly with increasing size and increasing substitution. In contrast, the solubility of the aliphatic oil components is very low relative to that of aromatic hydrocarbons and is considered to be negligible. The solubility of crude oils and petroleum products was investigated by Shiu et al. (1990)

using several methods in two different laboratories and under a variety of conditions. Table 3.1 contains examples of whole oil solubilities.

Table 3.1 : Examples of whole oil solubility data (NRC, 2003)

Oil Type	Solubility mg/L	Temperature °C	Salinity %
Prudhoe Bay	29	22	distilled
Lago Media	24	22	distilled
Lago Media	16.5	22	33
Diesel fuel	3	20	distilled
Diesel fuel	2.5	25	33
Bunker C	6	22	distilled
Automotive gasoline	98	22	distilled

Dissolution is thoroughly studied experimentally as well as theoretically by Mackay et al. (1980a, 1983b, Mackay and McAuliffe 1988) and Payne et al. (1983, 1991) and Payne and Phillips (1985). Dissolution was studied in an oil weathering model by Payne et al. (1983) by two distinctly different modeling approaches. A component-specific model predicts individual component concentration in the surface slick and in the water column, based on thermodynamic properties (e.g., mass transfer coefficients). A drawback of the component-specific description of oil with a complex composition is that it does not account for the overall mass balance of the oil slick. Thereore, Payne and his coworkers developed the approach with a limited number of pseudocomponents based on the fractional distillation cut characteristics, well known in the petroleum industry for many crude and refined oils. In this approach the bulk oil is divided into a number of pseudocomponents. The fate of the pseudocomponents (especially evaporation and dissolution) is described by the bulk properties of each pseudo-component. The limited number of pseudocomponents allows also the prediction of the overall oil mass balance (ASCE, 1996).

The kinetics of dissolution have remained largely unstudied. In oil spill models, dissolution is often assumed to occur immediately (Hibbs et al., 1999). Some models have incorporated the effect of oil droplet size in the water column and used this parameter to create a kinetic behavior model (Mackay and Leinonen, 1977). In groundwater, kinetics of dissolution are often modeled using a depletion concept and based on the rate of water flow (Mackay et al., 1991).

3.6 Development of Oil Spill Models

Many people assume that the principal objective of oil spill models is to forecast the future distribution or physicochemical character of the pollutant based on the initial or present distribution of oil. However, this function is only one of the potential ways to use models. Forecasts of where the oil will go are very useful for immediate response activities, but they are limited by the length of time that weather forecasts are available. Most major spills last longer than available weather forecasts. For major spills advanced planning must cover contingencies well beyond the time scales that are reliably covered by direct forecasts. To provide information for this longer range, planning and analysis techniques are available (ASCE, 1996).

A few quasi three-dimensional (3D) and 3D oil spill models are currently available. However, for some cases a two-dimensional (2D) surface model is all that is needed. Many of the models available have user-friendly interfaces and are developed based on state-of-art algorithms describing the physics of the oil spill processes. However, often the understanding of the physical processes is not complete and is subject to many scientific and computational limitations. Therefore, experienced personnel should interpret results. Without them the results may be of marginal use, or perhaps even misleading. In spite of the fact that computational models cannot always accurately simulate the fate and the transport of an oil slick, they are still a substantial help in the combat of oil spills (ASCE, 1996).

3.6.1 Two-Dimensional Oil Spill Models

During the early stages after the oil spill has occurred, the transport of spilled oil is mainly governed by: the spreading due to the gravity, inertia, viscosity and surface tension forces; the advection and turbulent diffusion due to current and wind; evaporation, dissolution and vertical dispersion. If the oil slick moves towards the islands or shoreline, the shoreline deposition and re-entrainment will also be considered. Based on these studies, 2-D trajectory and fate models are developed to simulate the movement of the surface oil slick (Chao et al., 2000).

3.6.2 Three-Dimensional Oil Spill Models

Because of spreading, advection, horizontal diffusion, evaporation and dissolution, the oil slick becomes thinner and thinner. Under the action of turbulent shear and breaking waves, the oil slick will disperse and become small particles. Delvigne and Sweeney (1989) and Delvigne (1994) has studied the vertical dispersion of surface oil slicks based on experimental data, and obtained the dispersion rate. The small oil particles can advect and diffuse in the water column because of the turbulent waters. Some of them float back to the water surface, while some of them form water-in-oil or oil-in-water emulsions. Since the density of emulsion oil is close to that of water, it can stay in the water column for a long time. In order to simulate the distribution of oil particles in the water column, a 3-D oil spill numerical model is necessary. As the fate and transport processes of oil spills in the water column are very complex, there has been little published research on the 3-D oil spill models (Chao et al., 2000).

4. NUMERICAL MODELING

4.1 Introduction

In recent years there has been a growing concern over the increasing contamination of water bodies and adjacent shoreline areas by oil spills. Some processes, such as industrial discharge, oil exploration and transport, oil storage facilities, etc., have increased the risk of oil spill accidents. Oil spill accidents are very harmful to the ocean environment and the health of mankind (Chao et al., 2000).

Generally, the transport and fate of spilled oil can be affected by the physical, chemical and biological processes. These include spreading, advection, evaporation, dissolution, emulsification, photo-oxidation, sedimentation, and biodegradation.

The environmental concern over oil spills has led to the development of mathematical models that simulate the transport and fate of oil slicks. Although over 50 models have been developed over the years, only a few are used extensively today. These models are used for spill response during accidents, environmental impact assessment, contingency planning, and response training (ASCE, 1996).

The oil spill model was developed as a numerical tool to study the behaviour and approximate trajectory of oil spills in water bodies. It is a two-dimensional model that simulates the sea surface fate of oil spills solving the equation for advection and diffusion of passive constituents. Typical processes associated with oil fate in water such as evaporation, spreading and entrainment are included in the two-dimensional oil spill models (Fragoso et al., 2002).

4.2 The Lagrangian Discrete Particle Algorithm

At the present time two basic methods of application exist. The models use either Lagrangian spillets or Lagrangian discrete parcels. The Lagrangian spillets method is implemented by assuming that a continuous spill consists of a number of discrete spills, discharged at specified time intervals. The spreading theories are then

applied to each discrete spillet. In the Lagrangian discrete parcel approach, the oil slick is represented as an ensemble of a large number of small parcels. Each parcel has a set of time-dependent spatial coordinates and a mass associated with it. The spreading theory is applied after considering the volume of parcels in grids or pie shaped segments that move with the slick (ASCE, 1996).

Each particle is then allowed to move with the drift velocity $\vec{V}_t$ during each time step. The drift velocity is given as (Shen and Yapa, 1987)

$$\vec{V}_t = \vec{V} + \vec{V}' \quad \textbf{(4.1)}$$

where $\vec{V}_t$ is the drift velocity of an oil particle; $\vec{V}$ is the mean drift velocity which represents the surface drift due to the combined effect of wind or ice cover and current; $\vec{V}_t'$ is the turbulent fluctuation of the drift velocity which simulates the horizontal diffusion of the oil slick (Wang et al., 2005).

4.3 The Weathering Mechanism

Oil or petroleum products spilled on water undergo a series of changes in physical and chemical properties that, in combination, are termed "weathering." Weathering processes occur at very different rates but begin immediately after oil is released into the environment. Weathering rates are not consistent and are usually highest immediately after the release. Both weathering processes and the rates at which they occur depend more on the type of oil than on environmental conditions. Most weathering processes are highly temperature dependent, however, and will often slow to insignificant rates as the temperature approaches zero. Table 4.3.1 is a summary of the processes that affect the fate of petroleum hydrocarbons from seven major input categories. Each input is ranked using a scale of high, medium, and low that indicates the relative importance of each process. The table is intended only to convey variability and is based on many assumptions. Nevertheless, it does provide a idea of the relative importance of these processes. Clearly one of the biggest problems in developing such a table is that the importance of a particular process will depend on the details of the spill event or release. Table 4.3.1 attempts to account for this to a limited extent in the case of accidental spills by including subcategories for various oil types. This table emphasizes the role various environmental processes can play in spills of widely varying types. This in turn underscores how just one facet of

the complex set of variables may vary from spill to spill, making each spill a unique event. Thus, the chemical and physical character of crude oils or refined products greatly influence how these compounds behave in the environment as well as the degree and duration of the environmental effects of their release (NRC, 2003).

Table 4.1 : Processes that move petroleum hydrocarbons away from point of origin (NRC, 2003)

Input Type	Persistance	Evaporation	Emulsification	Dissolution	Oxidation	Horizontal Transport or Movement	Vertical Transport or Movement	Sedimentation	Shoreline Stranding	Tarballs
Seeps	years	H	M	M	M	Horizontal	Movement	M	H	H
Spills										
Gasoline	days	H	NR	M	L	L	NR	NR	NR	NR
Light Distillates	days	M	L / L	H	L	M	H	L	L	NR
Crudes	months	M	M	M	M	M	M	M	H	M
Heavy Distillates	years	L	M	L	L	H	L	H	H	H
Produced water	days	M	NR	M	M	L	L	L	L	NR
Vessel operational	months	M	L	M	L	M	L	L	L	M
Two-stroke engines	days	H	NR	M	L	L	L	NR	NR	NR
Atmospheric	days	H	NR	M	M	H	NR / NR	NR	NR	NR
Land based	U	M	L	L	L	M	M	M	NR	U

NOTE: H = high; L = low; M = moderate; NR = not relavant; U = unknown

The physical and chemical changes that spilled oil undergoes are collectively known as 'weathering'. Although the individual processes causing these changes may act simultaneously, their relative importance varies with time. Together they affect the behaviour of the oil and determine its ultimate fate. These processes are illustrated in Figure 4.1 for a spill of a typical medium crude oil under moderate sea conditions (ITOPF, 2002).

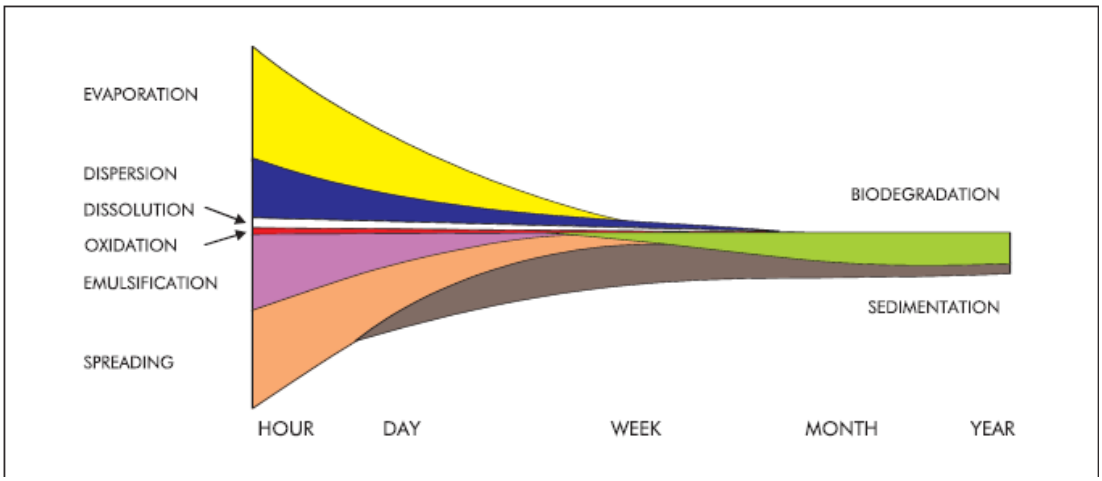

Figure 4.1 : A schematic representation of the fate of a crude oil spill showing changes in the relative importance of weathering processes with time - the width of each band indicates the importance of the process (ITOPF, 2002).

The processes described previously are summarised in Figure 4.2. Spreading, evaporation, dispersion, emulsification and dissolution are most important during the early stages of a spill whilst oxidation, sedimentation and biodegradation are longer term processes which determine the ultimate fate of oil. An understanding of the way in which weathering processes interact is important when attempting to forecast the changing characteristics of an oil during the lifetime of a slick at sea (ITOPF, 2002).

It should be appreciated that the movement of an oil slick on the sea surface is due to winds and surface currents, and may be influenced by the combined weathering processes. The actual mechanisms governing spill movement are complex, but experience shows that oil drift can be predicted from a simple vector calculation of wind and surface current direction, based on about 3% of the wind speed and 100% of the current velocity. Reliable prediction of slick movement is clearly dependent upon the availability of good wind and current data. Accurate current data are sometimes difficult to obtain. For some areas it is presented on charts or tidal stream atlases but often only general information is available. In shallow waters near the coast or among islands, currents may be complex and are often poorly understood, rendering accurate prediction of slick movement particularly difficult (ITOPF, 2002).

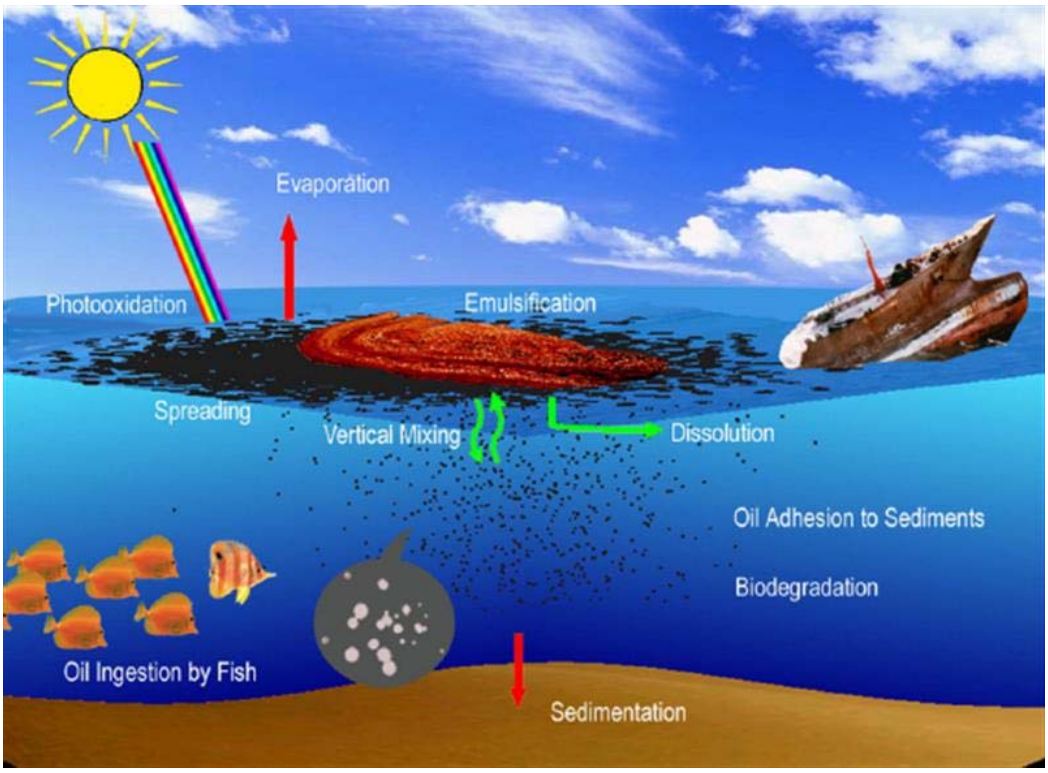

Figure 4.2 : Processes acting on spilled oil (Xie et al., 2007).

4.3.1 Evaporation

Evaporation is a very significant mass loss for many kinds of oil and it had profound effect on density and viscosity and other properties of oil. Evaporation can account for the loss of up to 60% of spilled light crude oil. Rates of evaporation depend on the oil vapour pressure, as influenced by composition and temprature, and on transport characteristics of the air-sea boundary layer influenced primarily by the wind. The vapour pressure changes as hydrocarbon fractions are lost into atmosphere (Korotenko et al., 2000).

Evaporation is usually the most important weathering process. It has the greatest effect on the amount of oil remaining on water or land after a spill. Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of a heavier Bunker C oil evaporates. The evaporation rates of different types of oil are shown in Figure 4.3. The rate at which an oil evaporates depends primarily on the oil's composition. The more volatile components an oil or fuel contains, the greater the extent and rate of its evaporation. Many components of heavier oils will not evaporate at all, even over long periods of time and at high temperatures (Fingas, 2000).

Oil and petroleum products evaporate in a slightly different manner from water and the process is much less dependent on wind speed and surface area. Oil evaporation can be considerably slowed down, however, by the formation of a "crust" or "skin" on top of the oil. This happens primarily on land where the oil layer does not mix with water. The skin or crust is formed when the smaller compounds in the oil are removed, leaving the larger compounds, such as waxes and resins, at the surface. These then seal off the remainder of the oil and prevent evaporation. Stranded oil from old spills has been re-examined over many years and it has been found that when this crust has formed, there is no significant evaporation in the oil underneath. When this crust has not formed, the same oil could be weathered to the hardness of wood (Fingas, 2000).

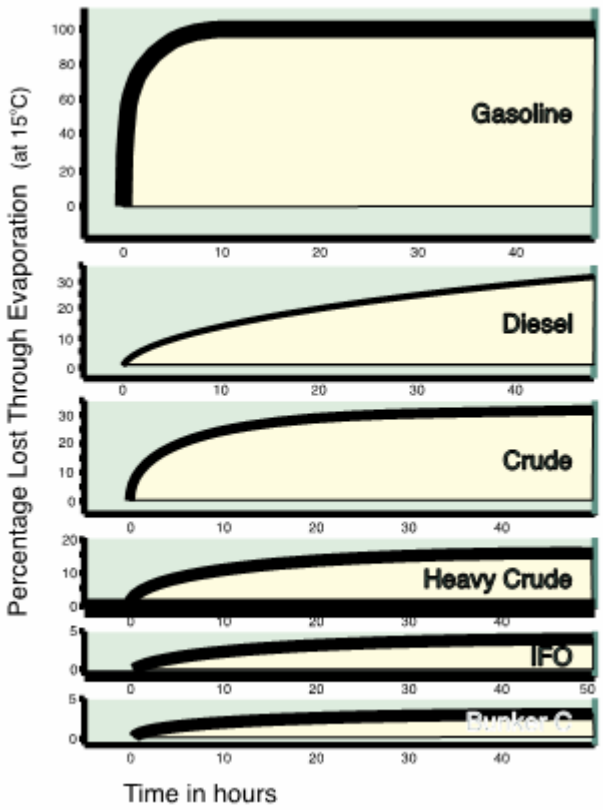

Figure 4.3 : Evaporation rates of different types of oil at 15°C (Fingas, 2000).

The properties of an oil can change significantly with the extent of evaporation. If about 40% (by weight) of an oil evaporates, its viscosity could increase by as much as a thousandfold. Its density could rise by as much as 10% and its flash point by as much as 400%. The extent of evaporation can be the most important factor in determining properties of an oil at a given time after the spill and in changing the behaviour of the oil (Fingas, 2000).

The more volatile components of an oil will evaporate to the atmosphere. The rate of evaporation will depend on ambient temperatures and wind speed. In general, those oil components with a boiling point below 200°C will evaporate within a period of 24 hours in temperate conditions. The greater the proportion of components with low boiling points, the greater the degree of evaporation. The initial spreading rate of the oil affects evaporation since the larger the surface area, the faster light components will evaporate. Rough seas, high wind speeds and warm temperatures will also increase the rate of evaporation. Any residue of oil remaining after evaporation will have an increased density and viscosity, which affects subsequent weathering processes and the effectiveness of clean-up techniques (ITOPF, 2002).

The volume fraction of oil evaporated is given by the following equation Mackay et al. (1980)

$$F_V = \left[\ln P_0 + \ln\left(CK_E t + 1/P_0\right)\right]/C \quad \textbf{(4.2)}$$

where

$$K_E = K_M A V_M /\left(RT_o V_0\right) \quad \textbf{(4.2a)}$$

$$K_M = 0.0025 V_w^{0.78} \quad \textbf{(4.2b)}$$

K_M is the mass transfer coefficient (m/s); V_w is the wind speed at 10 m above the water surface (m/s); A is the area of the oil slick (m^2); V_M is the molar volume (m^3/mol), the value of it can vary between $150x10^{-6}$ and $600x10^{-6}$ m^3/mol; R is the gas constant, $8.206x10^{-5}$ (atm m^3/K mol); T_o is the surface temperature of the oil (K), which is generally close to the ambient air temperature, T_E; and V_0 is the initial spill volume (m3). The initial vapor pressure P_0 in atmosphere at the temperature T_E is (Wang et al., 2005)

$$\ln P_0 = 10.6\left(1 - T_0/T_E\right) \quad \textbf{(4.2c)}$$

where T_E is the ambient air temperature (K); and T_0 is the initial boiling point (K). Mackay et al. (1980) showed that $T_E C$ is a constant for a given oil. Values of C at T_E=283 K, and the initial boiling point T_0 are given by Mackay et al. (1980). Using these values, Shen et al. (1986) obtained the following functional relationships for oils

$$C = 1158.9\,API^{-1.1435} \quad \textbf{(4.2d)}$$

$$T_0 = 542.6 - 30.275\,API + 1.565\,API^2 - 0.03439\,API^3 + 0.0002604\,API^4 \quad \textbf{(4.2e)}$$

The evaporative loss fraction (F_e) of a given hydrocarbon is also described by the following equation (Buchanan & Hurford):

$$\frac{dF_e}{dt} = \frac{KA_0}{V_0}\exp\left[A - \frac{B}{T_p}\left(T_i + T_G F_e\right)\right] \quad \textbf{(4.3)}$$

where

$$K = 2.5\times10^{-3} U_v^{0.78} \quad \textbf{(4.3a)}$$

T_p is the product temperature (°K); T_i is the initial temperature (when F_e = 0); A = 6.3; B = 10.3; T_G is the distillation curve gradient (°K); μ is the dynamic viscosity (cP); A_0 is the oil slick area (m^2); and V_0 is the oil volume (m^3).

4.3.2 Dissolution

Through the process of dissolution, some of the most soluble components of the oil are lost to the water under the slick. These include some of the lower molecular weight aromatics and some of the polar compounds, broadly categorized as resins. As only a small amount, usually much less than a fraction of a percent of the oil, actually enters the water column, dissolution does not measurably change the mass balance of the oil. The significance of dissolution is that the soluble aromatic compounds are particularly toxic to fish and other aquatic life. If a spill of oil containing a large amount of soluble aromatic components occurs in shallow water and creates a high localized concentration of compounds, then significant numbers of aquatic organisms can be killed (Fingas, 2000).

Gasoline, diesel fuel, and light crude oils are the most likely to cause aquatic toxicity. A highly weathered oil is unlikely to dissolve into the water. On open water, the concentrations of hydrocarbons in the water column are unlikely to kill aquatic organisms (Fingas, 2000).

Dissolution occurs immediately after the spill, and the rate of dissolution decreases rapidly after the spill as soluble substances are quickly depleted. Some of the soluble compounds also evaporate rapidly (Fingas, 2000).

Dissolution of hydrocarbons from a slick is generally unimportant for the spill mass balance because less than 1% of the oil slick may dissolve. Such a low dissolution of oil is a result of three factors: (1) the low dissolution mass transfer coefficient; (2) the very small water solubility driving force; and (3) the presence of relatively small quantities of the more soluble hydrocarbons, most of which are more susceptable to evaporation (Korotenko et al., 2000).

The rate and extent to which an oil dissolves depends upon its composition, spreading, water temperature, turbulence and degree of dispersion. The heavy components of crude oil are virtually insoluble in sea water whereas lighter compounds, particularly aromatic hydrocarbons such as benzene and toluene, are slightly soluble. However, these compounds are also the most volatile and are lost very rapidly by evaporation, typically 10 to 1,000 times faster than by dissolution. Concentrations of dissolved hydrocarbons in sea water thus rarely exceed 1 ppm and

dissolution does not make a significant contribution to the removal of oil from the sea surface (ITOPF, 2002).

The amount of oil mass dissolved into the water column may be computed according to a multi-component theory developed by Mackay (1980). The amount of oil component i, M_{di} (moles), lost by dissolution can be estimated by the following expression:

$$M_{di} = K_d . A . X_i . S_i . t \quad \textbf{(4.4)}$$

Here K_d (=3x10^{-6} m/s) is a dissolution mass transfer coefficient and S_i is the solubility of the particular component i. The rate of total oil dissolution is calculated as:

$$S_d = \sum_{i=1}^{m} M_{di} / t = K_d . A . \sum_{i=1}^{m} X_i S_i \quad \textbf{(4.5)}$$

Another method is developed by Cohen et al. (1980). In this method, the rate of dissolution is demonstrated as follows

$$S_d = K_d A S \quad \textbf{(4.6)}$$

where S_d is the total dissolution rate of the oil slick (g/h); K_d is a dissolution mass transfer coefficient (m/h); A is the area of the oil slick (m^2); S is the oil solubility in water. The solubility of oil decreases rapidly after the spill due to weathering. Huang and Monastero (1982) suggested that for a typical oil the solubility can be simulated by

$$S = S_0 e^{-\alpha t} \quad \textbf{(4.6a)}$$

where S_0 is the solubility for fresh oil; α is a decay constant; and t is time (h). Lu and Polak (1973) provided values for S_0 and α for three different types of oils.

4.4 Movement of Oil

4.4.1 Spreading

Spreading is the horizontal expansion of an oil slick due to gravity, inertia, viscous and surface tension forces. After an oil spill on water, the oil tends to spread into a slick over the water surface. This is especially true of the lighter products such as gasoline, diesel fuel, and light crude oils, which form very thin slicks. Heavier crudes and Bunker C spread to slicks several millimetres thick (Fingas, 2000).

The speed at which oil spreads over the surface depends to a great extent on the viscosity of the oil and the volume spilled. Fluid, low viscosity oils spread more quickly than those with a high viscosity. Liquid oils initially spread as a coherent slick but quickly begin to break up. Solid or highly viscous oils fragment rather than spreading to thin layers. At temperatures below their pour point, oils rapidly solidify and hardly spread at all and may remain many centimetres thick (ITOPF, 2002).

Oil spreads horizontally over the water surface even in the complete absence of wind and water currents. This spreading is caused by the force of gravity and the interfacial tension between oil and water. The viscosity of the oil opposes these forces. As time passes, the effect of gravity on the oil diminishes, but the force of the interfacial tension continues to spread the oil. The transition between these forces takes place in the first few hours after the spill occurs (Fingas, 2000).

The rates of spreading under ideal conditions are shown in Figure 4.4. As a general rule, an oil slick on water spreads relatively quickly immediately after a spill. The outer edges of a typical slick are usually thinner than the inside of the slick at this stage so that the slick may resemble a “fried egg.” After a day or so of spreading, this effect diminishes (Fingas, 2000).

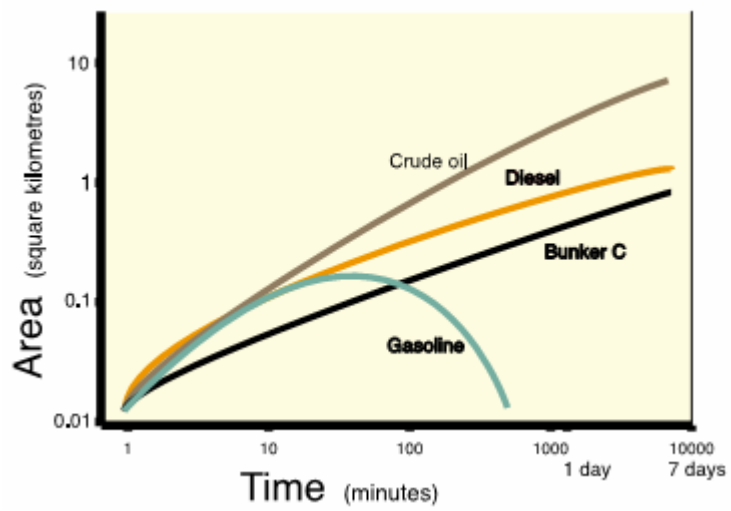

Figure 4.4 : Comparison of spreading of different oils and fuels (Fingas, 2000).

The rate at which oil spreads or fragments is also affected by tidal streams and currents - the stronger the combined forces, the faster the process. There are many examples of spills spreading over several square kilometres in just a few hours and over several hundreds of square kilometres within a few days, thus seriously limiting the possibility of effective clean-up at sea. It should also be appreciated that, except in the case of small spills of low viscosity oils, spreading is not uniform and large variations of oil thickness from less than a micrometre to several millimetres can occur (ITOPF, 2002).

Three stages have been identified in the spreading of an oil slick (Fay, 1969, Hoult, 1972, Buckmaster, 1973, U.S. Coast Guard, 1994). In the first stage gravity and inertial forces control the spreading of oil across the surface. In the second stage, the inertial forces become negligible in comparison with viscous drag across the surface. In the third stage interfacial forces become dominant and provide the driving force to propel spreading. Thus, at equilibrium the floating oil could spread across the surface or it could form a lens.

Fay (1972) considered the spreading of an oil slick passing through three phases and the axi-symmetrical spreading diameter and one-dimensional spreading width in each of phase are summarized in Table 4.2 Fay observed that the changes in the oil slick properties caused by weathering may result in the eventual cessation of the mechanical spreading. According to a lot of field observations, Fay suggested that

$$A = 10^5 V^{3/4} \quad \textbf{(4.7)}$$

where A is the final slick area (m^2); and V is the total volume of the slick (m^3). Equation 4.7 indicates that the cessation of the mechanical spreading occurs when the slick thickness reduces to $10^{-5} V^{1/4}$ m.

Table 4.2 : Spreading law for oil slicks

Spreading Phase	Width (L_e)	Radius (R_e)
Gravity-inertia	$1.39\left(\Delta g A t^2\right)^{1/2}$	$1.14\left(\Delta g V t^2\right)^{1/4}$
Gravity-viscous	$1.39\left(\Delta g A^2 t^{3/2} v^{-1/2}\right)^{1/4}$	$0.98\left(\Delta g V^2 t^{3/2} v^{-1/2}\right)^{1/6}$
Surface tension viscous	$1.43\left(\sigma^2 t^3 \rho_w^{-2} v^{-1}\right)^{1/4}$	$1.60\left(\sigma^2 t^3 \rho_w^{-2} v^{-1}\right)^{1/4}$

However, due to non-consideration of the influence of wind and associated turbulence, the prediction of oil spreading using Fay's formula has been found to be underestimating the horizontal spreading compared to that observed from field measurements. Lehr et al. (1984) formulated a modified Fay-type spreading equation considering the influence of wind:

$$A = 2270\left(\frac{\Delta\rho}{\rho_0}\right)^{2/3} V^{2/3} t^{1/2} + 40\left(\frac{\Delta\rho}{\rho_0}\right)^{1/3} V^{1/3} U_{wind}^{4/3} t \quad \textbf{(4.8)}$$

where A is the area of the oil slick (m^2);

$$\Delta\rho = \rho_w - \rho_o \quad \textbf{(4.8a)}$$

V is the total volume of the spilled oil in barrels; U_{wind} is the wind speed in knots; and t is the time in minutes. Based on the Lehr formula, the area of the oil slick due to spreading at every time step can be obtained.

Buckmaster also outlines a solution approach for computing the size and shape of lens as a function of time. Ultimately Buckmaster derived from this theory an expression for the radius of a slick, R, as

$$R(t) = 1.76(g\Delta\rho)^{0.25} V^{0.3333} v^{-0.125} t^{0.375} \quad \textbf{(4.9)}$$

Viscosity of sea water can be obtained from ITTC (1999) formula:

$$v_s = \left(\left(0.659\times10^{-3}\left(T-1.0\right)-0.05076\right)\left(T-1.0\right)+1.7688\right)\times10^{-6} \quad \textbf{(4.9a)}$$

where T is the water temprature (°C).

4.4.2 Advection

The shape and track of the oil slick are very important for predicting the oil movement. In 2-D oil spill models, the initial oil slick area is divided into a number of small grids, and a set of plane coordinates are assigned to each grid. It is assumed that these grids advect with the surrounding water body and diffuse as a result of random processes. Based on the flow fields on the water surface and the wind velocity, the advection and diffusion properties of each grid point can be computed. Then the velocity and displacement of each grid can be solved. After calculating the grid coordinates at every time step, the shape and track of the oil slick can be decided.

Advection is accounted for by simulation of the movement of the centroid of the oil slick due to large scale circulation, tidal and buoyancy driven and wind-induced transient currents. In the general case, the advection due to the combined effect of these components is described by their vector sum (Korotenko et al., 2000)

$$V_i = V_i^{wid} + V_i^{wad} + V_i^{d} + V_i^{c} + V_i^{T} + V_i^{B} \quad \textbf{(4.10)}$$

where V_i^{wid} and V_i^{wad} corresponds to velocity due to wind drift and wave (Stokes) drift component, respectively which, generally, do not coincide in the direction; V_i^{d} is the wind-induced component; V_i^{T} is the tidal component; V_i^{B} is the buoyancy-driven component, and V_i^{c} denotes the large scale component. The sum of the wind induced and Stokes drift components, $V_i^{wid} + V_i^{wad}$, is expressed in terms of wind speed U_A at 10 m above the water surface as (Korotenko et al., 2000)

$$V_i^{wid} + V_i^{wad} = 0.03U_A \quad \textbf{(4.10a)}$$

On the other hand, the drift velocity of the surface oil is usually considered to be a vector sum of a wind-induced drift and a water-current drift. Therefore, the drift velocity of the surface oil $\vec{V}_s$ is written as a vectorial addition

$$\vec{V}_s = \alpha_w D\vec{V}_w + \alpha_c \vec{V}_c \quad \textbf{(4.11)}$$

where $\vec{V}_w$ is the wind velocity at 10 m above the water surface; $\vec{V}_c$ is the surface water current velocity, it can be obtained from hydrodynamic models; α_w is the wind drift factor, usually adopted as 0.03 (Stolzenbach et al., 1977) and ac is the factor to account for the contribution of the oil slick drift on the water surface due to the

current, α_c is selected as 1.1. D is the transformation matrix which allows to introduce a deviation angle

$$D = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \quad \textbf{(4.11a)}$$

where $\theta = 40° - 8\sqrt{\vec{V}_w}$ **(4.11b)**

when $0 \le \vec{V}_w \le 25$ m/s and $\theta = 0$ when $\vec{V}_w \succ 25$

4.4.2.1 Displacement of Each Grid

The advective displacement of each grid point at every time step can be computed as:

$$L_x(\Delta x) = U_{dx}\Delta t + \Delta S\cos\theta \quad \textbf{(4.12)}$$

$$L_y(\Delta x) = U_{dy}\Delta t + \Delta S\sin\theta \quad \textbf{(4.13)}$$

where $L_x(\Delta t)$ and $L_y(\Delta t)$ are the displacements of each point in the x and y directions, respectively; U_{dx} and U_{dy} are the advective velocities in the x and y directions, respectively; and

$$\theta = 2\pi[R]_0^1 \quad \textbf{(4.14)}$$

Then the x and y coordinates of each point on the oil slick at every time step can be obtained, and the shape and track of the oil slick at every time step can be obtained (Chao et al., 2000).

4.4.2.2 Effects of Wind, Wave, and Current Fields

The spilled oil is subject to the action of wind and water movement. The wind elongates the slick and the action of wind and water currents separates the surface slick into windrows of thicker layers of oil, aligned in the direction of the prevailing wind, with areas of sheen oil or essentially open water between windrows. This results in long but narrow slicks, extending for several kilometers in the wind direction and only for a few hundred meters in the cross wind direction; the slick area, however, may approximate the area of the semi-empirical expressed previously. Within this slick, the oil is unevenly spread and its thickness varies considerably (Papadimitrakis et. al, 2004).

Advection of oil is also the result of wind, current and wave fields. The current field is, generally, calculated as the vectorial sum of wind-, tidally-, density-, and pressure gradient-induced currents. Frequently, the residual current is small and may be

neglected in many calculations, particularly in open seas where the oil will be moved mainly by the action of wind. The present model employs some simple expressions for describing the slick advection by the wind and wave-induced currents. The surface wind- and wave-induced currents, U_{sw} and U_{sww} respectively, may be given by the expressions proposed by (Wu, 1985; Wu, 1980; and Sobey and Barker ,1997)

$$U_{sw} = 0.01\exp(1.03 + 0.14U_w)U_w \quad \textbf{(4.17)}$$

$$U_{sww} = 0.015U_w \quad \textbf{(4.18)}$$

where the wind speed, expressed in m/s now, is measured at the elevation of 10 m above the mean sea level. The wind drift vector is rotated by an angle θ, with respect to the wind direction, to account for Coriolis effects. The deflection angle, θ, can be estimated as a function of the wind speed using an empirical expression proposed by Samuels et. al (1982)

$$\theta° = 25\exp(-10^{-8}U_w^3 / g\nu_w) \quad \textbf{(4.19)}$$

Here g is the acceleration of gravity and ν_w is the kinematic viscosity of water. Tidal currents are also included in the advection scheme of oil slicks (Papadimitrakis et. al, 2004).

4.4.2.3 Horizontal Turbulent Diffusion

The turbulent diffusive transport is generally calculated by a random walk procedure. Based on Fischer et al.'s study (1979), the fluctuation velocity component $\vec{V}'$ is calculated by

$$V' = (4E_T / \delta t)^{1/2} \quad \textbf{(4.20)}$$

$$\vec{V}' = V'R_n e^{i\theta'} \quad \textbf{(4.21)}$$

where

$$E_T = 0.4n_b V g^{1/2} h^{5/6} \quad \textbf{(4.20a)}$$

is the turbulent diffusivity (Sayre and Chang, 1969); h is the water depth; δt is the time step; R_n is the random number in the interval 0–1. The directional angle θ' is assumed to be a uniformly distributed random angle in the interval 0–π.

The diffusive velocity component can be modeled by a homogeneous random walk model. Based on Al-Rabeh et al.'s study (1989), the distance that any element (grid) travels by horizontal diffusion is:

$$\Delta S = [R]_0^1 \sqrt{12 D_h \Delta t} \quad \textbf{(4.22)}$$

where $[R]_0^1$ is the random number in the interval 0-1; D_h is the horizontal diffusion coefficient and in the present study we select D_h as 7 m^2/s.

5. OIL SPILL MODEL DEVELOPMENT

In this thesis, the numerical model developed for the oil slick trajectory is two-dimensional. Hence, the model is limited with processes that are effective on the sea surface. These include evaporation, dissolution, spreading and advection.

Data and empirical models suggest circular spreading of oil slicks in calm waters. Three different spreading formulae are used to obtain oil slick radii at each time step. In wind and current presence, circular shape of the oil slick will be deformed and elongate varyingly. Hence, in order to simulate these effects advection formulae are utilized. Moreover, evaporation and dissolution effects are considered as well.

To test the hypothesis and to quantify combined influence of the processes on the slick shape, the following numerical experiments are completed. First, a rectangular domain is considered with a width of 2000 meters and a length of 4000 meters. Afterwards, using 2-D ADAM hydrodynamic model (Ip et al., 1998) flow field of the computational domain is computed. Flow field is combined with the empirical formulae for spreading, advection, evaporation and dissolution and oil slick trajectory is simulated.

In the second numerical experiment the flow field in Bosphorus is computed with the ADAM model and then the oil slick trajectory is simulated assuming an oil spill scenario.

All the processes are simulated using MATLAB. MATLAB code of each process is given in appendice.

5.1 Computational Domain for the Rectangular Pool

The computational domain covers an area of 4000x2000 m, as shown in Figure 5.1. It consists of 231 nodes and 400 elements. The computational domain has a V-shaped bathymetry as shown in Figure 5.2.

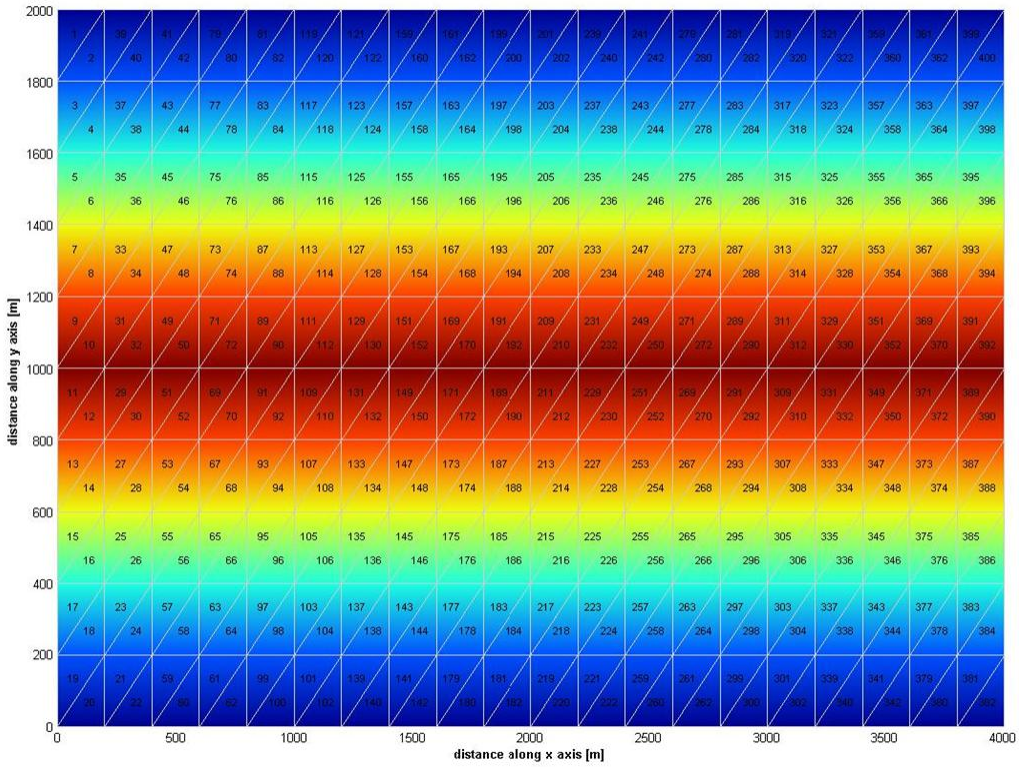

Figure 5.1 : Bathymetry and computational mesh of the rectangular pool.

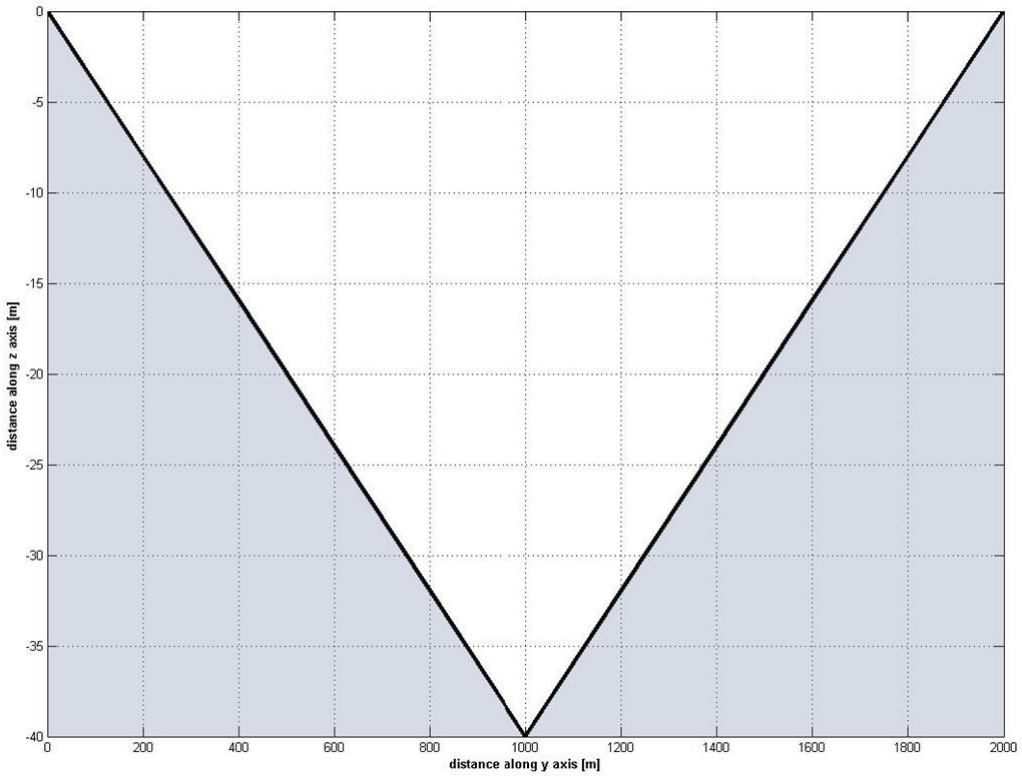

Figure 5.2 : Cross-section of the rectangular pool.

5.2 Simulation of Tidal Currents

To simulate the flow fields, ADAM model is used. In this 2-D model, the non-linear diffusion equation is discretized with linear finite elements by Galerkin method in space and solved implicitly by iteration in time. The boundary is forced with 12 hour tidal elevation for 6 tidal cycles. Each tidal cycle is divided into 300 time steps. Figure 5.3 shows the surface elevation versus time step at node 69 in the 6th tidal cycle computed from the ADAM model.

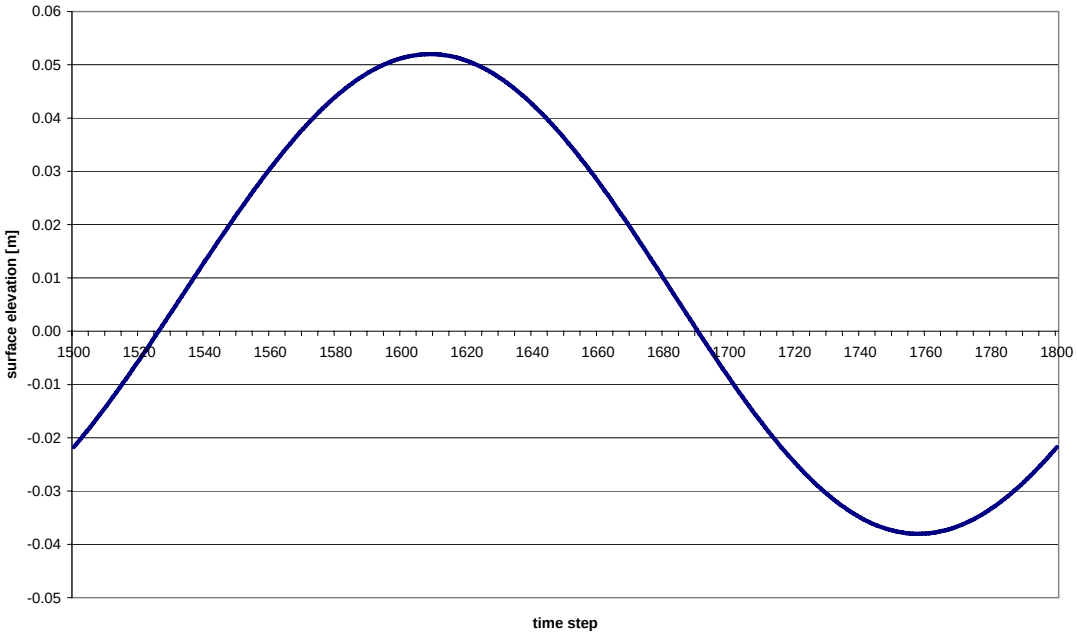

Figure 5.3 : Surface elevation versus time step at node 69 in the 6th tidal cycle.

5.3 Simulation of Weathering Processes

5.3.1 Evaporation

Evaporation occurs when the lighter or more volatile substances within the oil mixture become vapors and leaves the surface of the water. Figure 5.4 shows the percentage of evaporation versus time for different types of oil using Equation 4.2 . It can be observed that the evaporation mainly happens in the first 1-2 days. Boiling point of the oil greatly affects the evaporation rate. Hence, gasoline, whose boiling point is the lowest compared to other types, has the greatest evaporation rate as expected.

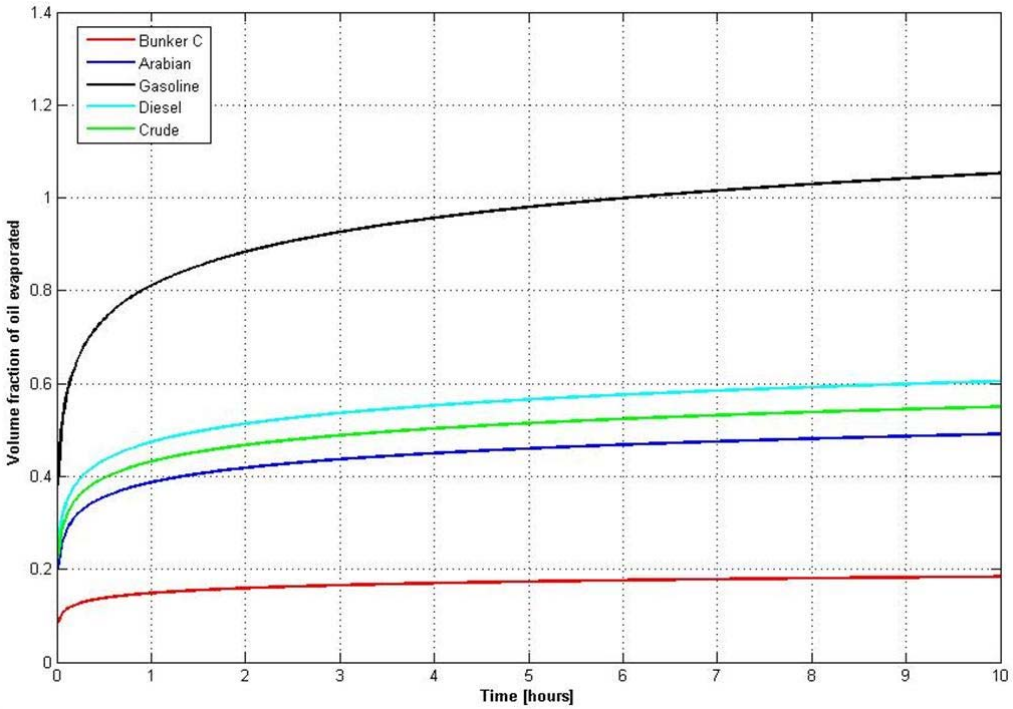

Figure 5.4 : Volume fraction of oil evaporated versus time for different types of oil.

5.3.2 Dissolution

Water soluble compounds in an oil may dissolve into the surrounding water. This depends on the composition and state of the oil, and occurs most quickly when the oil is finely dispersed in the water column. Figure 5.5 shows the total dissolution rate of Fuel oil No.2 in 6 hours.

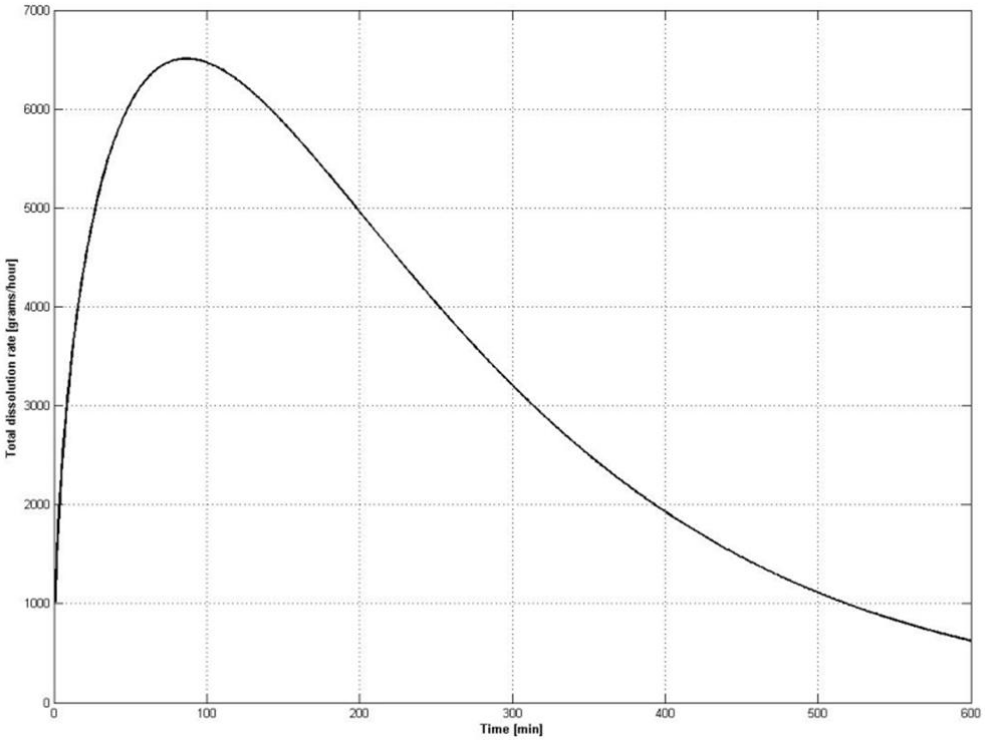

Figure 5.5: Total dissolution rate of fuel oil No.2

5.4 Simulation of the Movement of the Surface Slick

5.4.1 Spreading

As soon as oil is spilled, it starts to spread over the sea surface. The spreading of an oil slick is one of the most important processes in the early stage of the oil slick transformation, because of the influence of the surface area of the oil slick on weathering processes such as evaporation and dissolution. The spreading of an oil slick is determined by the balance between gravitational, viscous and surface tension forces. Primary factors that affects spreading process are viscosity of the oil and the volume spilled. In Figure 5.6 change of oil slick radius with time according to Equation 4.8 is given. Besides, change of oil slick radius with time for different types of oil is compared in Figure 5.7. The comparison is done using Equation 4.8 as well. In Figure 5.8 spreading of an oil slick is simulated. Effects like wind and current are not considered for this simulation. Only the spreading process is simulated.

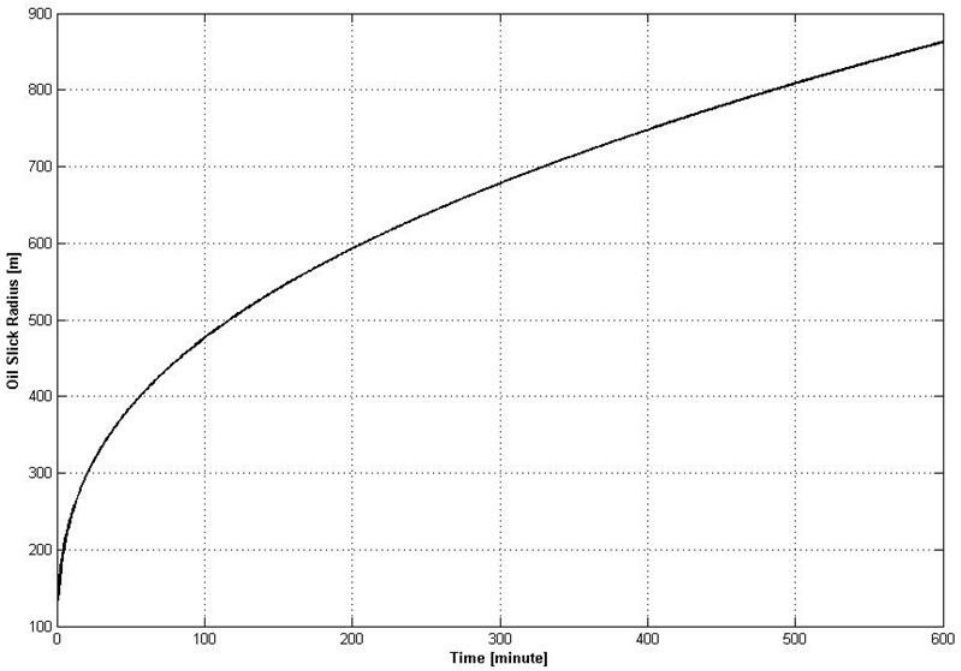

Figure 5.6 : Change of oil slick radius for 300 cubic meters of oil with time according to Lehr's formula

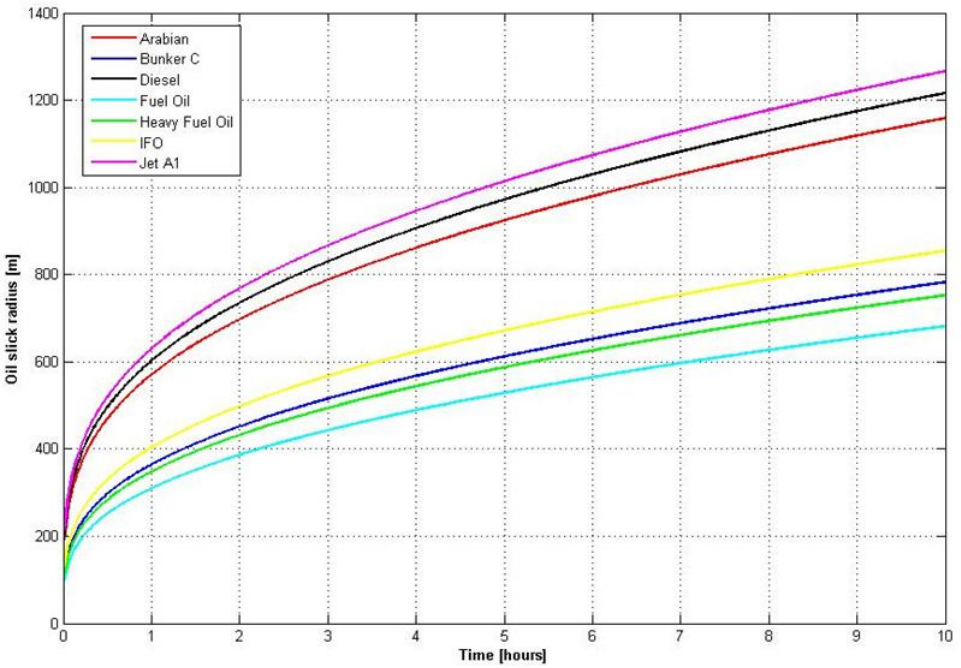

Figure 5.7 : Change of oil slick radius for 300 cubic meters of oil with time according to Lehr's formula for different types of oil

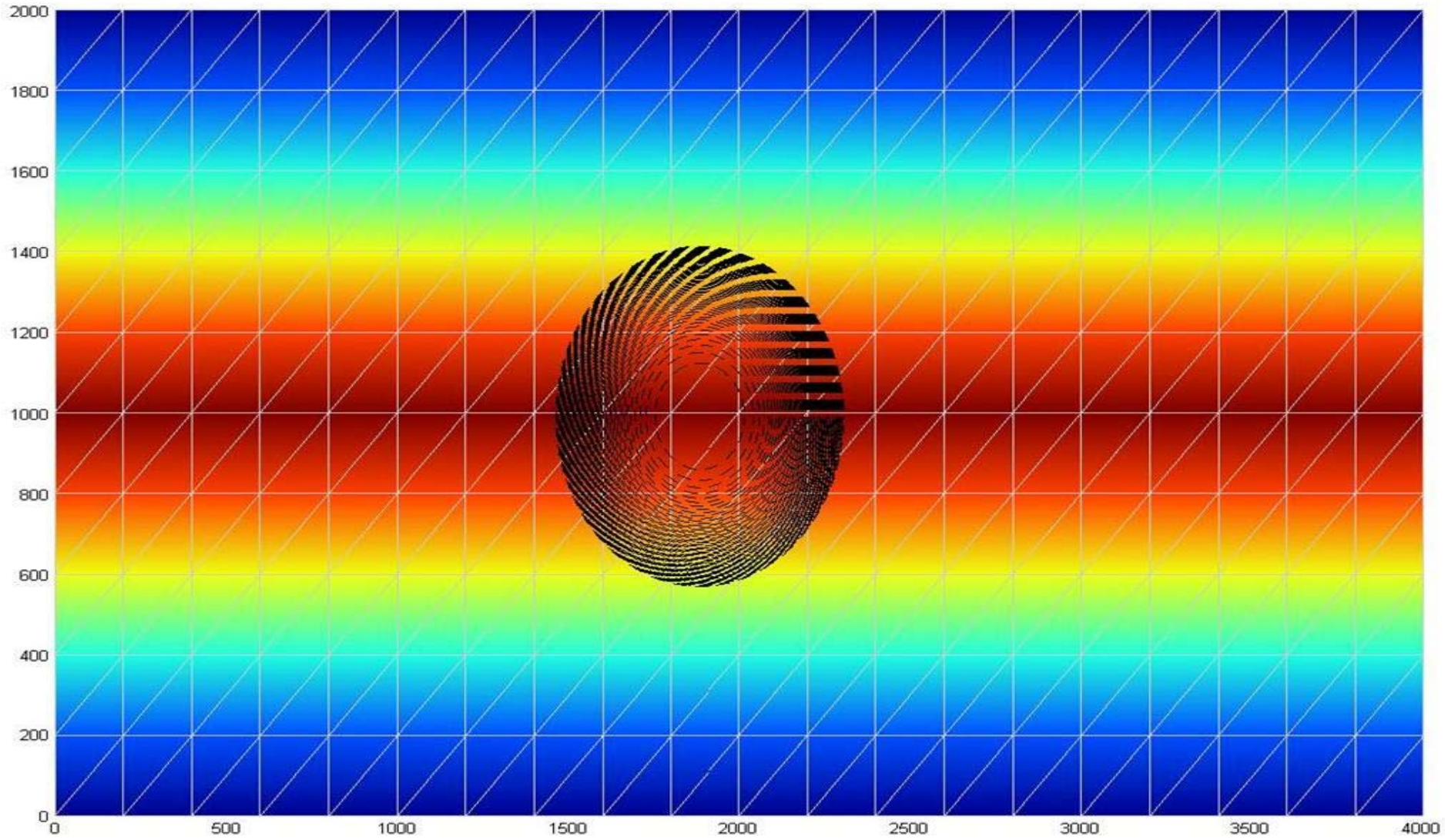

Figure 5.8 : Spreading of an oil slick with time according to Lehr's formula

5.4.2 Advection

Oil moves horizontally in the marine environment under forcing from wind, waves, and currents. Based on the flow fields and and the wind velocity, the advection properties of each grid can be computed. Figure 5.9 shows an example simulation for an oil slick. The arrows show the flow field. The dotted orbitals indicate the oil slick. Due to wind and flow field, the oil slick loses its circular shape. Its new shape and location is now determined by the effects of wind and the flow field.

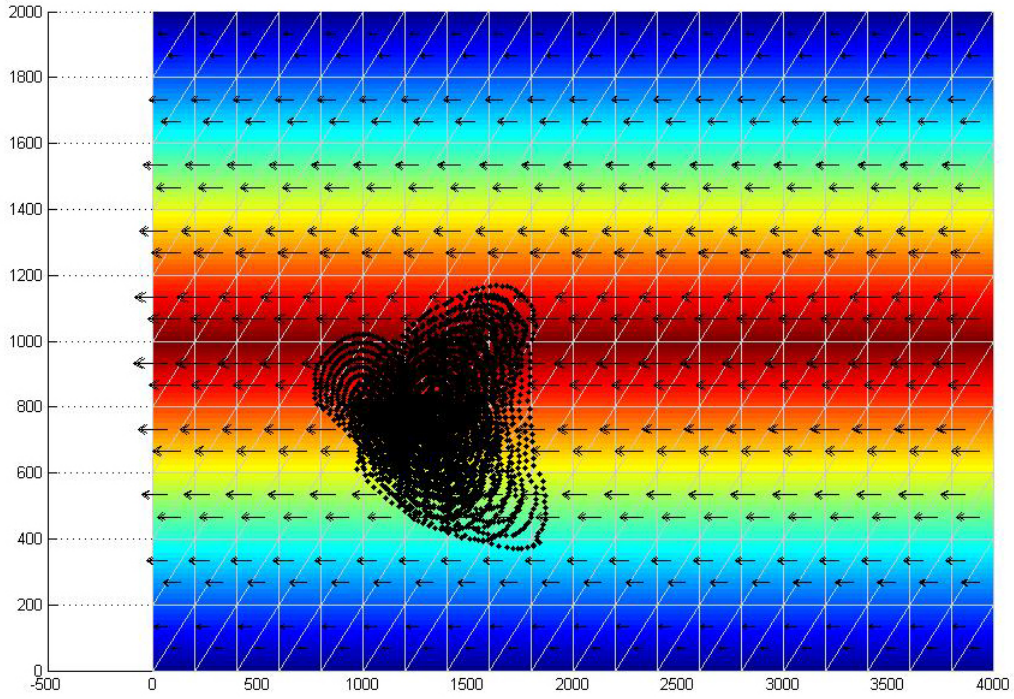

Figure 5.9 : Advection of an oil slick

5.5 Simulation of the Combined Processes

Oil spilled in water undergoes a variety of physical and chemical processes. In this thesis, four of these processes are analyzed. At first, all the processes are examined separately. However, for a real time oil slick trajectory, combination of these processes is needed. Figure 5.10 examplifies combination of processes in the chosen computational domain. Flow field is indicated with arrows. Oil slick is represented with dashed lines. With the effects of four processes, oil slick moves in the wind and current direction.

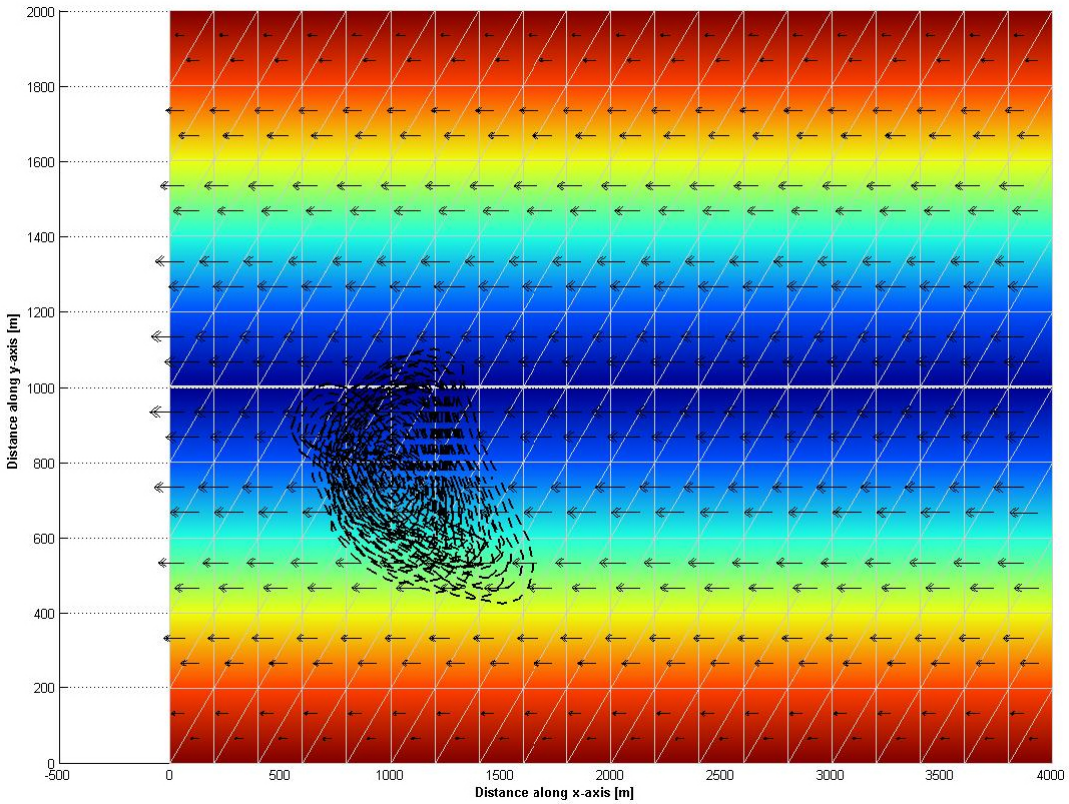

Figure 5.10 : Simulation of combined processes

5.6 Graphical User Interface

5.6.1 Model Inputs

The model operates on a spill scenario basis. It consists of four main modules for each process separately. Each process module has also sub modules enabling user to select between different formulae and different conditions.

The input parameters for each spill scenario are entered via a series of data input boxes. Figure 5.11 and Figure 5.12 shows the summary box for the scenario data entry. Inputs such as the density of spilled oil and oil spill volume can all be entered via these boxes. After entering inputs, user can select the desired simulation type. In Figure 5.11 and 5.12, on the left side of the modules, there is a user input section. Below it, output section is placed.

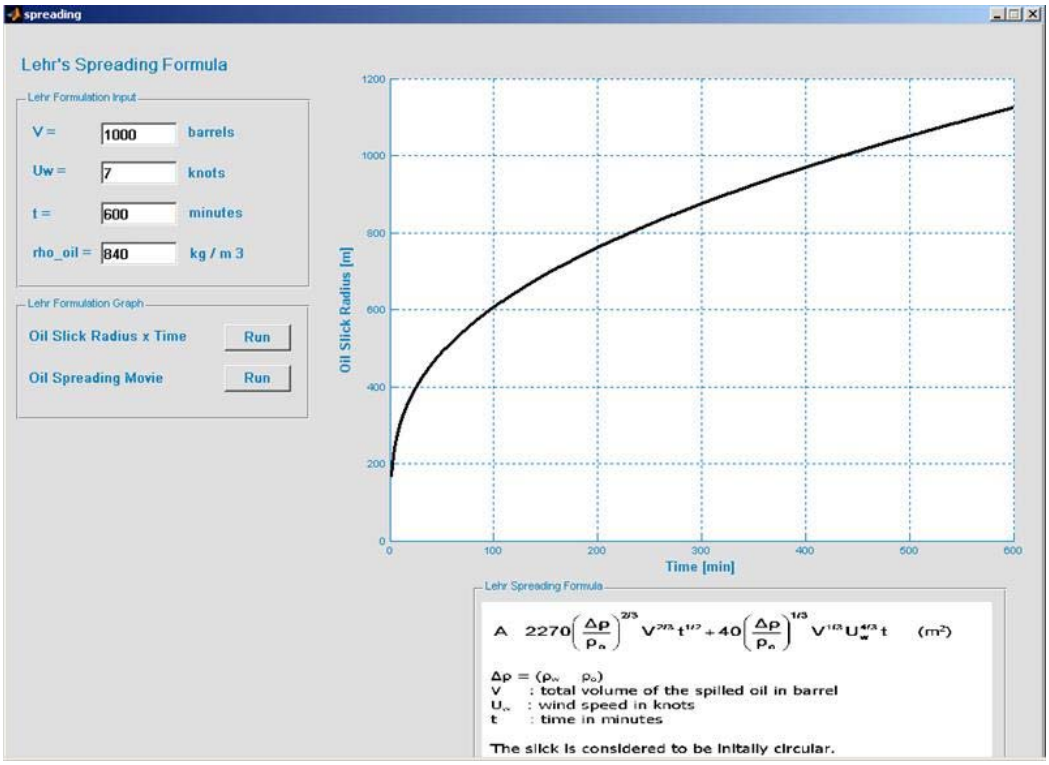

Figure 5.11 : Spreading module of the oil spill model (Lehr Formulation)

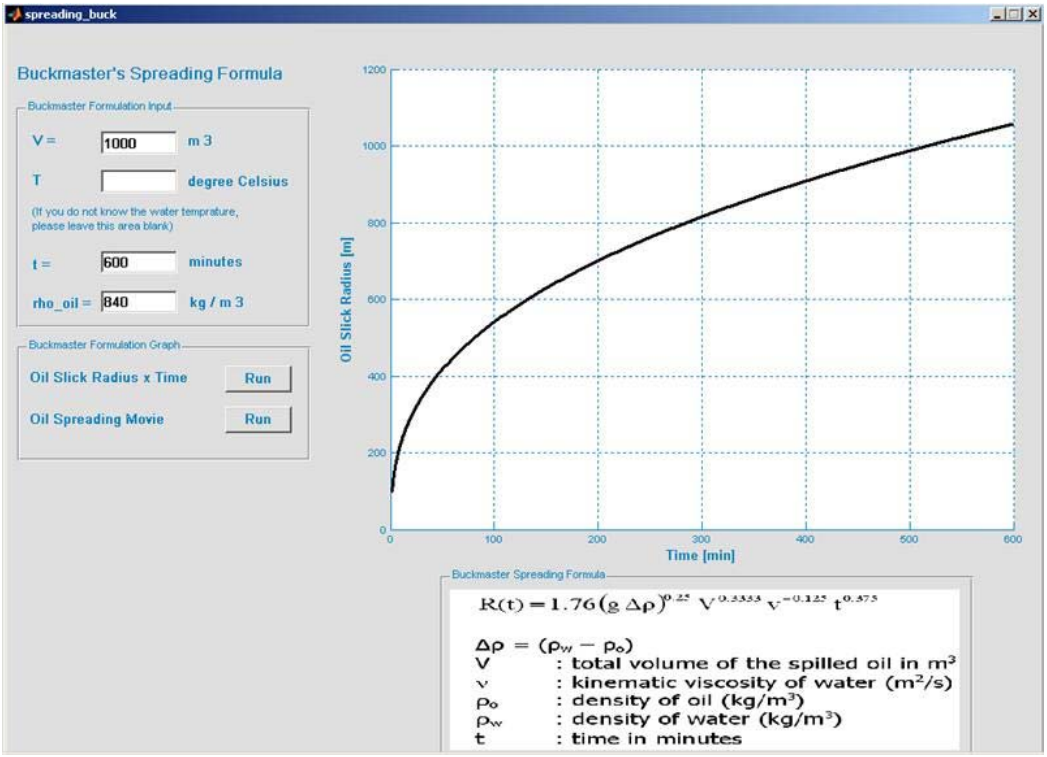

Figure 5.12 : Spreading module of the oil spill model (Buckmaster Formulation)

5.6.2 Model Outputs

The oil spill model developed can compute oil slick radius versus time with the selected inputs. In addition, the user can follow spreading of the oil slick at each time step. Formulation is of each process is also shown in each module. By this way, the user sees information about each formulae. In Figure 5.11 and Figure 5.12, on the right-hand side of the modules an output screen is created. This enables the user to simulate results.

5.7 Application of the Model to an Oil Spill Scenario in Bosphorus Strait

Bosphorus Strait is approximately 30 km long, with a maximum width of 3,700 meters at the northern entrance, and a minimum width of 700 meters between Kandilli and Aşiyan; and 750 meters between Anadoluhisarı and Rumelihisarı.

By some estimates, as many as 60 ships per day carrying oil and other hazardous materials pass through the straits. On the whole, 45,000 ships of various sizes pass, with an average of 1,350 per day. On average, 5 ships in excess of 80 DWTs now pass each day, representing a potential floating catastrophe in the very middle of Istanbul. Turkish officials estimate that 60% of the yearly traffic carries hazardous materials such as natural gas, agricultural and other chemicals, oil, nuclear waste and derivatives through the straits. Twenty billion gallons of oil and chemicals pass through the straits each year (Erdem, 1995).

The combination of the physical characteristics with heavy traffic has already had predictable results. Between 1988 and 1992 there were 155 collisions in the Bosphorus. In March of 1994, the oil tanker Nassia collided with an empty cargo ship at the entrance of the Bosphorus, resulting in 30 deaths. The Nassia, carrying 19 million gallons of crude oil from Novorssyisk, suffered 3 of its 10 tanks ruptured, and drifted unguided and burning for nearly a week. The accident resulted in $1 billion in damages, and the waterway was closed for a week. The spill eventually washed out to sea, away from Istanbul. An earlier accident, in 1979, occurred when a Greek freighter collided with a Romanian tanker near the lower entrance of the Bosphorus. The explosion shattered windows onshore, and the load of diesel carried by the tanker burned for weeks. The slick was washed into the Sea of Marmara, and onward through the Dardanelles to the Aegean Sea (Kohen, 1994).

Due to these facts, creating oil spill scenarios and simulating the fate of the spilled oil for Bosphorus Strait is essential. Hence, an oil spill scenario is created in Bosphorus Strait and 2D oil spill model developed is used to simulate the accident. The simulated result of the oil slicks after the spillage are presented and discussed.

5.7.1 Computational Domain for Bosphorus Strait

As shown in Figure 5.13, the computational domain covers an area of about 3 km x 32 km and the Cartesian coordinate system is used. The computational domain consists of 1170 nodes and 2038 elements. The depth of the Bosphorus Strait varies from 36 to 124 metres in midstream. Bathymety of Bosphorus Strait is shown in Figure 5.14.

For two-dimensional problems, the fundamental element shapes are triangular and rectangular, and the best results are obtained when the first is equilateral and the second square. The corners of triangular elements should be near to 60º. Considering this, computational mesh of Bosphorus Strait is not good enough but can be improved. Size of the elements in the narrowest location is about 300 meters and in the widest location it is about 833 meters.

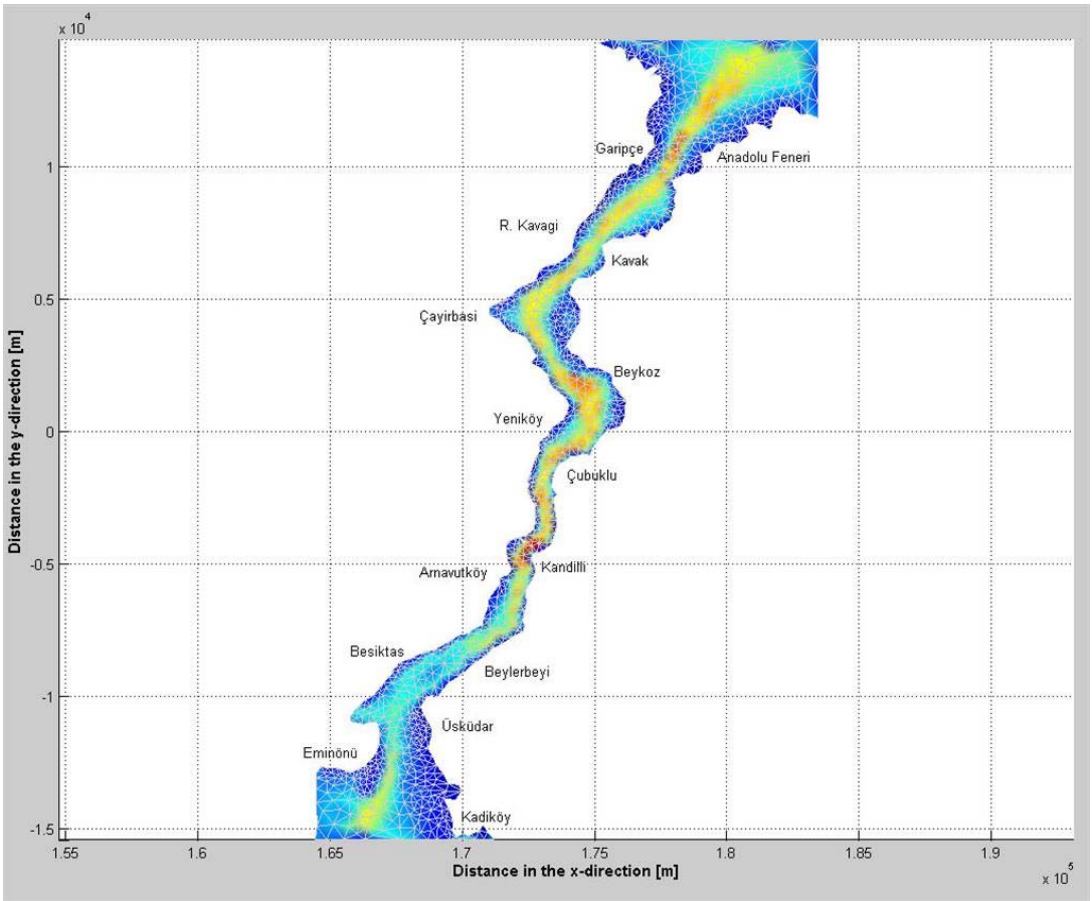

Figure 5.13 : Computational mesh of Bosphorus Strait.

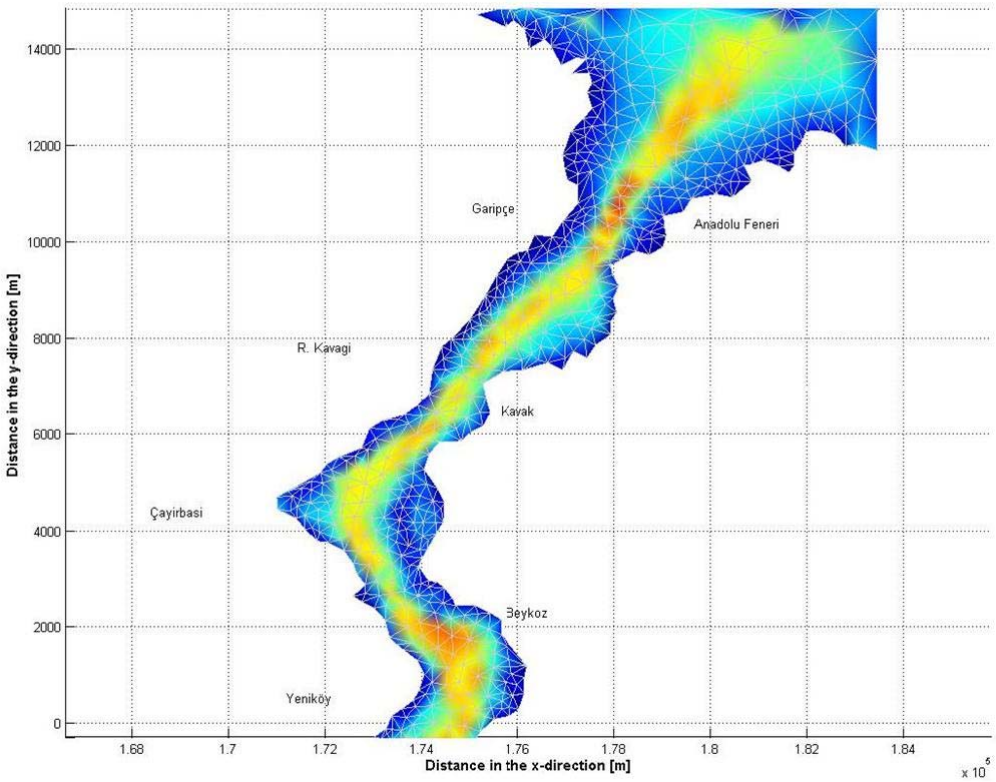

Figure 5.14 : Closer view of the computational mesh of Bosphorus Strait (north).

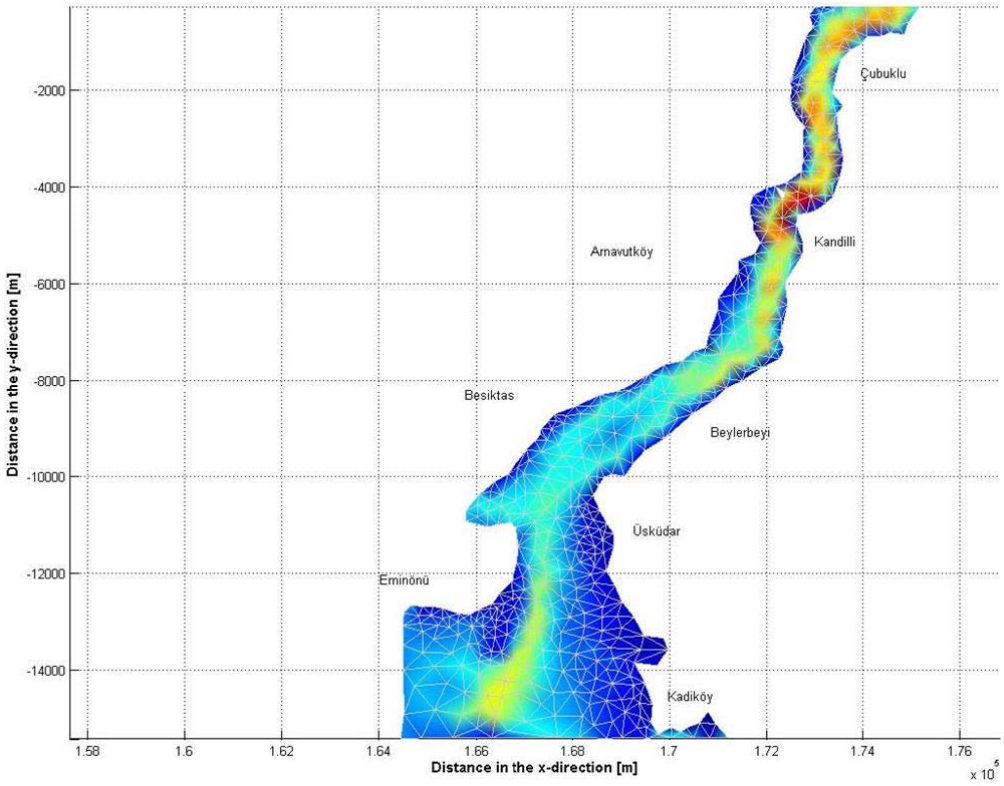

Figure 5.15 : Closer view of the computational mesh of Bosphorus Strait (south).

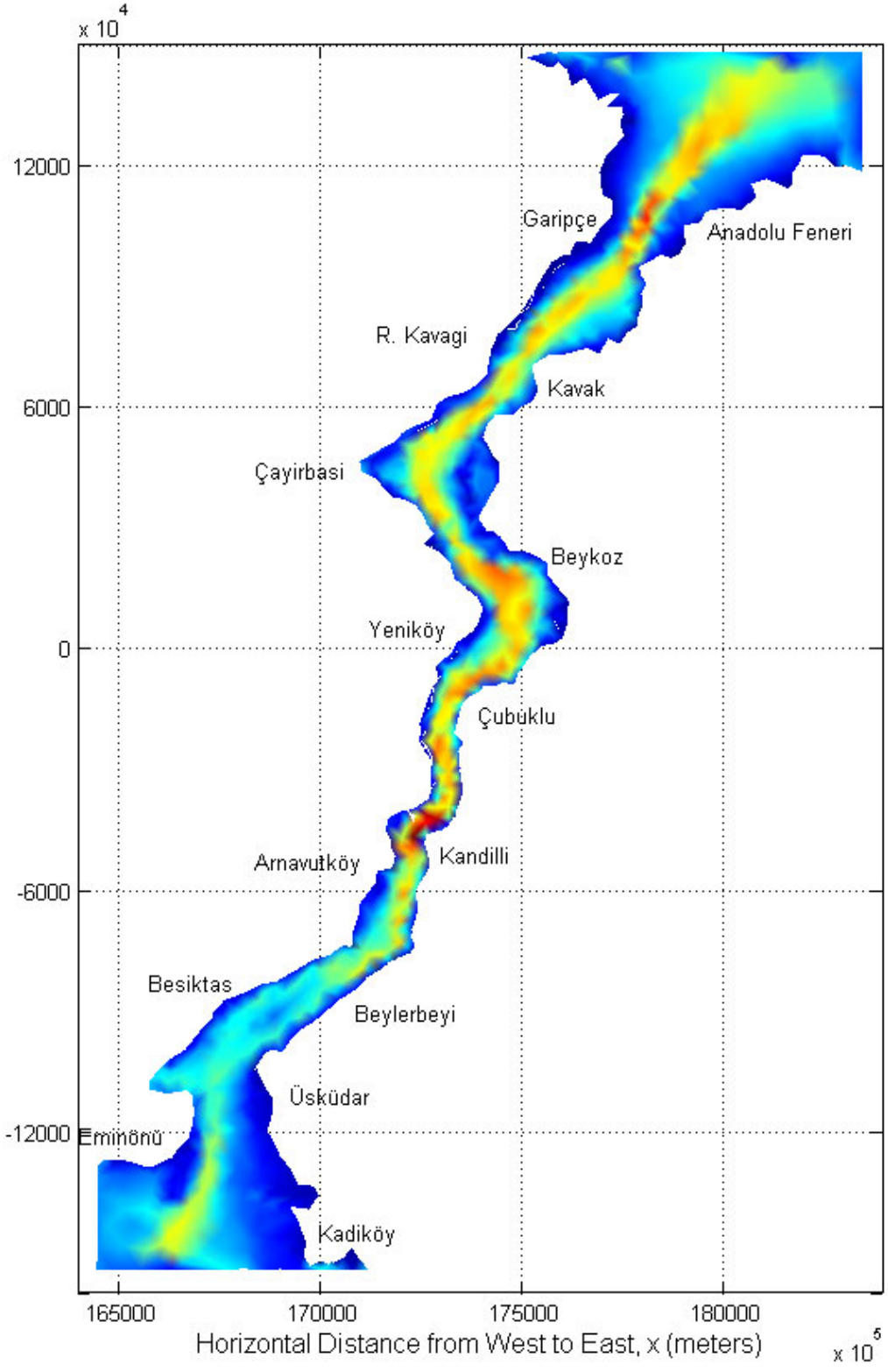

Figure 5.16 : Bathymetry of Bosphorus Strait.

5.7.2 Input Data

For flow field calculation 2D ADAM hydrodynamic model is used. The duration of the simulation is 5.2 hours. Since particle tracking method is used, it is assumed that during this period of time 100 oil particle was released. The wind speed is taken as 5 knots (2.572 m/s). Type of oil chosen is heavy fuel with a specific gravity of 0.965. The input data are summarized in Table 5.1.

Table 5.1 : Input parameters for sample simulations

Parameter	Case
Simulation time (hours)	5.2
Initial oil particle number	100
Spill condition	Instantaneous
Spill volume (m^3)	300
Oil type	Heavy fuel (sp. gr. = 0.965)
Wind velocity (knot)	5
Air temprature (ºC)	10
Surface tension (N/m)	0.02
Solubility parameter α (day-1)	0.423
Solubility parameter KS_0 ($g^{-2}h^{-1}$)	0.0184

5.7.3 Simulation of Combined Processes

Figure 5.15, Figure 5.16, and Figure 5.17 reveals the position of the oil slick at 1.6^{th}, 3.2^{th} and 4.8^{th} hours respectively. The net movement of the surface slick was dominated by wind-induced drift and residual flow of the current. The current direction in Bosphorus Strait is shown with arrows in the figures and it can be seen that oil slick movement agrees the current direction. The results show that using this 2D oil spill model, it is possible to forecast the transport of the oil slick on the sea surface. Even though the hydrodynamic data is not suuficient enough, the model can give a first order prediction of the oil slick displacement.

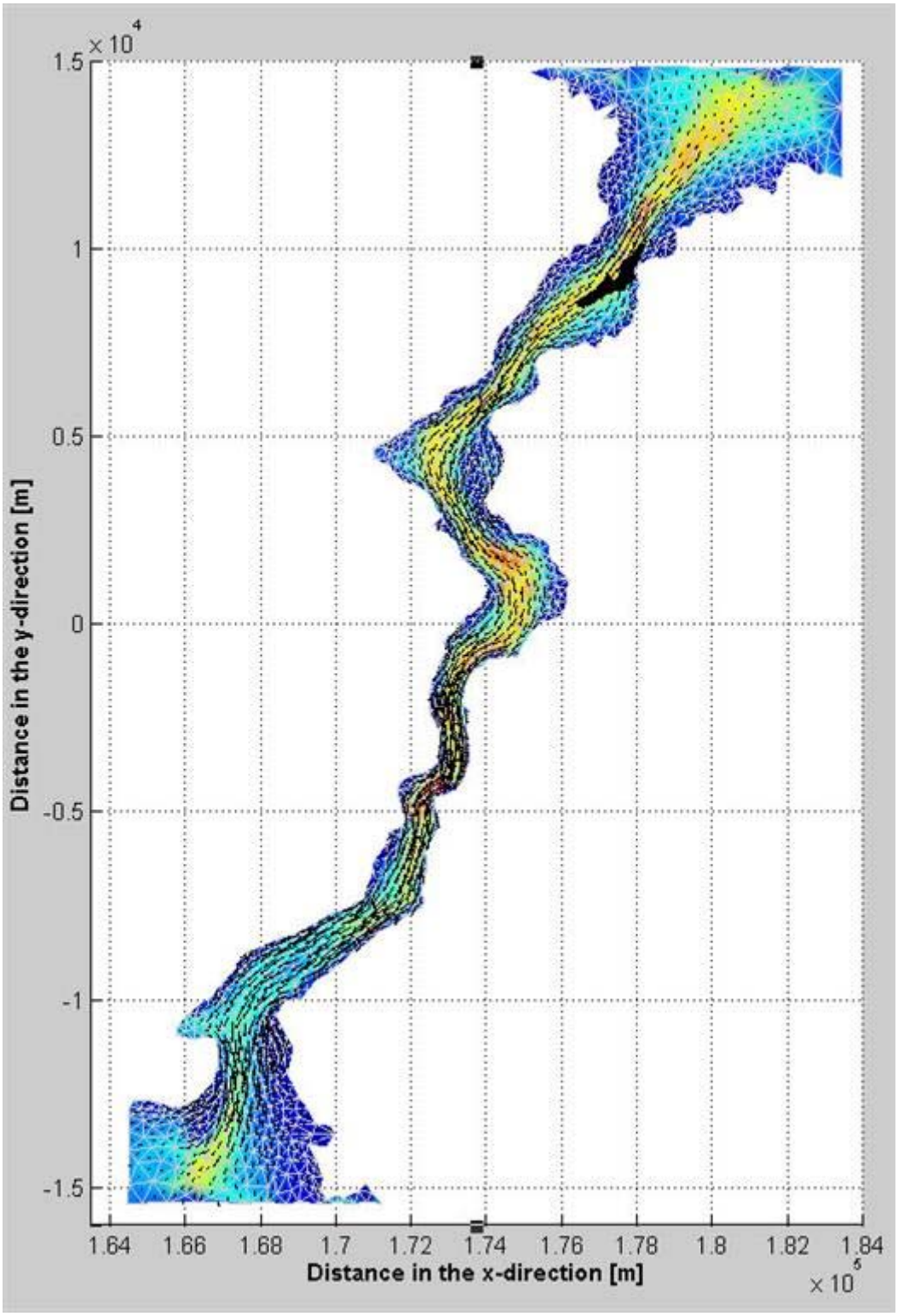

Figure 5.17 : The distribution of the oil particles on the surface at 1.6th hour.

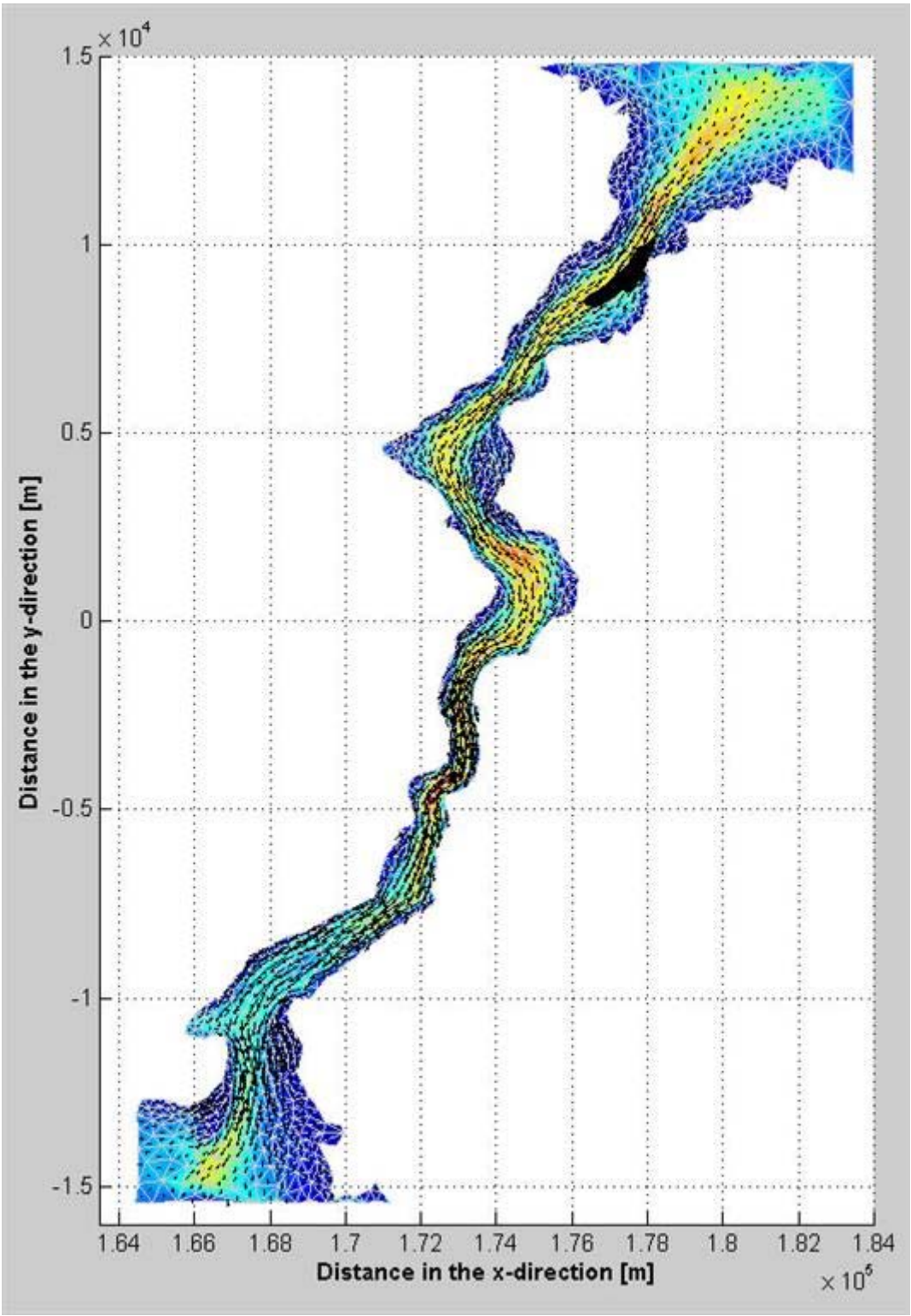

Figure 5.18 : The distribution of the oil particles on the surface at 3.2th hour.

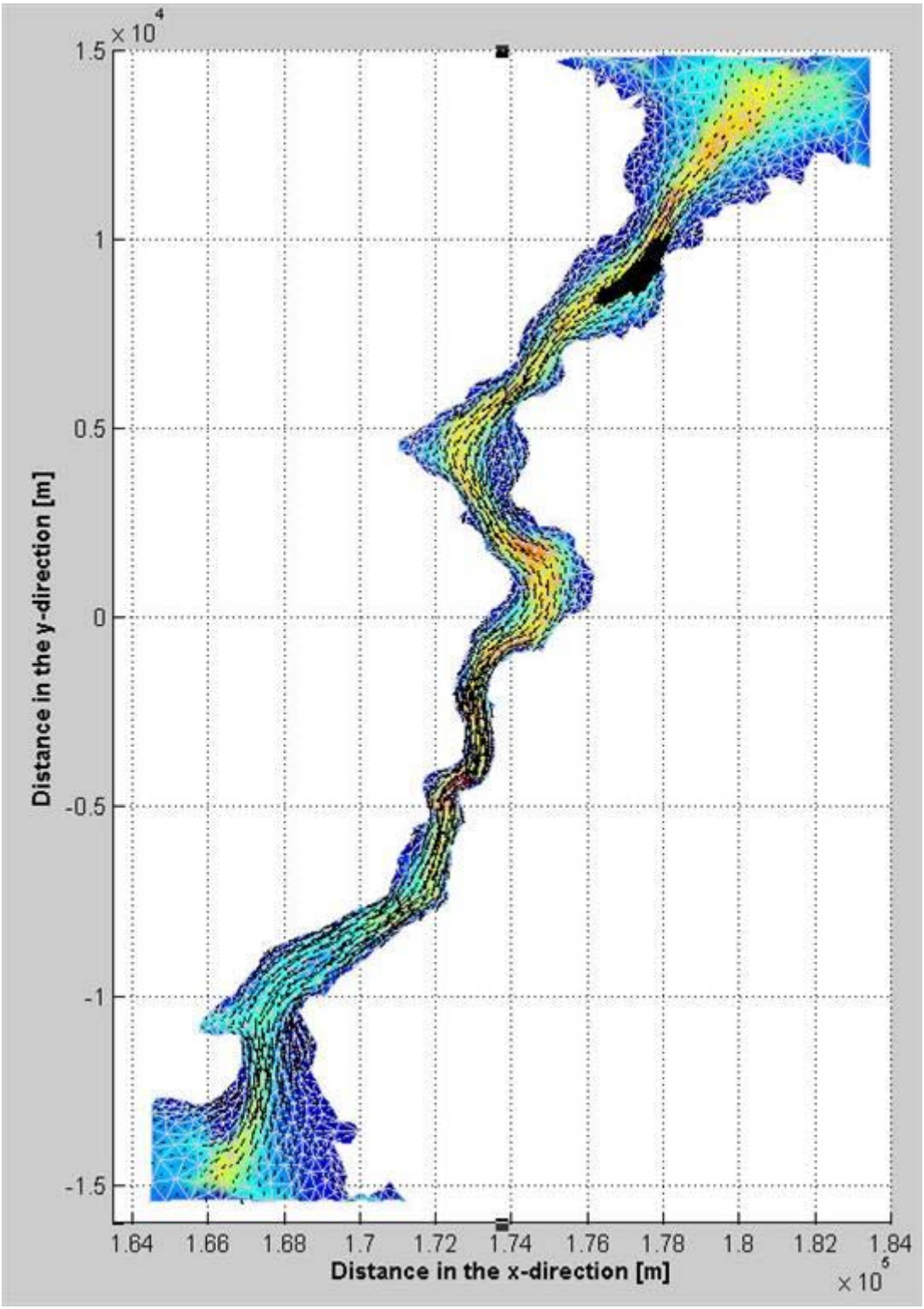

Figure 5.19 : The distribution of the oil particles on the surface at 4.8th hour.

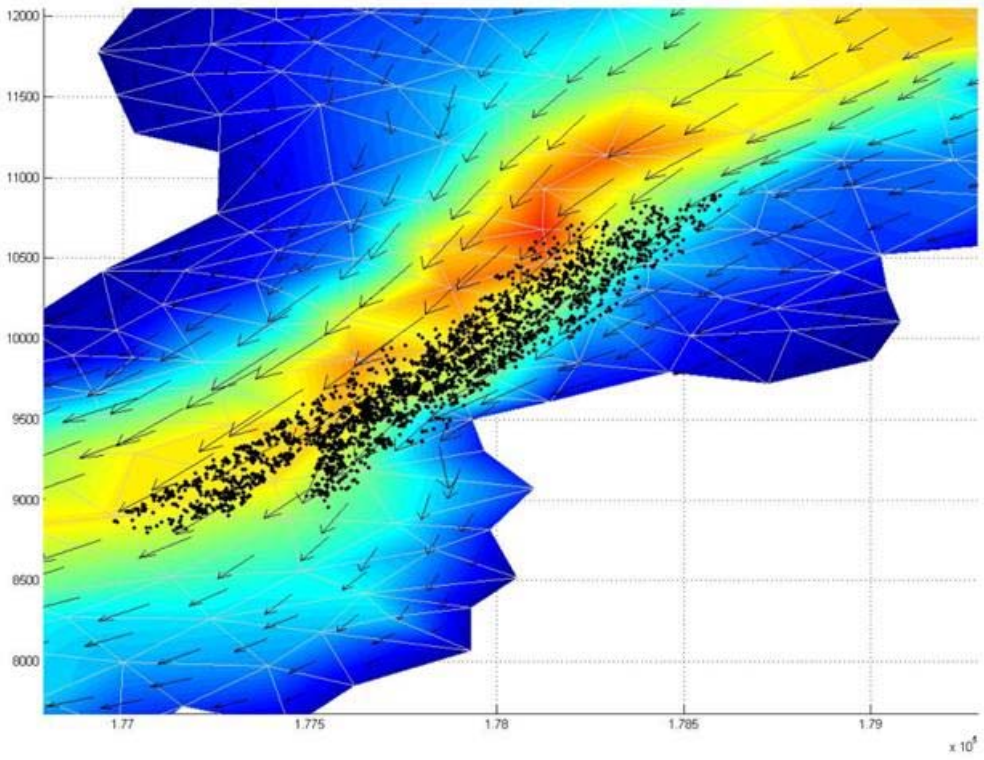

Figure 5.20 : Closer view of the distribution of the oil particles on the surface.

6. RESULTS AND DISCUSSION

Oil's composition affects the rate at which an oil evaporates. The rate of evaporation will be greater as the volatile components of an oil increases. This can be seen clearly in Figure 5.4 which shows the volume fraction of oil evaporated for different types of oil. Gasoline is more volatile then other types and as a result it is expected to evaporate more.

Computed results are qualitatively similar to available observations. If no wind and current is present, then the slick maintains circular shape as it can be seen in Figure 5.8. If wind and current are present, but droplet vertical exchange is prohibited, then the slick is moving in the combined wind and current direction.

The main parameters affecting oil spreading are oil volume and viscosity of the oil. The more viscous the oil becomes, the less quickly it will spread. In Figure 5.7, spreading of oil for different types of oil is given. It can clearly be seen from the figure that Jet A1, whose viscosity is the lowest, spreads more rapidly compared to other oil types.

The model has been applied to an oil spill scenario created in Bosphorus Strait. The results from the numerical test look realistic. In order to get more realistic results, further studies should be done.

A 2-D oil trajectory model is developed to predict the movement of a surface oil slick. After obtaining the surface currents from the ADAM hydrodynamic model, the advection properties of the oil slick are obtained. The simulation results from the 2-D model can show the user the processes of the oil slick moving on the water surface. The major movement direction and polluted area of the surface oil slick are successfully predicted using this 2-D model. In addition to predicting trajectory, this model can estimate the amount of evaporation and the amount of dissolution. Then, these results are included in the model and combination of processes are obtained for a realistic oil slick trajectory forecasting.

6.1 Future Work

Future development of the model will focus on the updating the oil spill behaviour algorithms as new data and models become available. A Graphical User Interface (GUI) is developed, but has not been improved yet. In the future the GUI for the oil spill model will be improved.

The oil spill model developed is two-dimensional and hence, it does not include all the processes occurred after an oil spill. The current model can be upgraded to a three-dimensional model. Thus, a more realistic oil slick trajectory and fate model can be achieved.

In general, the simulated results show that the model is useful to study the behavior of oil spreading, advection, evaporation and dissolution on the water surface. Even though the model need to be improved, it can still give a first order prediction of the oil slick displacement.

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APPENDIX A

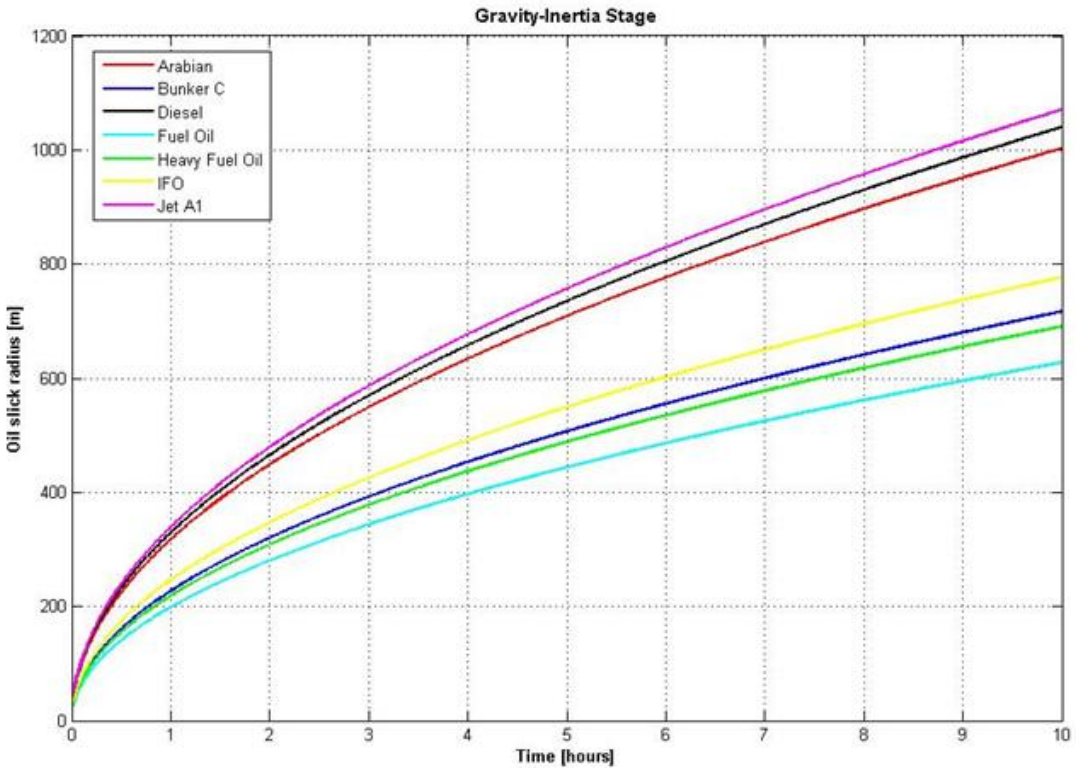

Figure A.1 : Change of oil slick radius for 300 cubic meters of oil with time according to Fay's formula for different types of oil at gravity-inertia stage.

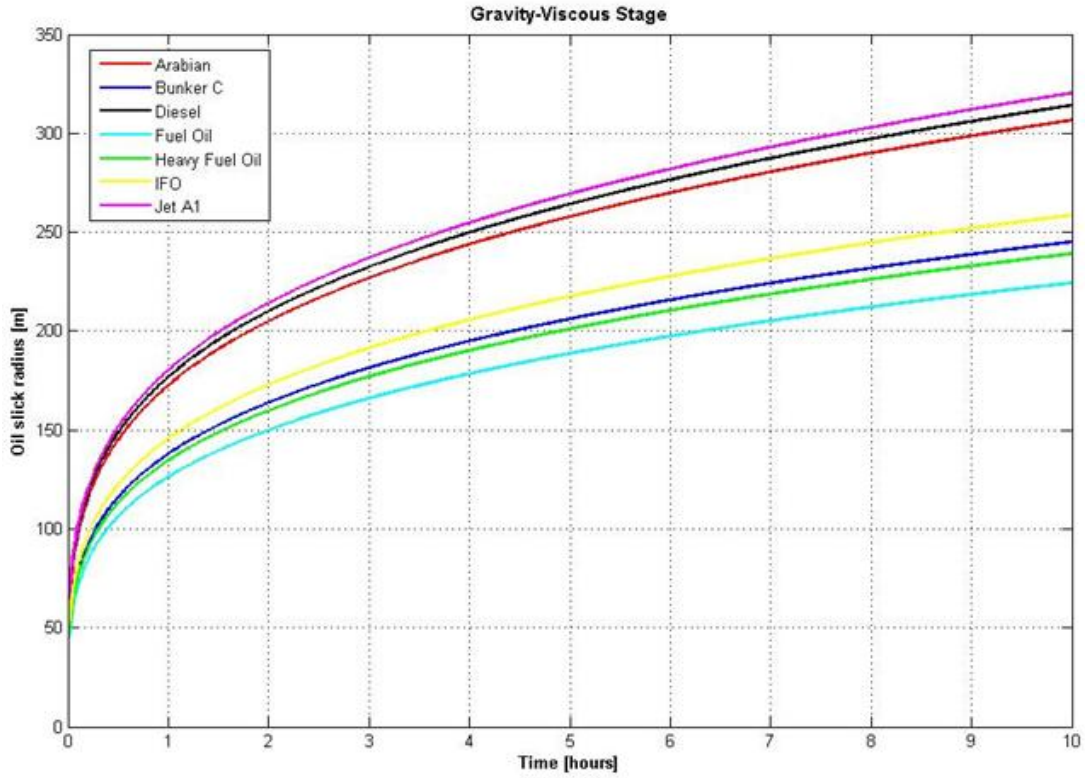

Figure A.2 : Change of oil slick radius for 300 cubic meters of oil with time according to Fay's formula for different types of oil at gravity-viscous stage.

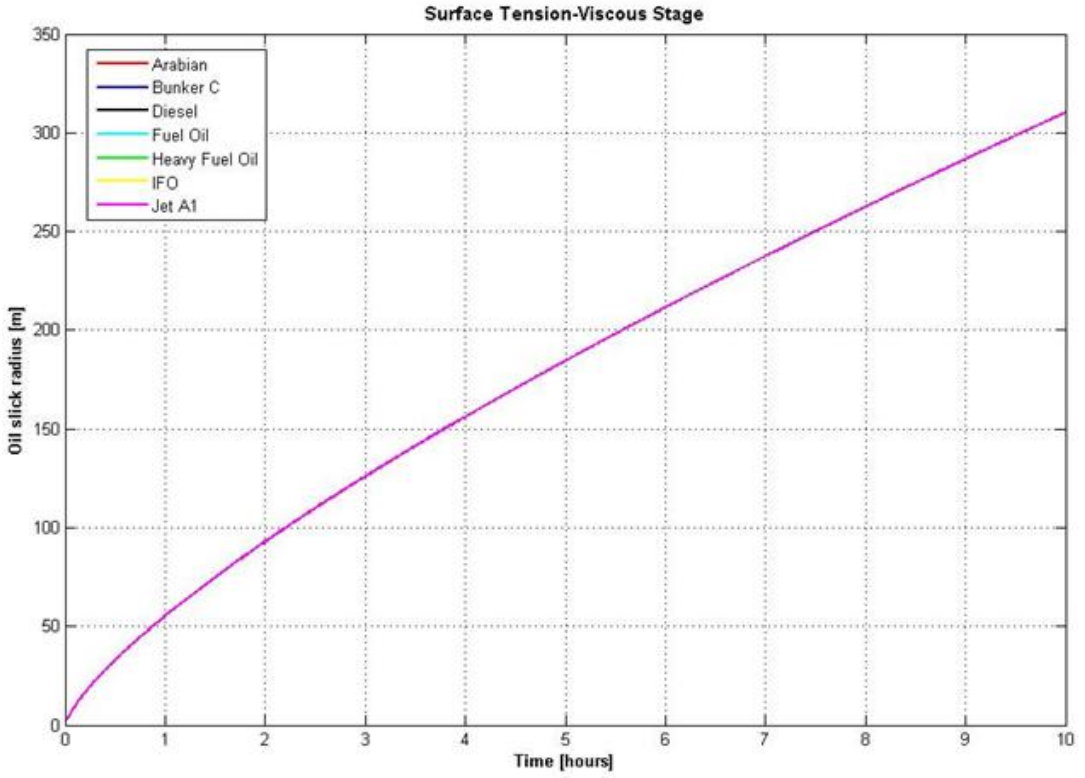

Figure A.3 : Change of oil slick radius for 300 cubic meters of oil with time according to Fay's formula for different types of oil at surface tension-viscous stage.

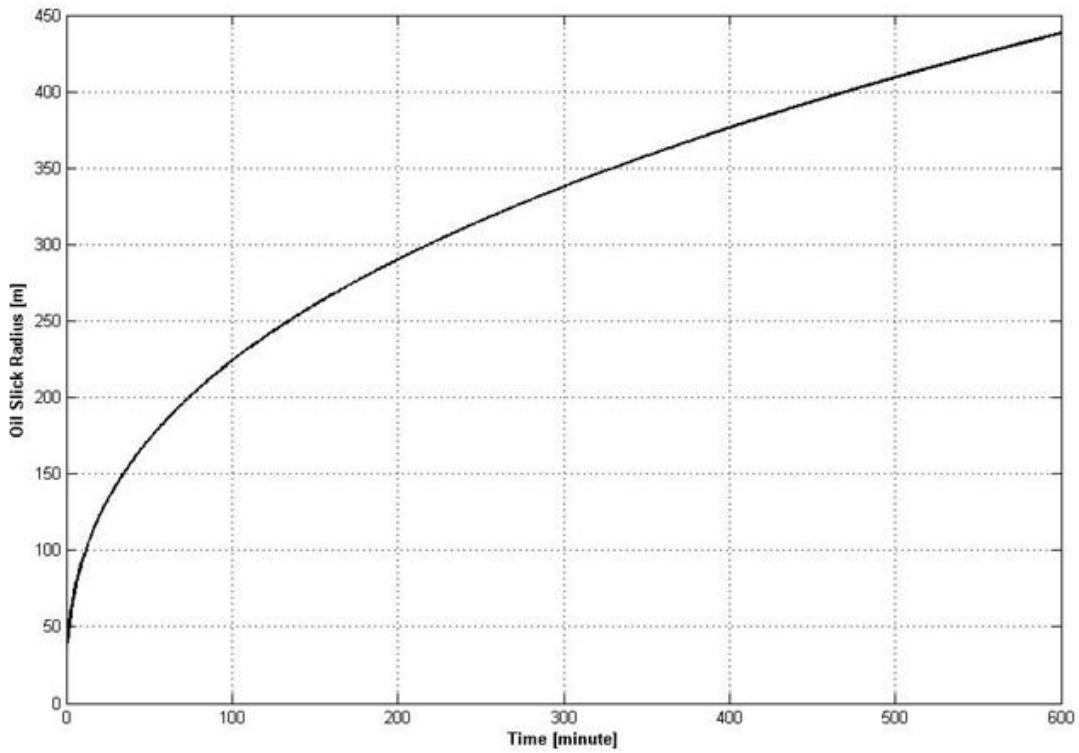

Figure A.4 : Change of oil slick radius for 300 cubic meters of oil with time according to Buckmaster's formula

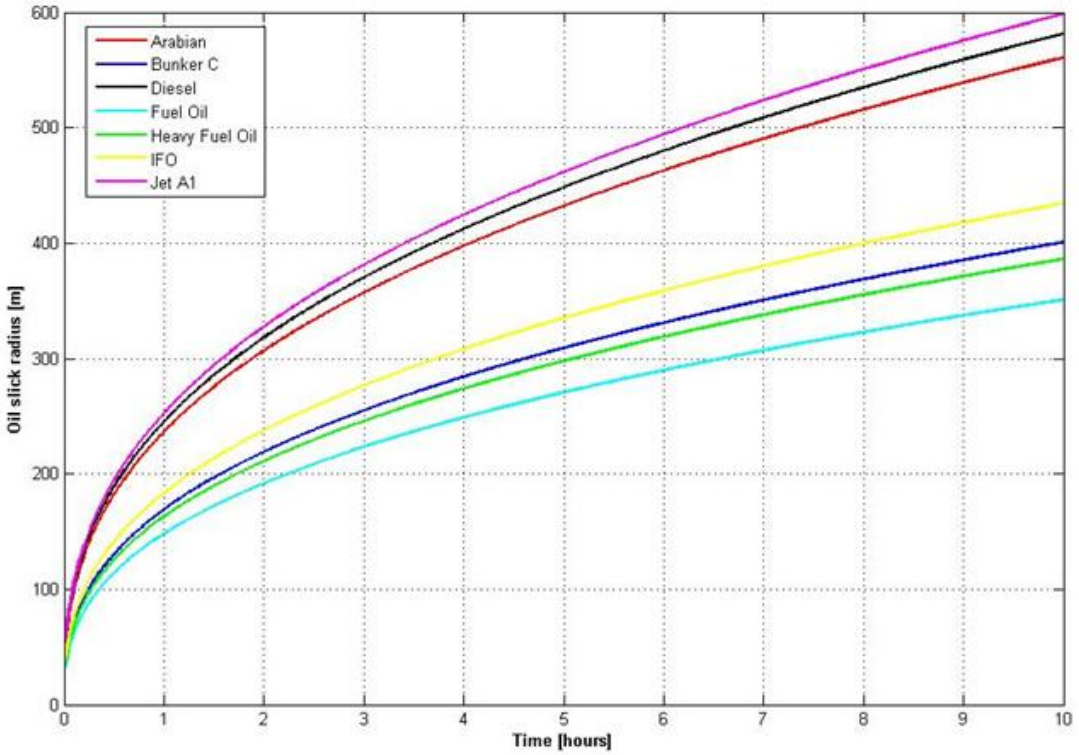

Figure A.5 : Change of oil slick radius for 300 cubic meters of oil with time according to Buckmaster's formula for different types of oil.

RESUME

Çiğdem Akan was born in 1982 in the city of Samsun. She completed her secondary school education in Samsun Anatolian High School in Samsun in 1999. Afterwards, she began her education in Istanbul Technical University, Faculty of Naval Architecture and Ocean Engineering in 2000, and graduated with honours degree by ranking second in her department in 2005. At present, she continues her education in Istanbul Technical University, Institute of Science and Technology, Ocean Engineering Program and working as a research assistant at Naval Architecture and Ocean Engineering Faculty, Oceanography Division.