

Uncertainty Analysis in Oil Spill Modelling

Sensitivity and Forcing Analysis for a spill in the Portuguese Coast and Tagus Estuary

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ABSTRACT

Oil spill modelling has evolved greatly throughout the last decades, triggered by increased oil consumption and exploitation that have resulted in large scale accidents and in the contamination of the marine environment. This study focuses on an uncertainty analysis. Models should not only provide a "best guess" estimate for the trajectory of the spilled oil but also a quantification of its uncertainty. This will provide a greater degree of confidence in numerical models for decision makers and make response teams more efficient through the "minimum regret" concept.

To test the model uncertainty three approaches were used: (1) a sensitivity analysis of the model parameters; (2) a forcing analysis to evaluate which parameter and forcing had the most impact on the slick properties; (3) the evolution of the centre of mass, as a way to evaluate the influence on the slick trajectory.

The sensitivity analysis in the four scenarios studied showed that variations in the API gravity and reference viscosity had the most impact on the model results. Wind forcing also showed a significant influence in those results. Changes in the trajectory of the slick were mostly affected by the wind coefficient and spill site.

These impacts are important for oil spill response teams to adjust their behaviour and have a more efficient plan of action, mitigating the impacts of these spills.

Keywords: Oil spill modelling; Sensitivity analysis; Forcing Analysis; MOHID.

Resumo

A modelação de derrames de hidrocarbonetos evoluiu grandemente nas últimas décadas, motivada por acidentes de larga escala e consequente poluição marítima, devido a um aumento no consumo e exploração de petróleo. Este estudo focou-se numa análise de incerteza para modelação de derrames de petróleo. Estes modelos devem apresentar não só a melhor estimativa da trajetória da mancha de óleo, mas também uma quantificação da sua incerteza. Isto resultará numa maior confiança por parte dos decisores em modelos numéricos e também numa maior eficiência das equipas de resposta através do conceito do menor arrependimento.

Para estudar as incertezas do modelo foram usadas 3 abordagens: (1) uma análise de sensibilidade aos parâmetros do modelo; (2) uma análise ao forçamento, nomeadamente a componentes do vento e ondas; (3) a evolução da latitude e longitude do centro de massa, como forma de avaliar o impacto na trajetória.

A análise de sensibilidade nos quatro cenários estudados mostra que as variações na gravidade API e na viscosidade de referência tiveram o maior impacto nos resultados do modelo. O forçamento do vento teve também uma grande influência. Alterações no coeficiente de vento e local da descarga resultaram no maior desvio da trajetória da mancha de óleo.

O conhecimento de como o modelo reage a estas incertezas é relevante para equipas de resposta, para que possam ajustar o seu comportamento e pôr em prática planos de ação mais eficientes, mitigando assim o impacto destes derrames.

Palavras-Chave: Modelação derrames hidrocarbonetos; Análise de sensibilidade; Análise ao forçamento; MOHID.

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NOTATION AND ACRONYMS

ADIOS	Automated Data Inquiry for Oil Spills
API	American Petroleum Institute
AsphC	Asphaltenes Content
Avg	Average
BP	British Petroleum Company
Fortran	Mathematical formula translation system
GDP	Gross Domestic Product
IST	From the Portuguese: Instituto Superior Técnico
LAT	Latitude
LONG	Longitude
MARETEC	Marine Environment and Technology Research Center
MDisp	Mass dispersed
MEvap	Mass evaporated
MM5	Mesoscale Meteorological Model 5
MOHID	From the Portuguese: Modelo Hidrodinâmico
Moil	Oil mass
MWC	Mass Water Content
NOAA	National Oceanic and Atmospheric Administration
OWP	Oil Weathering Processes
PCOMS	Operational Model for Portuguese Coast
PPoint	Pour Point
RefVisc	Reference Viscosity
ResC	Resin Content
SA	Sensitivity Analysis
SatC	Saturate Content
SI	From the French: Système International d'unités
Std Dev	Standard Deviation
Thick	Thickness
US	United States
USA	United States of America
VBA	Visual Basic for Applications
Voil	Oil volume
Vol	Volume
Windx	X component of the wind velocity
Windy	Y component of the wind velocity

NOMENCLATURE

Latin Symbols	Definition
Α	Empirical constant
A _s	Slick area
В	Empirical constant
BP_i	Boiling point
C _b	Empirical coefficient used in dispersion
C _{oil}	Experimental parameter
C _{oil}	Concentration of oil in the water column
C _{sed}	Concentration sediments water column
$C_{z,i}$	Empirical constant
d_0	Particles diameter
D_{ba}	Waves Dissipation area per unit of superficial area
D_s	Diameter of the slick
Ε	Rate of dissipated energy at water surface
F _e	Volumetric fraction of evaporated oil
f_s	Surface fraction covered by oil
F _{wc}	Fraction of sea surface hit by breaking waves
F_{wv}	Volumetric water fraction incorporated in the emulsion
g	Gravity acceleration
h	Oil spill thickness
H_0	Wave height
Κ	Mass transfer coefficient
<i>K</i> ₁	Constant
<i>K</i> ₂	Constant
K _a	Adhesion Parameter
K_e^i	Mass transfer coefficient
K_w	Empirical constant
M _i	Molar mass for each fraction
m _{oil}	Oil mass that remains at the surface
P_0	Atmospheric pressure
P_I^{sat}	Vapour pressure
R	Radius of the slick
R	Perfect gas constant
S	Solubility of oil
S ₀	Solubility of fresh oil
Sc _i	Schmidt number for fraction i
t	Time after the spill
Т	Oil temperature
T_0	Initial boiling point
T_{G}	Gradient of distillation curve
T_w	Wave period
V_e^i	Evaporated volume
v_w	Kinematics viscosity of water

W	Wind velocity
W_i	Wind velocity to start rupturing
Zi	Intrusion depth of the oil particles in the water column

Greek Symbols	Definition
α	Decay rate
<i>α</i> _{1,2,3}	Empirical constants used for spreading
Δz	Compressibility factor
ΔS	Variation of entropy
μ	Dynamic viscosity
$ ho_{oil}$	Oil density
$ ho_W$	Water Density
σ_n	Inertial tension oil-in-water
Xi	Molecular fraction

1. INTRODUCTION

1.1 OVERVIEW

Oil spill trajectory models have been developed for years in response to concerns for pollution in the marine environment. With increasing consumption of oil across the world promoting oil exploration, the marine environment is facing a major long term threat (Mishra et al. 2015).

In the last decade major accidents, such as the Atlantic Empress (1979), ABT Summer (1991) and more recently the BP deep horizon (2010), have also highlighted the relevance of numerical models to aid in response efforts (Afenyo et al. 2015, ITOPF 2016). Numerical models are of utmost relevance because they not only reproduce the dynamics of the system in study but also because they predict the oil spill behaviour (Mateus et al. 2008).

To model oil spills correctly it is fundamental to understand the mechanisms that affect fate and trajectory, which can be extremely complex, that are governed by transport processes and oil weathering processes. Oil transport is achieved through spreading, dispersion and sedimentation and oil weathering happens due to evaporation, emulsification, dissolution, biodegradation and photo-oxidation (Afenyo et al. 2015). Oil weathering modifies oil properties significantly, namely oil density and viscosity. It is also important to note that the initial conditions of the spill also influence the evolution of the slick (Mishra et al. 2015). However, there are some uncertainties when modelling oil spill trajectories, namely in prediction motion, tendency for the oil to break into smaller slicks and also information about initial and discharge conditions, that are not included in most oil spill modelling software available.

Oil slicks are a mixture of hundreds of different organic compounds, each with unique characteristics that influence the behaviour of the slick, which then effects oil toxicity and its impact on the environment and the effectiveness of clean-up strategies (Lehr 2001). The main properties that influence oil spill behaviour are the API gravity, pour point, viscosity, surface tension, flash point and thickness.

Environmental factors also play a major role on the fate of an oil slick, by affecting the oil weathering processes, they're occurrence or significance. Wind and temperature influence evaporation rates, sea state is also relevant for spreading, dispersion and emulsification since wind and breaking waves break oil into small drops (Lehr 2001). Solar radiation and sediment loading influence processes like emulsification and sedimentation respectively.

Oil transport processes like spreading, dispersion and sedimentation are key to model oil spills. Spreading is defined as the expansion of the oil slick due to the tendency oil has to spread in still water, it is a process that occurs within the first hours for most spills and is very important to compute the slick area. Fay (1969) analysed the forces that act on the oil slick in order to develop equations that describe oil spreading, he assumed a circular spill with a homogenous thickness. He suggested that spreading can be divided into three phases depending on the major driving and retarding forces, the first phase is gravity-inertial, then gravity-viscous and lastly surface tension-viscous (Lehr 2001). This formulation however does not explain spreading for non-circular spills, non-viscous oils, tar balls and for subsurface

and continuous releases (Reed et al. 1999). Other authors proposed equations which required physical knowledge of the oil, hindering the use of such models. Dispersion is an oil removal mechanism that consists in the uptake of oil droplets into the water column and happens due to breaking waves (Hackett et al. 2006) and is the main oil removal process during storm events (Fingas et al. 1993). Delvigne et al. (1988) proposed an empirical relation for the dispersion rate and is the most used method to calculate oil dispersion. Sedimentation is defined as the adhesion of solid particles in the water column (Lehr 2001), the significance of this processes depends on the sediment load, important in muddy rivers.

Oil weathering processes change the oil composition as soon as the spill occurs and the most relevant ones are evaporation, emulsification and dissolution, others like biodegradation and photooxidation are less relevant. Evaporation is a key process to understand, it accounts for a major portion of oil removal from the surface and starts immediately after the spill, and most of the volatile fraction is evaporated in the first hours of the spill. This process increases oil density and viscosity and is important to quantify to assess the lifetime of the spill. To calculate evaporation, the method of the Pseudocomponents (Yang et al. 1977, Payne et al. 1984) and the method of the evaporative exposure (Stiver et al. 1984) were presented. The first method has good results; however, it requires a lot of information on the oil. The second method does not require information but can be fallible for refined products. Emulsification is the entrainment of water in the oil, which has a significant impact on the volume, density and particularly in the viscosity of the oil slick, resulting in less efficient clean up strategies. As viscosity increases spreading and evaporation decrease, stable emulsions can also inhibit some chemical and biological reactions (Lehr 2001). Emulsion occurs in the first hours after the spill and can be up to 70-90% water (NOAA 2002), Mackay's formulation is used to compute emulsion. Dissolution is the fragmentation of soluble hydrocarbons in small particles that mix with the water, resulting in a homogenous mass. This process is more significant for compounds with low molecular weight that are more soluble (Afenyo et al. 2015). Usually is not the most relevant process, due to evaporation losses, but the components that dissolve into the water column are often very toxic to the environment (NOAA 2002). Biodegradation is the transformation of hydrocarbons in simpler compound by microorganisms. Photo-oxidation is a chemical process that degradates oil due to ultraviolet radiation resulting in a "thin, crusty skin" on the oil slick (NOAA 2002).

All the processes described previously interact amongst each other, inhibiting or enhancing their effect. For instances, evaporation and photo-oxidation facilitate emulsification, which in turn reduces dispersion, extending the lifetime of the oil slick. These and other processes interacting are a source of uncertainty and contribute greatly to the complexity that is oil spill modelling.

Traditional oil spill trajectory models are deterministic and provide a "best guess" of oil movement and fate; nonetheless as scientific knowledge evolves it has become evident that some indication of the model uncertainty is necessary. Uncertainty arises from input and environmental data necessary for the model (NOAA 2002) but also depends on the length and time scale of the spill (Mishra et al. 2015). This problematic is therefore the next step in oil spill modelling, providing a greater confidence in numerical models with the quantification of uncertainty.

1.2 OBJECTIVES

This study is within the scope of the development of the modelling tool to simulate oil spills, developed at IST in partnership with Action Modulers. This tool has been used for research projects, international projects (EROCIPS, DRIFTER, ARCOPOL, ARCOPOL+, ARCOPOLplatform, EASYCO, ISDAMP, MARPOCS), consulting services and operational support for accidents (Prestige).

The background for this work is directly linked to the problematic of the uncertainty associated with the prediction of the dispersion of hydrocarbons. Decision making by response teams in a scenario where uncertainty is unknown decreases the level of confidence in numerical models, hindering decision making or resulting in hasty decisions. In that scenario, it is only taken into account the most likely trajectory – if that solution turns out to be different from the truth actions become unsuccessful and confidence in these models tends to decrease.

Therefore, a correct quantification of model uncertainty can contribute to a more effective and prompt response by the authorities. Additionally, a correct identification of the relative weight of the uncertainty sources supports the development of probabilistic modelling. Later on contamination probability maps can be generated, these maps are very significant for authorities, allowing them to identify areas of "least regret" (areas where the probability of contamination is high enough to justify mitigation or response actions).

For a clear structure of this study three major sections are presented: State of the art; Methodology and Results. The first section gives an overview on the state of the art regarding oil spill modelling, focusing on the trends on oil exploitation and consumption that highlight the need for numerical models to support decision makers in spill events. The basis of oil spill modelling was also addressed, namely the most used methods in oil fate models, the main characteristics of oil that influence its behaviour (both physical and chemical), and main transport and weathering processes. Since environmental factors also influence oil fate, their effect was further described, there are also a source of uncertainty, which is a subject developed in the last part of the first section.

The methodology segment describes in detail the software used to model oil dispersion, the model domain used and the methods for the analysis performed. The areas of interest were selected based on their environmental, economic and social importance for Portugal, within each area two scenarios were simulated, with the purpose of understanding some of the more relevant variations in those areas. The study area selected was the Portuguese coast in two different scenarios, an upwelling event and a western wind scenario, and also in the Tagus estuary both in spring tide and neap tide periods. Results were later analysed using excel and VBA, and presented in the form of graphs, tables and maps with the complementary discussion and conclusion of this work.

2. STATE OF THE ART

Concerns for pollution in the marine environment due to oil spills have been increasing and accidents have shown the need for new tools to support decision spill response (Abascal et al. 2010). Oil consumption has been growing in the last years, promoting oil exploration (Figure 2), Figure 1 shows an increase in most regions of the world apart from Europe and North America that have decreased their consumption. Oil demand has also been increasing as shown by Figure 2.Figure 2Accidental releases pose a major long term threat for the marine environment (Mishra et al. 2015), some examples of accidents in the last few years are listed in Table 1 (Afenyo et al. 2015). It is also worth mentioning the BP oil spill in 2010, that released 486 000 tons of oil into the ocean, it was an unprecedented spill in U.S. waters with enormous economic impact, \$8.7 billion (Jolliff et al. 2014).

Ship name	Year	Location	Spill size (tons)
Deepwater Horizon (oil rig)	2010	Gulf of Mexico	486 000
Atlantic Empress	1979	Off Tobago, West Indies	287 000

TABLE 1 - MAJOR ACCIDENTS IN THE LAST FEW DECADES (BERNABEU ET AL. 2013, AFENYO ET AL. 2015, ITOPF 2016)

Atlantic Empress	1979	Off Tobago, West Indies	287 000
ABT Summer	1991	700 nautical miles off Angola	260 000
Castillo de Bellver	1983	Off Saldanha Bay, South Africa	252 000
Amoco Cadiz	1978	Off Brittany, France	223 000
Prestige	2002	130 miles of the Galicia coast, Spain	64 000
Exxon Valdez	1989	Prince William Sound, Alaska, USA	37 000

These accidents can result from human errors and mechanical failures, resulting in the collision of ships, bursting of pipelines, failure of oilrigs and contribute to even greater ecological damages to the marine environment. Oil at sea may enter the food chain, sink to the sea bed and affect vegetation, pollute harbours and damage sensitive shore resources (Mishra et al. 2015). It can also have relevant socio economic consequences (Mateus et al. 2008).

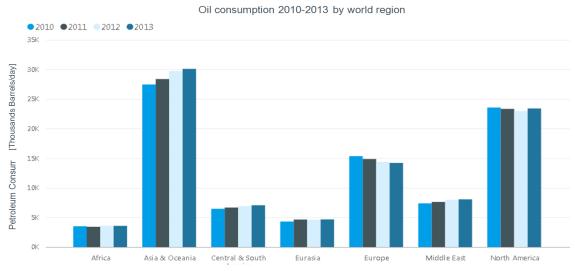


FIGURE 1 - TOTAL OIL CONSUMPTION BY REGION OF THE WORLD FROM 2010 TO 2013 IN THOUSAND BARRELS PER DAY (INTERNATIONAL ENERGY AGENCY 2016)

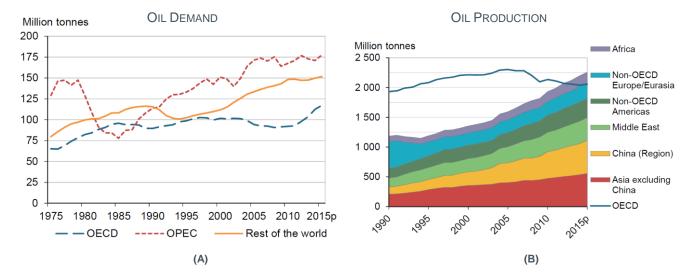


FIGURE 2 – (A) OIL DEMAND BY WORLD REGION (OECD – ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT; OPEC – ORGANISATION OF PETROLEUM EXPORTING COUNTRIES) FROM 1975 TO 2015 IN MILLION TONNES (B) OIL PRODUCTION BY WORLD REGION FROM 1990 TO 2015 IN MILLION TONNES (INTERNATIONAL ENERGY AGENCY 2016)

Numerical models are extremely helpful to assess the pollution of such accidents, since they not only describe the oil spill but also predict its behaviour, reproducing the dynamics of the system in study (Mateus et al. 2008).

This type of models intends to provide information that is not available otherwise to suit the needs of the community, private sector or public interests, providing continuous state estimates and forecasts of coastal ocean state. In addition, their development in the last decades is responsible for substantial scientific and technological achievements associated to operational oceanography, and have become irreplaceable tools to link oceanography to marine affairs (Mateus et al. 2012). Their ability to predict and simulate the trajectory of an oil spill is essential to the development of pollution response and contingency plans, as well as to the evaluation of environmental impacts assessments (Neves 2007).

In order to model oil spills in a good manner it is necessary to understand the mechanisms that affect its fate and trajectory, and this is a complex process and is governed by transport processes like spreading, dispersion, sedimentation and oil weathering processes (OWP). Such as evaporation, emulsification, dissolution, biodegradation and photo-oxidation (Afenyo et al. 2015). OWP significantly modify the slick properties, namely crude density and viscosity. Initial spill conditions and initial oil properties are also relevant concerning the evolution of the spill (Mishra et al. 2015).

2.1 OIL SPILL MODELLING

The need for numerical models is clear, they are essential to support oil spill response efforts, in particular with growing concerns about oil spills and their impact on the marine environment. A large number of numerical models have been developed in order to provide such information, such as MOHID (Neves 2007), used in this study.

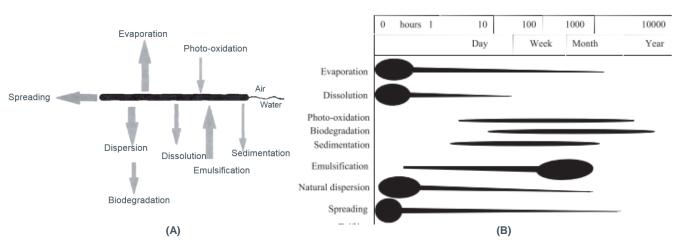
The main intention of these models is to predict where oil is likely to go after a spill, is therefore useful for decision makers since these models can point out areas that could be affected by the spilled oil, and how long will that take to happen (Abascal et al. 2010). This information is key to response teams, knowing the most likely trajectory of the spill will guide and help them make decisions to protect their resources and also aid in clean up strategies (NOAA 2002). To answer these questions models use data from ocean currents, winds, waves and other environmental factors (Afenyo et al. 2015).

The structure of an oil spill model can be split into three main components: input, weathering and transport algorithms (that quantify the processes involved), and output (that answer the questions mentioned above). The latter can be a representation of the spatial distribution of the spill, a geographical distribution or properties of the spill as a function of time (Afenyo et al. 2015). After a spill, the physical and chemical characteristics of the oil start changing almost immediately due to oil weathering processes that are described in the following sections. Models used nowadays use lagrangian tracers, which means that they represent oil as a collection of discrete particles, each representing a certain mass of oil (Hackett et al. 2006).

However, oil spill modelling can be challenging due to uncertainties in predicting motion, deformation and tendency of the oil to break up into smaller slicks, in part due to the interaction of the different physical processes, addressed in section 2.6, and also due to the incomplete information at the start of the response (NOAA 2002, Hackett et al. 2006).

The type and location of release is also important (and a source of uncertainty) to oil spill modelling; most models assume an instantaneous and surface release of the oil, which can be unrealistic for large spills and subsurface spills. Sunken vessels or ruptured pipelines result in subsurface release of oil, which due to low pressures typically form a "flower blossom" pattern, resulting in a thinner slick when compared with a surface release (Lehr 2001). These type of releases also mean that the oil will reach the surface altered, with gas or emulsified (Lehr 2001).

Figure 3 (A) and (B) show the main processes that affect spilled oil, and the evolution of weathering processes with time, respectively. The latter shows that evaporation, dissolution and spreading start right after the spill and are more significant in the first day, other processes such as emulsification are also relevant but after those processes occurred.





2.2 OIL PHYSICAL AND CHEMICAL PROPERTIES

Oil spills in the surface of the water result in slicks that are different from slicks made of pure chemicals; the latter usually do not change their properties during the lifetime of the slick, which is not true for oil spills (either of crude or refined petroleum products). This difference is due to the fact that oil is a mixture of hundreds of different organic compounds, each with unique characteristics that influence the nature and behaviour of the oil slick with time. That, in turn, will have significant consequences on the toxicity of the oil, its impact on the environment and effectiveness of clean-up techniques (Lehr 2001).

Crude oil's constituents are saturates, aromatics, resins and asphaltenes. Light crudes have a higher percentage of saturated hydrocarbons and aromatics.

In this section the most significant properties, such as density, pour point, viscosity, surface tension, pseudo-components, flash point and oil thickness, are explained.

2.2.1 API GRAVITY/DENSITY

API gravity is a scale developed by the American Petroleum Institute that is inversely proportional to the specific gravity of the oil at 15,6°C (Lehr 2001).

Fresh water has an API of 10 and most crude oils and refined products have higher API (that corresponds to smaller oil densities). These type of oil will float in freshwater, some heavier refined products and synthetic fuels can have lower API (Lehr 2001).

The US Coast Guard divides oil and oil products in groups according to their densities and consequently according to their API, see Table 2. Heavier oils, with API < 10, belong in group V oils, that is the group of oils that sink if spilled. In addition, those represent different clean-up challenges and weathering behaviour than floating slicks (Lehr 2001).

TABLE 2 – OIL CLASSIFICATION	ACCORDING TO	API GRAVITY
------------------------------	--------------	--------------------

Group	API (60ºF)
I	>45.0
II	35.0-45.0
111	17.5-35.0
IV	17.5-10.0
V	<10.0

2.2.2 POUR POINT

The oil Pour Point is the oil lowest temperature at which the oil flows under specified conditions. As oil weathers, its pour point will increase. This property is difficult to quantify and its measurements vary widely (Lehr 2001).

2.2.3 VISCOSITY

Viscosity measures the resistance to flow. In most cases, oil and oil products have higher viscosities than water, and are in the order of magnitude of several hundred centipoise.

Some weathering processes, like emulsification, can greatly increase the viscosity of the oil (Lehr 2001). Dispersion can be influenced by oil viscosity. Viscosity depends strongly on temperature, so it is necessary to know the reference temperature at which the viscosity is measured when using historical data (Lehr 2001).

Viscosity also influences greatly cleanup efforts since it lowers the efficiency of the machines used to clean spilled oil (Lehr 2001).

2.2.4 SURFACE TENSION

Surface tension is the force of attraction between surface molecules of a liquid and can be used by spreading and dispersion algorithms. Cleanup teams therefore use chemicals that reduce surface tension to promote dispersion (Lehr 2001).

2.2.5 PSEUDO COMPONENTS

Oil is assumed a mixture of discrete and independent components named pseudo-components. Petroleum hydrocarbons have different constituents that influence the way oils weather, and are listed below (Lehr 2001):

- Alkanes, or waxes characterized by single bonds, branched or unbranched chains of carbon atoms with attached hydrogen atoms;
- Aromatics which are organics that have a benzene ring, or rings as a part of their chemical structures;
- Naphtenes that also form rings but have single carbon bonds;
- Non-hydrocarbon compounds may contain oxygen, nitrogen, sulphur and various trace metals.

2.2.6 FLASH POINT

The flash point is an important temperature for oils since it is a measure of the flammability of the oil and can be changed as oil composition changes with evaporation (Lehr 2001).

2.2.7 OIL THICKNESS

Oil slicks form thin films on open waters, ranging from a tenth of a micron to hundreds of microns (NOAA 2002).

2.3 ENVIRONMENTAL FACTORS

This section will discuss the main environmental factors affecting oil spill modelling, such as water temperature, sea state and wind speed. Depending on the circumstances of the spill the following factors can also be important: solar radiation, air temperature, ice cover and sediment loading (Lehr 2001).

Solar radiation affects the photo-oxidation process that in turn can have a negative impact on other weathering processes, such as evaporation (Lehr 2001).

Wind and temperature influence oil dispersion (Bi et al. 2012), water temperature influences evaporation rates, the difference between the air temperature and water temperature is responsible for the sensible heat flux, and can be important for biological processes (Rayson et al. 2015).

Sea state is important for estimating spreading, dispersion, and emulsification (Lehr 2001), the reason being when a slick is exposed to turbulence, generated by wind and breaking waves, the oil forms small drops. Oil is then dispersed vertically and moves to the subsurface layer region (Reed et al. 1999).

Knowledge regarding the fate and transport of oil spilled in ice-covered waters is much more limited than oil spilled in open waters. Apart from the "usual" processes, others such as encapsulation occur. The driving forces of such processes are also different, for open waters the oceanographic forces are more relevant as in ice covered waters is the nature of the ice and seasonal variations (Afenyo et al. 2015).

Sediment loading influences sedimentation, which can be a significant removal process, for example in muddy rivers, where sediment load is substantial (Lehr 2001).

2.4 OIL SPILL TRANSPORT PROCESSES

2.4.1 SPREADING

Spreading can be defined as the expansion of the oil slick due to the tendency oil has to spread in still water. This process occurs rapidly and within the first hour for most spills, faster for lighter and less viscous oils than for heavier oils. Warm waters and warm oils can also accelerate this process (NOAA 2002). Spreading is a very complex phenomenon since it involves physical properties of the spilled product as well as the environmental characteristics of the surface water (Lehr 2001). However, it is very important to calculate it because of the slick area, clean up strategies and also due to some weathering processes, whose effect is proportional to the area of the slick.

Spreading is not uniform since wind can cause stretching and induce a thickening of the slick in the downwind direction, which will be surrounded by a larger, thinner sheen (Figure 4). However, most of the oil (around 90%) is found in that smaller area (usually around 10% of the area) (Lehr 2001, NOAA 2002).

Slick aging usually results in a fragmentation (Figure 5 (A)), due to wave actions or Langmuir effects (Figure 5 (B)). The latter refers to a pattern below the surface of repeating Langmuir cells, creating a system of ridges and troughs at the surface. Langmuir cells then become a collection area for floating oil, resulting on lines of oil that spread over a large geographical area but covering a small percentage of the water surface (Lehr 2001).



FIGURE 4 - TEST SPILL (50 BARRELS) SHOWING THE SEPARATION OF AN OIL SLICK INTO THICK PART AND SHEEN (LEHR 2001).

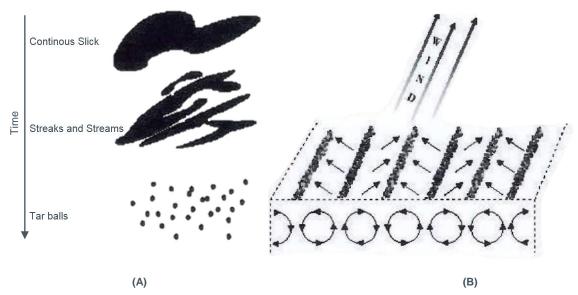


FIGURE 5 - (A) EVOLUTION OF AN OIL SLICK OVER TIME (B) FORMATION OF LANGUIMIR CELLS AND OIL STREAMERS

Fay (1969) analysed the forces acting on the oil slick in order to develop equations to describe the spreading of oil, assuming a circular spill and homogeneous thickness. He assumed that the oil slick spread axis-symmetrically and in a circular shape before and after spreading independent of wind, waves and currents (Mishra et al. 2015).

Therefore, according to Fay, spreading can be divided into three phases depending on the major driving and retarding forces. The first takes place right after the spill, in a matter of minutes, gravity forces determine spreading; the second, when the slick is relatively thick, oils spreads laterally due to gravity forces; later interfacial tension at the periphery will be the dominant spreading force. The main retarding forces are initially inertia followed by viscous drag of the water. As a result Fay labelled the three phases gravity-inertial, gravity-viscous and surface tension-viscous (Lehr 2001).

The Fay equation describes the force balances as follows:

$$\alpha_1(\rho_w - \rho_{oil})gh^2 + \alpha_2 \sigma_n = \frac{\alpha_3 \rho_w v_w^{1/2}}{t^{1/2}} R \frac{dR}{dt} + \rho_w h \left(\frac{dR}{dt}\right)^2, \qquad [1]$$

where R (*m*) is the radius of the spill assuming axi-symmetrical spreading, $\rho_w (kg/m^3)$ is the water density, $\rho_{oil} (kg/m^3)$ oil density, $\sigma_n (mN/m)$ the interfacial tension oil-water, g (m/s²) the gravity acceleration, t (s) the time after the spill, $v_w (kg/(s.m))$ the kinematic viscosity of water, h (m) the oil slick thickness, α_1 , α_2 and α_3 are dimensionless empirical constants.

Stolzenbach et al. (1977) suggested the following values for the empirical constants:

$$\alpha_1 = 0.42, \, \alpha_2 = 1.64, \, \alpha_3 = 0.86$$

Table 3 presents the same equation for each of the phases described, in S.I. units.

Spreading phase	L	R	D
Gravity-Inertial	$1.39 (\Delta g A t^2)^{1/3}$	$k_1 (\Delta g V t^2)^{1/4}$	$\frac{\pi k_1^2}{8} (\Delta g V t)^{1/2}$
Gravity-Viscous	$1.39 \left(\frac{\Delta g A^2 t^{3/2}}{v_w^{1/2}}\right)^{1/4}$	$k_2 \left(\frac{\Delta g V^2 t^{3/2}}{{v_w}^{1/2}} \right)^{1/6}$	$\frac{\pi k_2^2}{16} \left(\frac{\Delta g V^2 t}{v_w^{1/2}} \right)^{1/3} \frac{1}{\sqrt{t}}$
Surface Tension - Viscous	$1.43 \left(\frac{\sigma^2 t^3}{\rho_w{}^2 v_w}\right)^{1/4}$	$k_3 \left(\frac{\sigma^2 t^3}{\rho_w^2 v_w}\right)^{1/4}$	$\frac{3\pi {k_2}^2}{16} \Big(\!\frac{\sigma}{\rho_w v_w^{-1/2}}\!\Big)^{\!\!1/4} \frac{1}{\sqrt{t}}$

TABLE 3 - FORMULAS AND FAY COEFFICIENTS FOR THE DIFFERENT SPREADING REGIMES

Where L (m) is the characteristic length of the slick for unidmensional spreading, D (m^2/s) is the difusion coefficient, $\Delta = \frac{(\rho_w - \rho_0)}{\rho_w}$, V (kg^3) the volume of spilled oil, A = 0.5V is the length unit of the spill, k_1 , k_2 and k_3 are constants, Garcia-Martinez (1999) suggested the following values 0.57,0.75 and 0.5, respectively.

As said before the initial stage is very short and often not modelled, so the initial area and time are modelled at the beginning of the gravity-viscous phase, or the end of the first stage, as follows:

$$t_0 = \left(\frac{k_2}{k_1}\right)^4 \left(\frac{V_0}{\Delta g v_w}\right)^{1/3}$$
[2]

$$R_0 = \frac{k_2^2}{k_1} \left(\frac{\Delta g V_0^5}{v_w}\right)^{1/12}$$
[3]

The last stage is also often not applicable, since it occurs when the slick is extremely thin, which in reality would mean it would break in smaller slicks due to wave and wind action, which in turn means that Fay's assumptions are no longer correct. Therefore, it is common practice to use only the gravity-viscous phase to calculate spreading, assuming that when the slick reaches a certain thickness spreading stops. Mackay et al. (1980) and Reed (1989) use a 0.1mm thickness (h) for heavy oils, and a 0.01mm thickness for lighter oils.

As mentioned previously, Fay is a classical method to calculate spreading of an oil slick, as is widely used today, even though it is known that oil spreading cannot be fully explained by these equations. The major aspects not described by the equations are (Reed et al. 1999):

- Non-circular slicks;
- Spreading for viscous oils;
- Tar balls tendency of oil to break up into smaller patches;
- Discharge conditions subsurface and continuous releases.

Mackay et al. (1980) proposed an alteration, a "thick-thin" variation of the gravity-viscous equation, with the thickest part of the slick feeding oil to the thin part. However, physical knowledge on how the two phases of the slick relate is limited, hindering the use of this model.

In conclusion, the Fay equations are useful and provide accurate predictions for the thick part of the oil slick, where the majority of oil is found, and for the early stages of the spill.

The model developed in this study used the Fay method to compute spreading.

2.4.2 DISPERSION

Natural dispersion is an oil removal mechanism, as it is the uptake of oil droplets into the water column until they are no longer a part of the oil slick (NOAA 2002, Hackett et al. 2006). This happens due to breaking waves, with smaller oil droplets (diameters less than 50-70 microns) not being able to resurface due to natural turbulence of the water. The dispersed quantity of oil depends on oil properties, such as viscosity, (low viscosity implies that the oil is more likely to disperse than high viscosity crude) surface tension and water conditions, such as water temperature and sea state (NOAA 2002).

In oil spills during storms, dispersion can be the main removal mechanism of oil from the sea surface, whereas in normal conditions it would be evaporation. Some studies also show that high asphaltenes quantities can slow down oil dispersion (Fingas et al. 1993).

Delvigne et al. (1988) developed a series of laboratory studies about the natural dispersion of oil, and based on the results, developed an empirical relation for the dispersion rate of the oil due to breaking waves, equation 4, and is the most used method to calculate dispersion.

$$\frac{dm_t}{dt} = c_{oil} D_{ba}^{0.57} f_s F_{wc} d_0^{0.7} \Delta d , \qquad [4]$$

where f_s is the surface fraction covered by oil (wich is equal to the oil content in the oil-water emulsion); $d_0(m)$ is the particles diameters; $\Delta d(m)$ is the diameter interval of the particles; c_{oil} a parameter determined experimentally that depends on oil type; D_{ba} is the waves dissipation energy per unite of superficial area, and is computed by equations 5 and 6; F_{wc} is the fraction of the sea surface hit by the breaking waves per unit time, equation 7.

$$D_{ba} = 0.0034 \rho_W g H_{rms}^2$$
 , [5]

$$H_{\rm rms} = \frac{1}{\sqrt{2}} H_0 , \qquad [6]$$

where $H_0(m)$ is the wave height.

$$F_{wc} = \frac{C_b(W - W_i)}{T_w},$$
^[7]

where $C_b = 0.0032 \text{ sm}^{-1}$, W_i is the wind velocity to start rupturing 5ms^{-1} and T_w (*s*) is the wave period. For unknown wave height and period empirical formulas can be used, equations 8 and 9, based on wind velocity, as proposed for the ADIOS model (NOAA 1994):

$$H_0 = 0.243 \frac{W^2}{g}$$
 [8]

$$T_{\rm w} = 8.13 \frac{\rm W}{\rm g}$$
^[9]

Since turbulence energy is hard to determine Mackay et al. (1980) presented a simplified formulation, based on the square of the wind velocity, as shown below:

$$\frac{dm_d}{dt} = 0.11m_{oil}\frac{(1+W)^2}{1+50\mu^{1/2}h\sigma}$$
[10]

This equations determines the mass transfer rate per hour, where $m_{oil} (kg)$ is the mass of oil that remains at the surface, μ is the oil's dynamic viscosity (cP), h is the slick thickness (cm), W the wind velocity (m. s⁻¹) and σ the interfacial tension oil-water (dyne. cm⁻¹).

To compute dispersion the model used the Delvigne method to conduct this study.

2.4.3 SEDIMENTATION

Sedimentation is defined as the adhesion of oil to solid particles in the water column. It can be sorbed onto sediments in the water column increasing the mass of the particles and causing a downward movement, and can even be found in bottom sediments (NOAA 2002). Depending on the sediment load it can be an important removal process, for muddy rivers (where sediment load can exceed 0.5 kglm³) the removal by sedimentation can be significant and exceed the loss by dispersion, which means that the oil remains in the water column. For open waters, where sediment loading is less than 1% of that value, meaning that the oil will remain on the surface much longer, spreading the slick over a wider area (Lehr 2001, NOAA 2002).

Other phenomena can increase the mass of the slick or its droplets in the water column and therefore contribute to sedimentation, for example dispersion, incorporation of faeces of organisms that degrade oil.

NOAA (2000) used the following method to assess mass of oil sedimented per unit time (kgs⁻¹) in their model ADIOS2:

$$\frac{dm_{sed}}{dt} = 1.3 \sqrt{\frac{E}{v_w}} K_a C_{oil} C_{sed} z_i A_s \quad ,$$
[11]

where $v_w kg/(s.m)$ is the water's dynamic viscosity; K_a is the adhesion parameters $(1 \times 10^{-4} m^3 kg^{-1})$; z_i is the intrusion depth of the oil particles in the water column due to breaking waves, (Delvigne et al. 1988); E is the rate of dissipated energy at the water surface $(Jm^{-3}s^{-1})$, can be calculated through the energy of wave dissipation (D_{ba}) , equation 13; $C_{sed} (kg/m^3)$ is the sediments concentration in the water column; $C_{oil} (kg/m^3)$ is the concentration of oil particles in the water column, equation 14 (Delvigne et al. 1988):

$$z_i = 1.5H_0$$
 [12]

$$E = \frac{D_{ba}}{z_i T_w}$$
[13]

$$C_{oil} = \frac{\frac{dm_d}{dt}}{z_i T_w}$$
[14]

2.5 OIL WEATHERING PROCESSES

As discussed before, when an oil spill takes place physical processes occur and start to change the oil composition immediately, however these changes depend on its chemical compositions and on how it is spilled (Hackett et al. 2006). The main weathering processes discussed here are evaporation, emulsification and dissolution. Others, less relevant, such as biodegradation and photo-oxidation will also be explained, in less detail.

2.5.1 EVAPORATION

Evaporation is a very important process, accounting for a major portion of oil removal from the surface and starts right after the oil spill. In the first hours of the spill, most of the volatile fractions of the crude oil are removed (Mishra et al. 2015). Estimate losses due to evaporation are very important to asses the lifetime of the spill and estimate the evolution of oil properties with time (Reed, Johansen et al. 1999).

Oil is made of different components, the ones that have lower boiling points, and are therefore more volatile are the first to evaporate, reducing rapidly the volume and mass of the oil slick in the surface of the water. Crude oils, that have a high volatile fraction, have a significant portion of their total mass removed within a short period of time due to evaporation, other types (such as heavy fuel oils) lose relatively little to evaporation, Table 4 (Hackett et al. 2006).

Evaporation rates depend on multiple factors, such as boiling points of the components, surface area, slick thickness, vapour pressure of the oil and mass transfer coefficient, which depends on oil composition, wind velocities, sea state and air and water temperature and exposure time.

Oil	% Evaporated	Hour
Gasoline	94	1
Lagomedio	38	18
Diesel fuel oil	37	18
Prudhoe Bay	28	70

TABLE 4 – EXAMPLES OF PERCENTAGE OF OIL EVAPORATED FOR DIFFERENT OIL TYPES (NOAA 2002)

This process increases the density of the oil and its viscosity and the heavier fraction will continue to weather, evaporation is as shown previously the first process involved in oil removal and its importance decreases as time passes.

To compute the evaporation rate there are two frequent methods, the first is the pseudo-components model (Yang et al. 1977, Payne et al. 1984) and second an analytical model known as evaporative exposure (Stiver et al. 1984).

The first method, of the pseudo components, assumes that the crude oils and refined products are a mixture of discrete and independent components named pseudo-components. Each pseudocomponent is then treated as a singular substance with a vapour pressure associated, assuming a well mixed oil.

The evaporation rate for each pseudo-component, i, can be calculated according to the following equation:

$$\frac{dV_{e}^{i}}{dt} = K_{e}^{i} \frac{P_{i}^{sat} \overline{V}_{i}}{RT} A_{s} \chi_{i} , \qquad [15]$$

where $V_e^i (kg^3)$ is the evaporated volume of the fraction i, t is time, $K_e^i (ks/s)$ is the mass transfer coefficient, $P_i^{sat} (N/m^2)$ is the vapour pressure considered, R is the perfect gas universal constant, T is the oil temperature, $\overline{V}_i (m^3/mol)$ is the molar volume of the fraction i, $A_s (m^2)$ is the slick area and χ_i is the molar fraction of component i.

The molar volume for each pseudo-component is computed through a correlation between the molar volume and boiling point for a series of alkenes (C_3 - C_{20}):

$$\overline{V}_{i} = 7 \times 10^{-5} - (2.102 \times 10^{-7} . BP_{i}) + (1 \times 10^{-9} . (BP_{i})^{2})$$
^[16]

The saturated vapour pressure is calculated through the Antoine equation:

$$\ln \frac{P_{i}^{\text{sat}}}{P_{0}} = \frac{\Delta S_{i} (BP_{i} - C_{2,i})}{\Delta Z. R. BP_{i}} \cdot \left[\frac{1}{BP_{i} - C_{2,i}} - \frac{1}{T - C_{2,i}} \right],$$
[17]

where $P_0(Pa)$ is the atmospheric pressure, $\Delta S_i(JK^{-1}kg^{-1})$ is the variation of entropy from the vaporization of the fraction i, ΔZ is a compressibility factor (assumed 0.97), BP_i (⁰*C*) is the boiling point from component i, and C_{2,i} is an empirical coefficient.

$$\Delta S_{i} = 8.75 + 1.987 \log BP_{i}$$
[18]

$$C_{2,i} = 0.19. BP_i - 18$$
 [19]

As for the mass transfer coefficient, two equations are presented. The first according to (Mackay et al. 1973) and the second one, simpler, according to (Buchanan et al. 1988):

$$K_{e}^{i} = 0.029 W^{0.78} D_{s}^{-0.11} Sc_{i}^{-0.67} \sqrt{\frac{M_{i} + 29}{M_{i}}}$$
, [20]

$$K_e = 2.5 \times 10^{-3} W^{0.78}$$
 , [21]

where W is the wind speed in $m.h^{-1}$, D_s is the diameter of the slick (m), Sc_i is the Schmidt number for the fraction i, and M_i is the molar mass for each fraction (kg. mol⁻¹). K_e^i is therefore in $m.h^{-1}$.

In equation 21 the value of 2.5×10^{-3} is not consensual across literature, varying from 1.5×10^{-3} and 5.0×10^{-3} .

The evaporative exposure method is described with the following equations:

$$\frac{\mathrm{dF}_{\mathrm{e}}}{\mathrm{dt}} = \frac{\mathrm{K}_{\mathrm{e}}\mathrm{A}_{\mathrm{s}}}{\mathrm{V}_{\mathrm{0}}} \cdot \exp\left[\mathrm{A} - \frac{\mathrm{B}}{\mathrm{T}}(\mathrm{T}_{\mathrm{0}} + \mathrm{T}_{\mathrm{G}}\mathrm{F}_{\mathrm{e}})\right] , \qquad [22]$$

where F_e is the volumetric fraction of evaporated oil, A and B are empirical constants, T_0 is the initial boiling point and T_G is the gradient of the distillation curve. All of these are dependent of the type of oil, of they are unknown they can be estimated based on the API density, according to NOAA (1994):

$$A = 6.3$$
, $B=10.3$, [23]

$$T_0 = 532.98 - 3.1295. API$$
, [24]

$$T_0 = 654.45 - 4.6588.$$
 API, [25]

where Equation 24 and 25 are for Crude oils and refined products, respectively. T_G is determined by the second version of the ADIOS model (NOAA 2000):

$$T_G = 1356.7 - 247.36. \ln API$$
 [26]

The pseudo components method has good results; however, it requires a lot of information about the spilled oil. The fact that fractions are determined based on distillation temperatures may result in some shifts from reality. The second method explained, evaporative exposure, does not require information

about the oil composition but results can be fallible for oils with non-linear distillation curves (refined products).

The model used calculated the fraction of oil evaporated through the evaporative exposure method.

2.5.2 EMULSIFICATION

Emulsification is the entrainment of water in the oil, which is the opposite of dispersion, see section 2.4.2. This process has a significant impact in the volume, density and especially in the viscosity of the oil slick, Table 5. This has significant implications for removal strategies, since increased viscosity can decrease clean up strategies' efficiency (Lehr 2001).

TABLE 5 – EFFECT OF EMULSION ON VISCOSITY IN DIFFERENT OIL TYPES (NOAA 2002)		
Product	Viscosity at room temperature (cP)	Viscosity after emulsion (cP)
Water	1	-
Prudhoe Bay crude	46	250 000
Lagomedio	20	300 000

(10 1 1 0000)

This increase in viscosity results in less spreading and evaporation, if emulsions are stable and persistence they will hinder and inhibit some chemical and biological reactions, since they reduced the surface area in contact with air and water. Removal and clean-up operations are very impacted by this process since not only is the volume to be removed much greater, but also because the equipment used has a lower efficiency under these circumstances

It is important to note that not all oils emulsify, this process depends on other weathering processes occurring first, sea state, oil composition is also extremely important in determining if emulsification occurs, namely water content and asphaltenes content (this one being the most relevant). Waxes and asphaltenes can be considered as solutes in a solvent consisting of the lighter hydrocarbon components of the oil. Resin levels are important as well, since they help to maintain asphaltenes in solution and are emulsifiers by themselves. For example, light refined products usually do not emulsify, since they do not have the right components to stabilize the water droplets (Lehr 2001).

Emulsification usually occurs within a few hours of the spill (Figure 4) and emulsions can be up to 70 to 90% water, meaning that the combined volume of oil and water is much larger than the initial volume (NOAA 2002). Drift behaviour is also influenced by emulsion formation (Hackett et al. 2006).

An emulsion can be stable or unstable, in unstable emulsions water and oil separate easily under calm conditions and warm temperatures, as for stable emulsions water can remain in the oil for weeks or months (NOAA 2002). The stability of the emulsions is also a function of the asphaltenes and wax content, being at least 3% is necessary to have a stable emulsion.

Once emulsification starts, the water entrainment in the oil can be described through the Mackay's formula, Equation 27:

$$\frac{\mathrm{d}F_{\mathrm{wv}}}{\mathrm{d}t} = \mathrm{K}_{\mathrm{w}}(1+\mathrm{W})^{2} \left(1 - \frac{\mathrm{F}_{\mathrm{wv}}}{\mathrm{F}_{\mathrm{wv}}^{\mathrm{final}}}\right),$$
[27]

where F_{wv} is the volumetric water fraction incorporated in the emulsion; K_w is an empirical constant (1.6×10^{-6}) (NOAA 1994).

Rasmussen (1985) proposed Equation 32 that takes into account some oil properties:

$$\frac{\mathrm{dF}_{\mathrm{wv}}}{\mathrm{dt}} = \mathrm{R}_1 - \mathrm{R}_2 \,, \qquad [28]$$

where R_1 is the rate of water entrance (s⁻¹) and R_2 water exit rate (s⁻¹), and are given by Equation 29 and 30, respectively:

$$R_{1} = \frac{K_{1}}{\mu_{0}} (1 + W)^{2} (F_{wv}^{\text{final}} - F_{wv}), \qquad [29]$$

$$R_2 = \frac{K_2}{\text{Asph. Wax. }\mu_0} F_{wv}, \qquad [30]$$

where Asph is the oil asphaltenes content (%),Wax is the wax content (%),K₁ and K₂ are constants defined by Rasmussen (1985) ($K_1 = 5 \times 10^{-7} \text{kg} \cdot \text{m}^{-3}$; $K_2 = 1.2 \times 10^{-7} \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$)

2.5.3 DISSOLUTION

Dissolution is a process through which soluble hydrocarbons fragment in small particles and mix with water, resulting in a liquid homogenous mass, and can originate either in the superficial oil slick or in oil droplets present in water. Dissolution is more significant in compounds with lower molecular weight that are more soluble and volatile. Low levels of soluble hydrocarbons result in a small lost due to dissolution when compared with other processes.

Dissolution and evaporation are therefore two competing processes, the latter becoming more important in superficial slicks, where partial pressure exceeds lower molecular weight compounds solubility. Making dissolution more significant in cases where evaporation is small, for instances ice covered surfaces (Afenyo et al. 2015) or in oil droplets in the water column, in these circumstances the larger surface areas also justify the importance of the dissolution process. Therefore, this process varies with different factors, such as the ease of dispersion, spreading, composition, water temperature and sea state. So, after oil spill dissolution tends to increase, after a few minutes it decreases rapidly, due to evaporation losses. Dissolution is of minor importance when related with quantities of mass lost, usually less than 0.1% (in very heavy oils) to 2% (gasoline) of the spilled volume dissolves into the water column. However, the components that dissolve into the water column are often very toxic to the environment (NOAA 2002).

Equation [31] is used to assess dissolution losses:

$$\frac{d_{\text{Diss}}}{dt} = \text{K.}\,\text{f}_{\text{s}}.\,\text{A}_{\text{s}}.\,\text{S}\;,$$
[31]

where K (kg/s) is the mass transfer coefficient for dissolution, f_s is the fraction of surface covered by crude (the same as the oil content in the oil-water emulsion); $A_s(m^2)$ is the area of the oil slick and S ($g.m^3$) is the oil solubility in water. The latter can be calculated through the Equation 32, proposed by Huang et al. (1982) :

$$S = S_0. e^{\alpha t} , \qquad [32]$$

where S_0 is the solubility of fresh oil (30g.m³), α is the decay rate (0.1) and t the time after the spill.

The model used in this study calculated the dissolution through the Fingas method.

2.5.4 BIODEGRADATION

Hydrocarbons, found in oil slicks, are a food-source to many microorganisms that range from algae to bacteria and fungi, these transform hydrocarbons in simpler compounds, and this process is called biodegradation.

The rate at which biodegradation happens depends on the surface area of the slick in contact with water and bacteria, temperature (higher temperatures favours biodegradation) and nutrient (nitrogen and phosphorus) and oxygen availability. The type and composition of oil is also relevant since lighter fractions are preferred and more biodegraded.

This processes when compared with other like evaporation or dispersion has little impact on oil removal from the slick, since it is a slow (time scales ranging from weeks to years) and small-scale process (Fernandes 2001, NOAA 2002).

2.5.5 PHOTO-OXIDATION

Photo-oxidation is a slow acting (weeks to months) process that acts on the surface of the slick and can result in a "thin, crusty skin" on slicks (NOAA 2002). This is a chemical process through which oil degradates due to action of ultraviolet radiation, that transforms some of its chemical components by the addition of oxygen that happens slowly, which in turn increases the hydrocarbons hidrossolubility.

This process is favoured by spreading, since it occurs on the surface of the oil slick. Other factor that affects the oxidation rates are the thickness of the slick, the presence of salts in the water, the amount of radiation with a wavelength under 400nm and spill latitude. In areas with a greater incidence of radiation, photo-oxidation can be a significant process, mainly after the first week.

Photo-oxidation transforms some chemical components of oil into polar components increasing the resin and asphaltenes content. Therefore, it is likely that it increases the formation of emulsions. This process can result in a skin on the surface of the slick, which researchers think may limit evaporation since the lighter components of oil can no longer diffuse through the surface of the slick (NOAA 2002).

2.6 INTERACTIONS BETWEEN PROCESSES

The processes described earlier can also interact amongst them and enhance or inhibit other processes. In this chapter, these are going to be addressed and explained, Figure 6 is going to be the basis for this analysis, in blue are represented the processes that affect an oil slick and in orange the rates that occur.

Evaporation contributes to the formation of mousse and therefore facilitates emulsification; the evaporation of the oil lighter components yields the level of resin and asphaltenes necessary to stabilize emulsions. Resins can also cause water-in-oil emulsions that can be produced from photo-oxidation (Afenyo et al. 2015). These two processes, evaporation and emulsification, change oil properties such as viscosity and density that in turn affect oil spreading. With increased density, the oil becomes less buoyant (Lehr 2001).

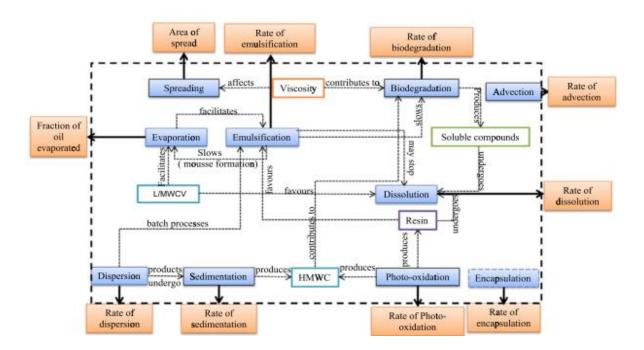


FIGURE 6 - INTERACTIONS BETWEEN PROCESSES THAT AFFECT AN OIL SPILL (AFENYO ET AL. 2015)

Emulsification and dispersion are a series of batch processes (Afenyo et al. 2015); the rate of natural dispersion is reduced with emulsion formation, which extends the lifetime of the slick, which in turn can alter the environmental impact of an oil spill and also how responders react to it (Hackett et al. 2006). The two process mentioned in the beginning of this paragraph are controlled by hydrodynamic factors and oil properties, such as frequency of breaking waves, mixing intensity and depth of mixing on one hand and viscosity and interfacial tension on the other (Afenyo et al. 2015).

Oil composition, this is, their lighter fractions are more susceptible to processes such as biodegradation, and so spreading, dispersion and dissolution promote biodegradation.

Spreading affects oil-weathering processes due to its influence on the oil slick thickness (Hackett et al. 2006) and it is affected by dispersion, evaporation and emulsification (Lehr 2001). The thickness of an oil slick is key since it computes the natural rate of dispersion which in turn determines the persistence (lifetime) of the oil at sea. Spreading is also related to the slick area, and this variable is of utmost importance since it is used to compute evaporation, which in turn determines the oil composition in time. These two variables: area and thickness are extremely important for oil spill combat methods and environmental impact assessment (Reed et al. 1999).

2.7 UNCERTAINTY IN OIL SPILL MODELLING

Input data, detailed spill data (location, volume lost, and product type) and environmental data (wind and current observations and forecasts) are necessary to model the fate and transport of an oil spill. Analysing those results and comparing them with field data enables the improvement of the model through feedback loops (NOAA 2002).

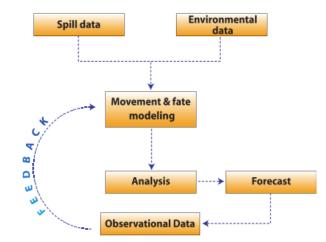


FIGURE 7 - OIL SPILL MODELLING SCHEME (NOAA 2002)

Traditional oil spill trajectory models outputs are deterministic and provide a "best guess" of oil movement and fate. However, as scientific knowledge evolves and new techniques appear it has become evident that trajectory analysis should not only include the "best guess" of the oil movement and fate, but also some indication of its uncertainty, namely in the spill and environmental data used to make the forecast. Table 6 indicates uncertainty for the most common input requirements in oil spill models.

Uncertainty depends also on the length and time scale of the spill and the model uncertainty is not necessarily proportional to model input uncertainty (Mishra et al. 2015). An uncertainty analysis would provide two different types of information, firstly it would calculate the relative importance of the uncertainty of each input parameter in the uncertainty of the global results of the model, and secondly it would calculate the global uncertainty in function of the uncertainties of each input parameter (Sebastião et al. 2006).

Category	Parameter	Uncertainty
Release Details	Spill Location	Low-Medium
	Time of release	Low-Medium
	Type of oil (density, viscosity)	Medium-High
	Potential Spill Volume	Low
	Actual Spill Volume	High
	Release Rate	High
Oil Weathering	Light refined products	Low
-	Intermediate fuel oils	High
	Heavily studied crude oils	Low
	Crude oils	Medium-High
Winds	Observations	Low
	24H to 48H forecast	Low-medium
	Wind drift	Low
Surface currents	River	Low
	Tidal areas with current stations	Low
	Shallow water lagoon	Medium
	Shelf area (wind setup)	
	Continental slope	Low
	Abyssal plain	High
Turbulence	Spreading	Medium
	Horizontal diffusion	Low-medium

TABLE 6 - MAJOR SOURCES OF UNCERTAINTY IN OIL SPILL MODELS

3. METHODOLOGY

3.1 METHODOLOGY OVERVIEW

A sensitivity and forcing analysis were carried out in order to better understand the MOHID oil spill model used and its sensitivity to oil parameters and forcing. For that an oil spill was modelled offshore of the Portuguese coast and Tagus estuary, Figure 8 (A) and (B) respectively.

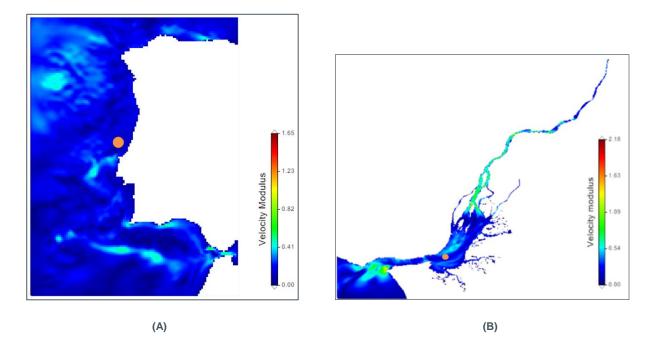


FIGURE 8 – (A) PORTUGUESE COAST OIL SPILL INITIAL DISCHARGE LOCATION (ORANGE) (B) TAGUS ESTUARY OIL SPILL INITIAL DISCHARGE LOCATION (ORANGE)

This study intends to provide a sensitivity analysis to an oil spill trajectory model, determining the relative weight of the parameters in the results of the model. Also a forcing analysis was carried out to understand the effect of wave and wind action in the model behaviour.

The sensitivity analysis was performed on the Portuguese western coast and on the Tagus estuary, hereafter referred as Setting 1 and 2, respectively. In addition, two scenarios were analysed for each setting. In the coastal area of Portugal, the first scenario consists of a typical upwelling event during the summer months and the second scenario with westerly winds, to evaluate the impact of the oil slick in the Portuguese shoreline, both with a seven-day duration. In the estuary, the two scenarios consisted of a neap tide and a spring tide with eight-day duration. Other parameters such as the wind coefficient and spill location were also subject to variations to assess their impact on the model outputs.

Regarding model outputs the evolution of selected oil properties was analysed, the evolution of the centre of mass, for the sensitivity analysis (S.A.) an index was calculated to quantify the impact of parameters in the output variables.

Oil spreading was computed using the Fay method, evaporation was calculated through the Evaporative Exposure Method, Dispersion through the Delvigne method and Emulsification with the Fingas algorithm. Oil sedimentation and dissolution, as well as removal techniques were not considered.

3.2 MOHID

The model used in these simulations of oil spreading and weathering is MOHID, which stands for *Modelação Hidronâmica*. This software is an open-source geo-physical circulation model based at *MARETEC*, a research group at *Instituto Superior Técnico* (IST). It is also a free-surface, baroclinic model that uses the hydrostatic and Boussinesq approximations and a rotating Cartesian reference frame with angular rotation rate following the seminal primitive ocean equations. MOHID provides solution for the advection-diffusion of temperature, salinity and horizontal momentum equations. It also solves the continuity equations to determine vertical velocity, water elevation, density is calculated using the UNESCO state equation as a function of salinity, temperature and pressure (Mateus et al. 2012).

This model is written in ANSI-FORTRAN-95 and has more than sixty modules and over 300 000 lines of code (Neves 2007). Each module has a specific task, and belongs in one of four main groups: modules related with the description of the computational grid, modules that manage data input and output, modules responsible for boundary conditions and lastly module to change the models state variables. This software also makes available for use a baroclinic hydrodynamic module for the water column and 3D module for the sediments and corresponding eulerian transport and lagrangian transport modules. Other parameters and processes have specific modules, such as turbulence, water content, ecology or transformation module, these and the main models are listed in Table 7.

To study the trajectory of the spilled oil it is assumed that oil can be considered a large set of small particles; therefore, the model used is based on a tracer's model. These particles move by advection, diffusion and spreading specific to oil slicks. MOHID oil spreading feature is based mainly in three submodels: one for the evolution of properties and oil specific properties (such as density, spreading velocity, evaporation, etc.); a hydrodynamic model to calculate wave or wind induced velocity fields; and a lagrangian model that computes the oil particles spatial evolution based on currents velocity (calculated in the hydrodynamic module), wind drift, oil spreading (computed in the oil module) and also the random velocity that represents diffusive transport.

TABLE 7 - MAIN MODULES USED BY MOHID

Module Name	Module Description
Model	Manages the information flux between the hydrodynamic module and the two transport modules and the communication between nested modules.
Hydrodynamic	Computes the water level, velocities and water fluxes through a 3D dimensional baroclinic hydrodynamic free surface model.
Water Properties	Eulerian transport model. Manages the evolution of the water properties (temperature, salinity, oxygen, etc) using an Eulerian approach.
Lagrangian	Lagrangian transport model. Manages the evolution of the water properties (temperature, salinity, oxygen, etc) using a Lagrangian approach. Can also be used to simulate oil dispersion.
Water Quality	Zero Dimensional water quality model. Simulates oxygen, nitrogen and phosphorus cycle.
Oil Dispersion	Simulates oil spreading due to thickness gradients and internal oil processes like evaporation, emulsification, dispersion, dissolution and sedimentation.
Turbulence	One dimensional turbulence model.
Geometry	Stores and updates information about the finite volumes.
Surface	Boundary conditions at the top of the water column
Bottom	Boundary conditions at the bottom of the water column
Open Boundary	Boundary conditions at the frontier with the open sea
Discharges	River or Anthropogenic water discharges
Hydrodynamic file	Auxiliary model to store the hydrodynamic solution in an external file for posterior usage.

3.2.1 HYDRODYNAMIC MODULE

The hydrodynamic module available in MOHID generates and updates information on flow, solving the Navier-Stokes equations in the three-dimensional space for incompressible fluids. The hydrostatic balance is assumed as well as the Boussinesq approximation. Spatial discretization is accomplished through a technique of finite volumes which allows for the usage of a generic vertical coordinate system. Time discretization is based on a semi-implicit scheme. This module is therefore extremely versatile and is the only tool needed to simulate flow, regardless of the spill location and geometry complexity.

3.2.2 LAGRANGIAN MODULE

The Lagrangian module is used to simulate localized processes with sharp gradients, as for example oil dispersion. The MOHID model uses the concept of lagrangian tracer and its position to assess spatial-temporal evolution of the oil slick contamination zone and also interacts with other modules such as the oil module (Figure 9) (Mateus et al. 2008). This interaction is necessary since tracers movement is

influenced by velocity fields from the hydrodynamic module, by wind from the surface module, by spreading velocity found in the oil dispersion module and by random velocity (Neves 2007).

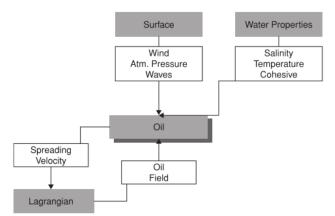


FIGURE 9 - INFORMATION FLUX BETWEEN THE OIL MODULE AND OTHER MODULES. (NEVES 2007)

The spatial evolution of the oil particles is calculated by the definition of velocity, Equation [33]:

$$\frac{dx_i}{dt} = U_i(x_i, t), \tag{33}$$

where the velocity, U, can be obtained by one of the following components:

- Currents velocities obtained in the hydrodynamic module;
- Wind drift velocity;
- o Random velocity representative of diffusive transport;
- Velocity from the oil slick spreading, from the oil module.

And is solved through an explicit method:

$$x_i^{t+\Delta t} = x_i^t + \Delta t. u_i'$$
^[34]

The temporal step used in the lagrangian model is independent of the one used in the hydrodynamic module, increasing the performance of MOHID with a shorter time step than the hydrodynamic model.

In this model the user also defines the type of emission, both spatially and temporally. The discharge can be set up in one origin or by multiple origins and each one corresponds either to a point discharge or an area defined by a polygon. Emissions can also be instantaneous, continuous or be defined by a time series, the latter is very useful to simulate accidents that occurred in the past, like oil spills that the oil amount that is released varies with time. The oil characteristics are also defined for each origin.

3.2.3 OIL MODULE

The oil weathering module was developed to predict the behaviour of spilled oil in coastal zones and enables the prediction of the behaviour of processes (such as transport or spreading) and properties with time, and uses mainly 3D hydrodynamics and 3D lagrangian transport models, Figure 9. This model also integrates some response methods. Oil properties and processes are included in this model namely, oil density and viscosity and oil spreading, evaporation, dispersion, sedimentation, dissolution, emulsification, beaching and removal techniques respectively.

As mentioned before oil trajectories are modelled considering oil as a large number of particles that move independently in water. Water properties and atmospheric conditions are used to determine oil processes and properties. All weathering processes and properties are assumed to be uniform for all tracers, apart from spreading and oil beaching, water properties and atmospheric conditions are considered equal to the same environmental conditions at the discharge location. In addition oil temperature is assumed equal to water temperature, neglecting solar radiation or any other energy transfer process.

3.3 MODEL DOMAIN

3.3.1 SETTING1 - PORTUGUESE COAST

Located in the western part of Europe the Portuguese coastal zone is the first study area (Figure 10) selected in this study. It is an intense shipping traffic zone (Figure 11) with more than 55 000 commercial vessels per year crossing this area. Several routes go through this area that is a mandatory passage point between the Mediterranean Sea and Northern Europe or the American Continent.

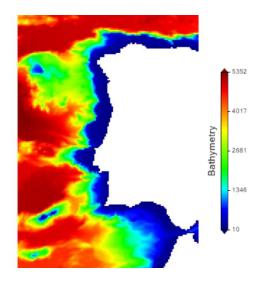


FIGURE 10 - BATHYMETRY OF THE STUDY AREA FOR THE FIRST SETTING, PORTUGUESE COAST

This area is also very important for other reasons, for instance the activities developed near shore represent a significant part of the Portuguese economy and are also socially and environmentally important. It has a high potential in natural resources, fishing, aquaculture, maritime commerce and port activity, leisure, sports and tourism activities (Fernandes et al. 2016).

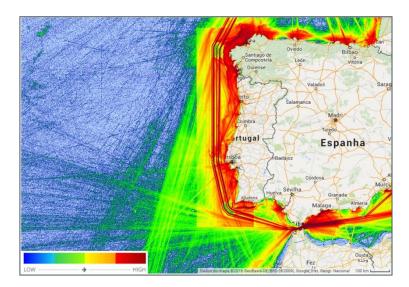


FIGURE 11 - SHIP DENSITY IN THE PORTUGUESE COAST IN 2014 (WWW.MARINETRAFFIC.COM ACCESSED ON 07/07/2015)

3.3.2 SETTING 2 - TAGUS ESTUARY

The Tagus estuary is located on the Portuguese west coast, covering an area of 320 km² (Figure 12). It is characterized by a deep, long and narrow tidal inlet that connects it to the Atlantic Ocean, and also by a shallow, tide-dominated basin with extensive tidal flats and marshes that cover up to 40% of the inner estuary (Monteiro et al. 2016).

In 2012 the Port of Lisbon had almost 3 000 ships, (Figure 13), representing more than 10 000 million tones of cargo and over 500 000 passengers. This estuary is a significant connection between the Mediterranean and northern Europe, and drives social and economic development of the Lisbon and Tagus Valley regions and for Portugal as well. It accounts for almost 5% of the regions GDP and maintains 40 000 jobs (Sá Pereira et al. 2014).

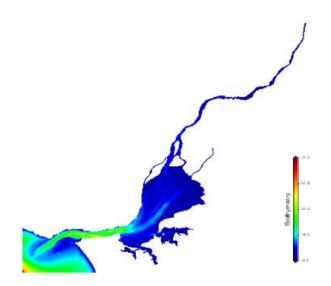


FIGURE 12 - BATHYMETRY FOR THE STUDY AREA IN THE SECOND SETTING, TAGUS ESTUARY

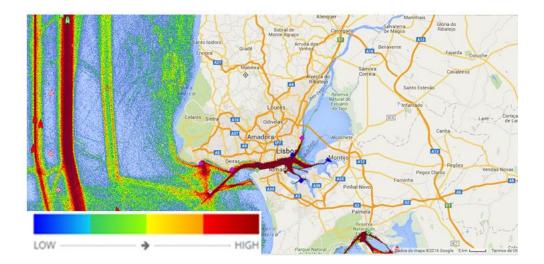


FIGURE 13 - SHIP DENSITY IN THE TAGUS ESTUARY IN 2014 (WWW.MARINETRAFFIC.COM ACCESSED ON 07/07/2015)

3.4 LAGRANGIAN TRANSPORT MODEL

This work was developed using the MOHID software described in previous chapter, the simulations of the oil spill were made using the MOHID oil spill fate and behaviour component, which is integrated in the MOHID Lagrangian transport model. In this module pollutants are represented by a cloud of discrete particles advected by wind, currents and waves and spread due to a random turbulent diffusion or mechanical spreading (Fernandes et al. 2016). This spill model has the ability to run integrated with the hydrodynamic solution or independently (when coupled to metocean models). This latter option was selected to optimize computational efficiency, taking advantage of models previously run (Fernandes et al. 2016).

3.4.1 METOCEAN DATA

The models used to obtain current and water properties and atmospheric conditions where the PCOMS-MOHID model and the MM5 model, respectively. The first is a 3D hydro-biogeochemical model of the Iberian western Atlantic region (Yang et al. 1977, Mateus et al. 2012). Ocean boundary conditions are provided by the Mercator-Ocean PSY2V4 North Atlantic and by tidal levels computed by a 2-D version of MOHID (NOAA 2000, Neves 2013), forced by FES2004, and running for a wider region. PCOMS has a horizontal resolution of 6.6 km and a vertical discretization of 50 layers with increasing resolution from the sea bottom upward, reaching 1 m at the surface. The MM5 model has a 9 km spatial resolution and is used as atmospheric forcing of the PCOMS-MOHID (Payne et al. 1984). The Tagus model is forced with the results from PCOMS.

The wave parameters, necessary for the first setting (Portuguese coast), are obtained from the Portuguese wave forecasting system implemented at MARETEC-IST, the WaveWatch III model that has a 5 km spatial resolution (Fernandes et al. 2016).

Some HDF5 handling was necessary for the Sensitivity Analysis and Forcing Analysis, namely to glue meteorological files and modify some components of the HDF5 files respectively.

3.5 SENSITIVITY ANALYSIS

Sensitivity analysis is a common approach to identify parameters that have a greater influence on model behaviour. This analysis was therefore carried out to evaluate the importance of each parameter on oil spill modelling. First a reference model was run to have a benchmark and to compare model results afterwards. Then each parameter listed on Table 9 was varied by $\pm 10\%$ sequentially in separate runs, while holding all other terms constant. This perturbation($\pm 10\%$) is frequently adopted (Stiver et al. 1984, Fingas et al. 1993) and therefore was chosen for this analysis as well.

So, to evaluate the sensitivity of the model some variables were selected and listed in Table 8, based mainly in two factors: The first relates to trajectory analysis and second with the usefulness to emergency responders in clean-up strategies. For instances the mass and volume have a great importance for the clean-up teams, as well as the density or viscosity of the oil forever since they affect significantly the efficiency of the equipment used.

To evaluate and later discuss results several outputs were analysed, oil slick properties and trajectory (Table 9). For the sensitivity analysis, the evolution of properties with time was very important, and graphics were developed for the chosen variables. A sensitivity index was calculated (see section 3.5.1) to quantify the impact of the selected variations on the model outputs. Excel and VBA were used to process the data from the 48 simulations performed.

The centre of mass was analysed to understand the impact of said variations in the trajectory of the oil, namely its evolution with time. Comparing with the reference run simple statistics were used to understand what variations impacted the results the most. For forcing analysis this index cannot be calculated since this variation is not a parameter variation which makes the index not applicable. For

variations of the wind coefficient and spill location graphical results were analysed as well as their centre of mass variations. As for the sensitivity index was calculated for the wind coefficient as location is not a model parameter and does not enable the use of the formula.

Variable	Units
Slick Area	m²
Slick Volume	m ³
Oil Volume	m ³
Oil thickness	m
Density	kg/m³
Viscosity	сР
Trajectory	-
Tracers position	-
Mass Dispersed	kg
Mass Evaporated	kg
Water Content (MWC)	%

TABLE 8 - MODEL OUTPUTS AND RESPECTIVE UNITS ANALYSED

TABLE 9 - PARAMETERS CHOSEN TO PERFORM THE SENSITIVITY ANALYSIS, THEIR REFERENCE VALUE, UNITS AND VARIATIONS.

Parameter	Reference Value	Units	+10%	-10%
API gravity	22.9	-	25.19	20.61
Pour point	-21	°C	-23.1	-18.9
Reference Viscosity	164	cP	180.4	147.6
Resin Content	17	%	18.7	15.3
Saturate Content	44	%	48.4	39.6
Asphaltenes Content	9	%	9.9	8.1

3.5.1 SENSITIVITY INDEX

In order to quantify parameter sensitivity it was necessary to choose an index that complied with the following criteria: simplicity, the ability to quantify normalized sensitivity and also the nature of the variation, positive or negative (Delvigne et al. 1988, Fingas et al. 1993).

The normalized sensitivity index proposed by Mateus (2015), $S_{(p)}$, is defined as the relative change in model output divided by the relative change in the parameter value, Equation [35].

$$S_{(p)} = \frac{(V_{(p)} - V_s)/V_s}{(p - p_s)/p_s},$$
[35]

where V stands for the value of the variable; p is parameter's value. The lower index s represents the standard case value.

This index will compute a negative index result or a positive one, the first when coupled with a negative parameter perturbation (in this case -10%) means a positive perturbation in the end result of a given property (a higher end value is obtained when compared with the reference simulation value), as for a positive index means a negative perturbation of the in the result (a lower end value when compared with the reference run value). On the other hand, a positive parameter perturbation (+10%) with a positive index stands for a positive end result and with a negative index will return a negative end result, as summarized in the Table 10.

	Positive index Value	Negative Index Value
Negative Variation (-10%)	Negative Impact	Positive Impact
Negative variation (-1076)	Lower value then reference	Larger value then reference
Positive Variation (+10%)	Positive Impact	Negative Impact
	Larger value then reference	Lower value then reference

TABLE 10 - SENSITIVITY INDEX INTERPRETATION ACCORDING TO INDEX SIGNAL AND PARAMETER VARIATION

The models degree of sensitivity (Table 11) towards a given parameter can either be: not sensitive, sensitive, highly sensitive and extremely sensitive; according with their index value. An index greater than 0.1 means that the model is sensitive which implies a change of more than 1% in the results when compared with the reference run. An index larger than 1 represents a change of more than 10% when compared with the reference value and therefore the model is highly sensitive. The model is extremely sensitive when the index is larger than 10, which represents a change of more than 100%. If this index is lower than 0.1 than the model is not sensitive to that parameter variation.

Index result	Sensitivity	Effect on the results
0 - 0.1	Not sensitive	-
0.1 – 1	Sensitive	> 1% change
1 - 10	Highly sensitive	> 10% change
> 10	Extremely sensitive	> 100% change

TABLE 11 - INTERPRETATION OF THE SENSITIVITY INDEX

One downside of a sensitivity analysis is that is also difficult to define the magnitude of the parameter perturbation while avoiding non-realistic values, and covering the actual range of the parameter.

Tables are presented to better understand the model sensitivity, showing colours that reflect the degree of sensitivity: green for a sensitive model, orange for a highly sensitive model and red for an extremely sensitive model to that parameter variation. No colour represents a model which is not sensitive. The signs on that same table also show if the variation of the model is positive or negative.

3.6 WIND COEFFICIENT AND SPILL LOCATION

Wind coefficient and spill location are also parameters found relevant for the oil modelling; the first is a parameter with large uncertainties, it is known that varies from 0.01 to 0.04 (Huang et al. 1982), but its exact value is uncertain. The spill site is also a major source of uncertainties in the first hour after an accident and modellers should know and account for these uncertainties.

A similar analysis to the one explained earlier was performed, varying one parameter at the time, keeping all other values constant, comparing the results with a reference run. The wind coefficient was

varied to 0.02 and 0.04, the spill site was changed one kilometre to the east, west, north and south. Later the results are going to be analysed in the same way as previously described.

3.7 FORCING ANALYSIS

A forcing analysis was carried out in the first scenario and first setting, in the Portuguese coast, in an upwelling event, where the oil slick does not reach the coastline and therefore its movement is not influenced by the shoreline.

To perform this analysis the forcing input meteorological files were modified and multiplied by factors to have a $\pm 20\%$ variation in the components found to be more relevant (listed below). This percentage was chosen due to the fact that it is an error common for the meteorological and wave models. Even though wave models usually have larger error we will assume that they have the same magnitude of error of 20%. This change was done one component at the time keeping all other model parameters unchanged.

The following wind components were changed:

- wind velocity, x component;
- o wind velocity, y component,

and the following wave components:

- wave height;
- wave period.

The evolution of the oil properties and centre of mass evolution with time are the main results to interpret and discuss. Since the sensitivity index is not applicable in this case, the effect on the weathering processes is assessed by calculating the difference to the reference run and simple statistics.

4. RESULTS

4.1 REFERENCE RUN

Two scenarios were used in the Portuguese coast, the first in an upwelling event and second in a westerly wind, both with a 7-day duration. The first occurs from 11th July 2015 to 18th July 2015 as for the second it occurs from 11th September 2015 to 18th September 2015. On the Tagus estuary two scenarios were also proposed: a neap tide scenario and a spring tide scenario, the first occurs from 10th July 2015 to 15th July 2015 and the second from 1st July 2015 to 7th July 2015. This subsection presents the results for the reference simulations for each setting and scenario.

4.1.1 SETTING 1 - SCENARIO 1

For the upwelling event the evolution of properties in time are shown in Figure 14 to Figure 20. As expected, the mass of oil (Figure 14), decreases with time due to weathering processes. Oil volume and total volume (Figure 15) differ because the first refers only to the volume occupied by oil and the second refers to the volume occupied by the oil slick, which can, by the interaction with its surroundings, be composed by oil, and water. So, as expected the total volume is greater than the oil volume, the oil volume tends to decrease due to weathering processes as the total volume increases mainly due to the formation of mousse. This large and sudden increase of total volume is due to the entrainment of water in the oil slick due to emulsion that is very important in the first hours after an oil spill.

The slick area increases with time due to the spreading effect (Figure 16) the opposite happens with the oil slick thickness that decreases with time as the oil slicks spreads out (Figure 17). The effect of weathering processes considered is assessed by comparing the amount of oil mass lost to evaporation and dispersion. As observed in Figure 19 the amount of oil lost to evaporation is several orders of magnitude larger than the amount of oil lost to dispersion. The MWC increases rapidly and stabilizes at its maximum, also showing the relevance of emulsion in the properties of the slick contributing to the large increase in the volume of the spill in the first hours (Figure 18). Both viscosity (Figure 20) and density (Figure 21) increase with time, due to mousse formation.

Figure 22 through Figure 24 show the evolution of the lagrangian tracers in three different instances, at the start of the simulation in the end and an intermediate time. The spreading of the slick is clear and towards south (due to north winds), it also drifts away from the shore due to the upwelling near shore. The slick moves around 200 km south from the spill site and the tracers spread over an area of around 2700 km².

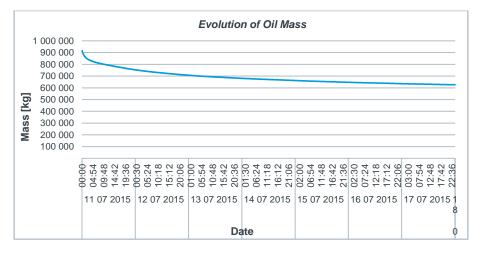


FIGURE 14 - EVOLUTION OF OIL MASS WITH TIME IN SETTING 1 - SCENARIO 1

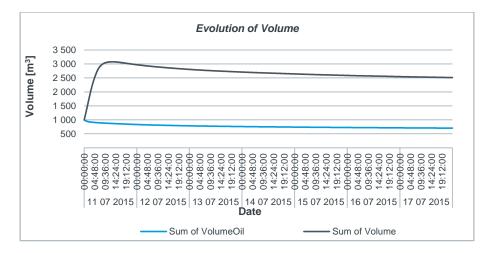


FIGURE 15 - EVOLUTION OF OIL VOLUME WITH TIME IN SETTING 1 - SCENARIO 1

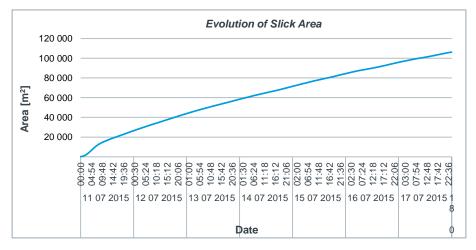


FIGURE 16 - EVOLUTION OF OIL SLICK AREA WITH TIME IN SETTING 1 - SCENARIO 1

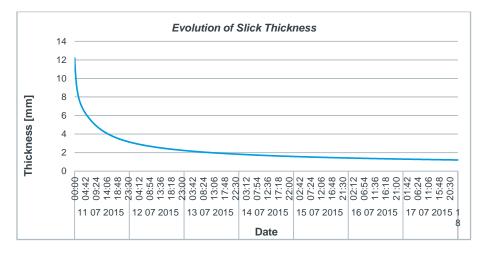


FIGURE 17 - EVOLUTION OF OIL SLICK THICKNESS WITH TIME IN SETTING 1 - SCENARIO 1

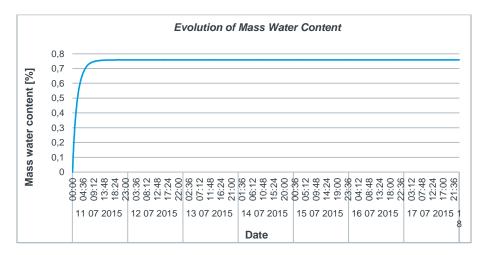


FIGURE 18 - EVOLUTION OF MASS WATER CONTENT WITH TIME IN SETTING 1 - SCENARIO 1

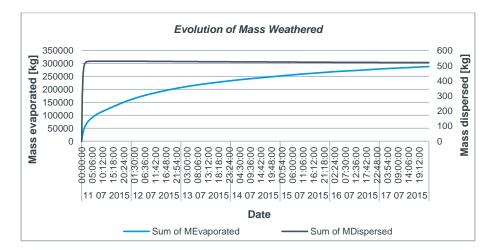


FIGURE 19 - EVOLUTION OF THE WEATHERED MASS, IN SETTING 1 - SCENARIO 1

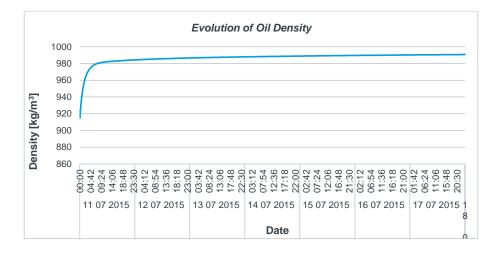


FIGURE 20 - EVOLUTION OF OIL VISCOSITY WITH TIME IN SETTING 1 - SCENARIO 1

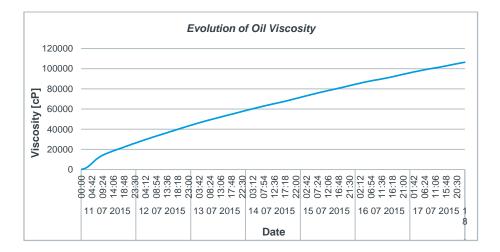


FIGURE 21 - EVOLUTION OF OIL SLICK DENSITY WITH TIME IN SETTING 1 - SCENARIO 1

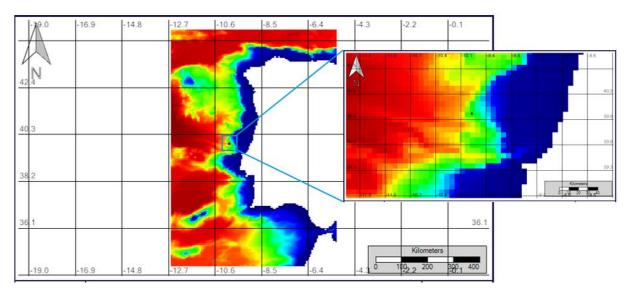


FIGURE 22 - OIL SICK LOCATION ON 11TH JULY

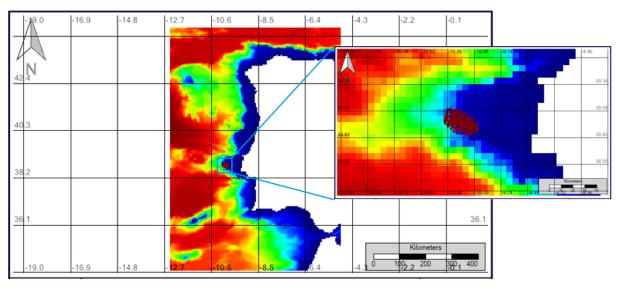


FIGURE 23 - OIL SICK LOCATION ON 14TH JULY

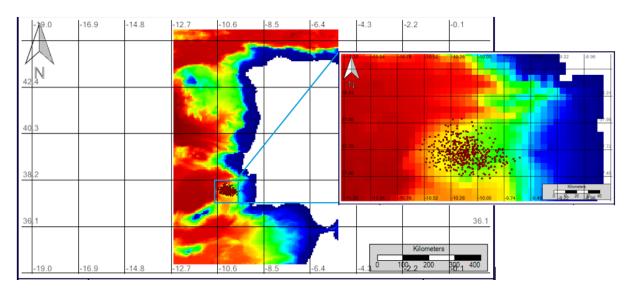


FIGURE 24 -OIL SICK LOCATION ON 18TH JULY

4.1.2 SETTING 1 – SCENARIO 2

Results obtained for this scenario were similar to the results shown in the previous section, with some changes occurring due to the fact that in this scenario the oil beaches, which implies that tracers leave the calculation grid.

For the oil mass (Figure 25) it is observed a decrease due to weathering processes. As total volume increases due to mousse formation and oil volume decreases (Figure 26). These volumes have a sudden drop in the sixth day of simulation (16th September) since the tracers left the calculation grid. Spreading implies an increase in the slick area (Figure 27) and a decrease in its thickness, (Figure 28). Weathering processes such as dispersion and evaporation start right after the spill, the first one being faster and stabilizing later (Figure 29). Evaporation however is several orders or magnitude larger and a much more significant process. Water content (Figure 30) also starts increasing immediately and stabilizes at its maximum value. This process implies mousse formation which increases oil density and viscosity, Figure 31 and Figure 32 respectively.

Figure 33 to Figure 35 shows the evolution of the lagrangian tracers in three different instances, at the start of the simulation in the end and an intermediate time, it can be observed that the slick moves initially to south but as the western wind becomes more relevant oil tracers reach the shoreline, starting at the 15th September and at the end of the time period some tracers are taken back into the ocean. The slick moves 71 km south in this circumstances.

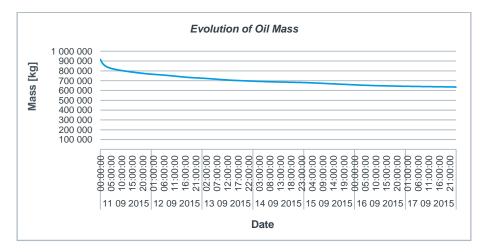
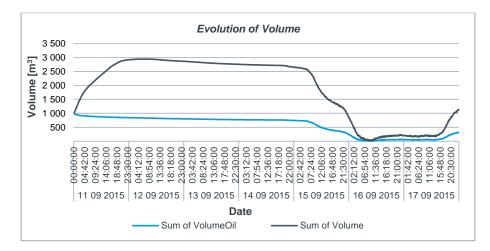


FIGURE 25 - EVOLUTION OF OIL MASS WITH TIME IN SETTING 1 - SCENARIO 2





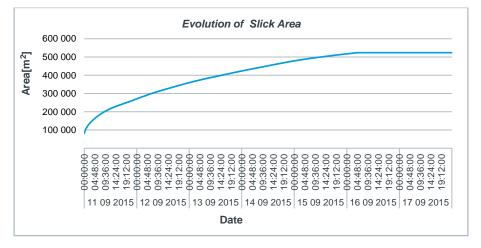


FIGURE 27 - EVOLUTION OF OIL SLICK AREA WITH TIME IN SETTING1 - SCENARIO 2,

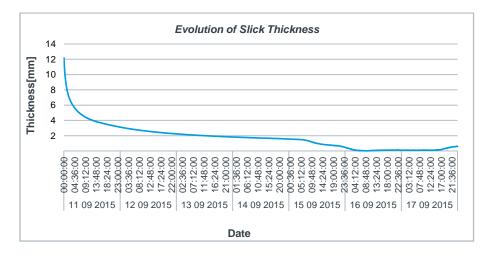


FIGURE 28 - EVOLUTION OF OIL SLICK THICKNESS WITH TIME IN SETTING1 - SCENARIO 2

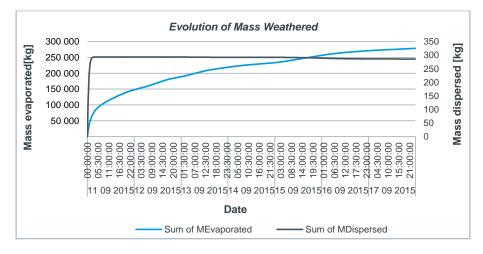


FIGURE 29 - EVOLUTION OF MASS WEATHERED WITH TIME IN SETTING 1 - SCENARIO 2

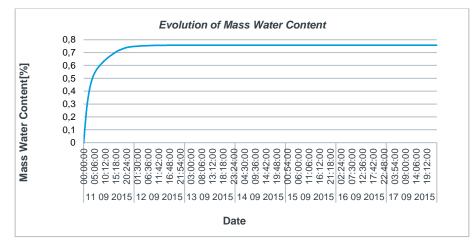


FIGURE 30 - EVOLUTION OF MASS WATER CONTENT WITH TIME IN SETTING 1 - SCENARIO 2

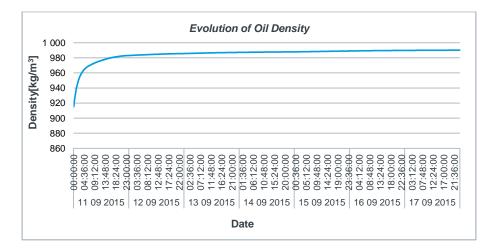


FIGURE 31 - EVOLUTION OF OIL DENSITY WITH TIME IN SETTING 1 - SCENARIO 2

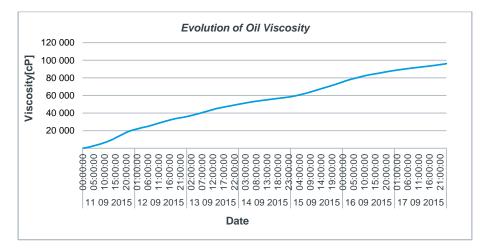


FIGURE 32 - EVOLUTION OF OIL VISCOSITY WITH TIME IN SETTING 1 - SCENARIO 2

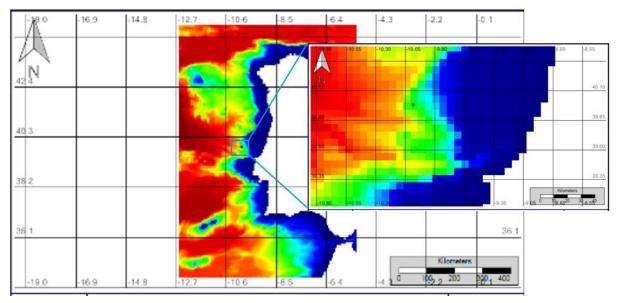


FIGURE 33 – OIL SLICK ON THE 11TH OF SEPTEMBER

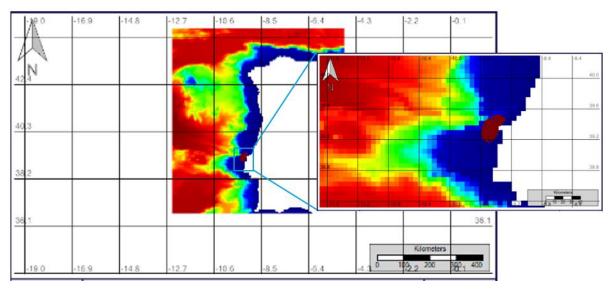


FIGURE 34 – OIL SLICK ON THE 15TH SEPTEMBER

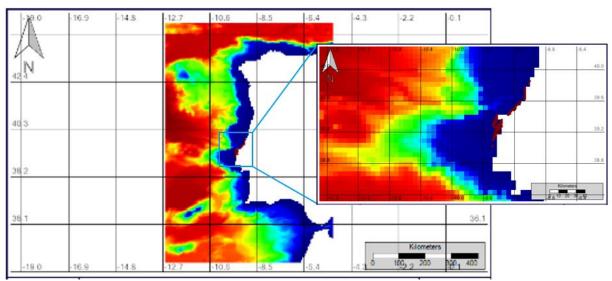


FIGURE 35 - OIL SLICK ON 18TH SEPTEMBER

4.1.3 SETTING 2 - SCENARIO 1

In the Tagus estuary, the first scenario analysed was the neap tide scenario. For this scenario, which occurs between 10th July and 15th of July 2015 the model results show the same behaviour seen in the first setting. Oil mass (Figure 36) decreases slowly due to weathering processes that transfer mass either to the water column either to the air. Emulsification increases the volume of the slick (Figure 37) due to mousse formation, oil volume however decreases as oil is being transferred from the slick. The variations seen on this figure are a result of oil tracers leaving the calculation grid since they reach the shoreline and are trapped. Due to water movement associated with tides some tracers are released back into the river. Area (Figure 38) increases as spreading occurs, which also decreases thickness (Figure 39). Figure 40 shows that evaporation is much more significant than dispersion and that both evaporation and dispersion start immediately after the spill. The MWC increases rapidly after the spill and stabilizes around its maximum value (Figure 41). Density and viscosity increase mainly due to evaporation, Figure 42 and Figure 43 respectively.

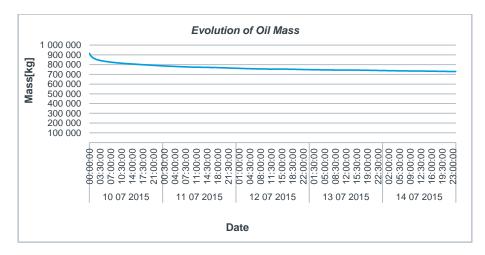


FIGURE 36 - EVOLUTION OF OIL MASS WITH TIME IN SETTING 2 - SCENARIO 1

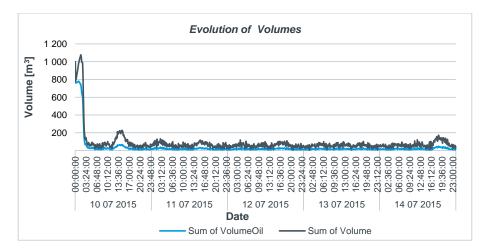


FIGURE 37 - EVOLUTION OF VOLUME WITH TIME IN SETTING 2 - SCENARIO 1

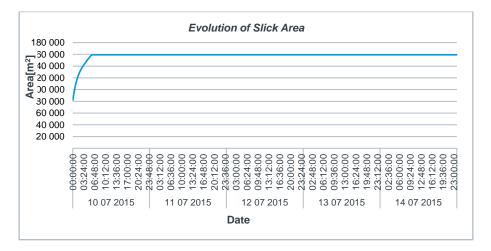


FIGURE 38 - EVOLUTION OF SLICK AREA WITH TIME IN SETTING 2 - SCENARIO 1

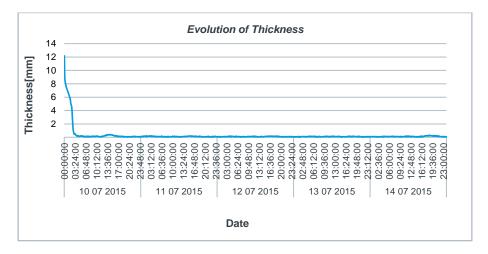


FIGURE 39 - EVOLUTION OF SLICK THICKNESS WITH TIME IN SETTING 2 - SCENARIO 1

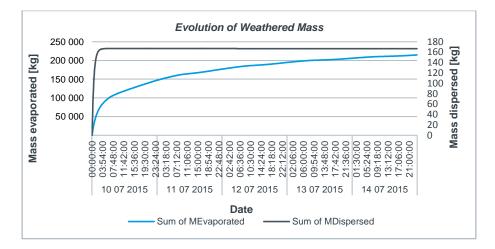


FIGURE 40 - EVOLUTION OF MASS WEATHERED WITH TIME IN SETTING 2 - SCENARIO 1

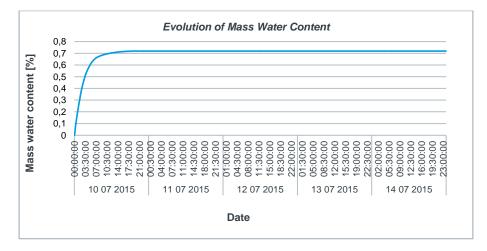


FIGURE 41 - EVOLUTION OF MASS WATER CONTENT WITH TIME IN SETTING 2 - SCENARIO 1

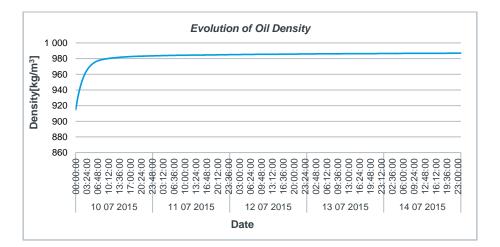


FIGURE 42 - EVOLUTION OF OIL DENSITY WITH TIME IN SETTING 2 - SCENARIO 1

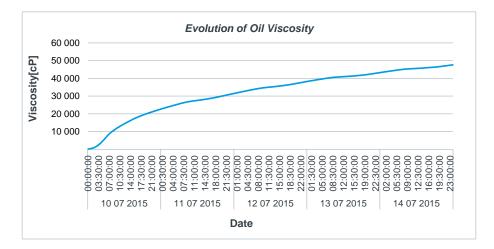


FIGURE 43 - EVOLUTION OF OIL VISCOSITY WITH TIME IN SETTING 2 - SCENARIO 1

4.1.4 SETTING 2 – SCENARIO 2

The spring tide scenario resulted in Figure 44 to Figure 51. The model results in this scenario show great similarity with previous results, all of the properties analysed show the same behaviour. However, it is worth pointing out that the oscillations in these scenarios are larger due to spring tides.

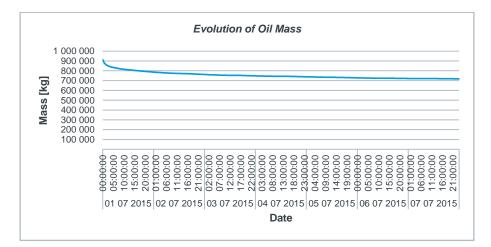


FIGURE 44 - EVOLUTION OF OIL MASS WITH TIME IN SETTING 2 - SCENARIO 2

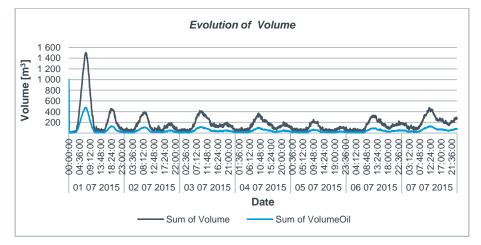


FIGURE 45 - EVOLUTION OF VOLUMES WITH TIME IN SETTING 2 - SCENARIO 2

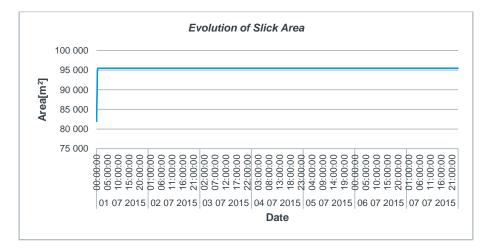


FIGURE 46 - EVOLUTION OF OIL SLICK AREA WITH TIME IN SETTING 2 - SCENARIO 2

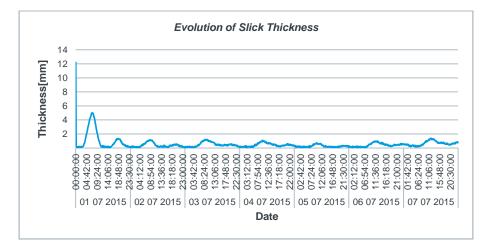
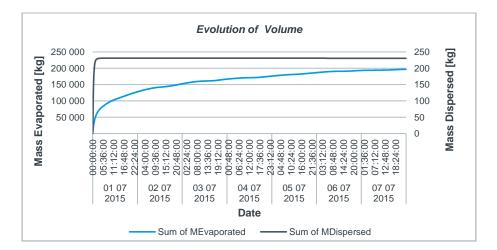


FIGURE 47 - EVOLUTION OF OIL SLICK AREA WITH TIME IN SETTING 2 - SCENARIO 2





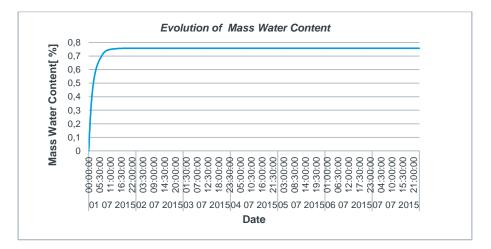


FIGURE 49 - EVOLUTION OF MASS WATER CONTENT MASSES WITH TIME IN SETTING 2 - SCENARIO 2

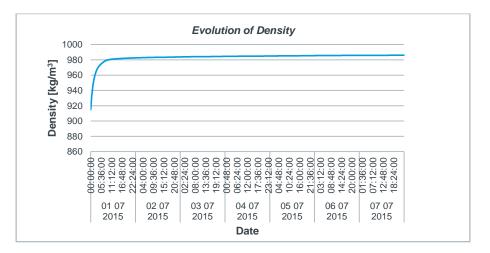


FIGURE 50 - EVOLUTION OF DENSITY WITH TIME IN SETTING 2 - SCENARIO 2

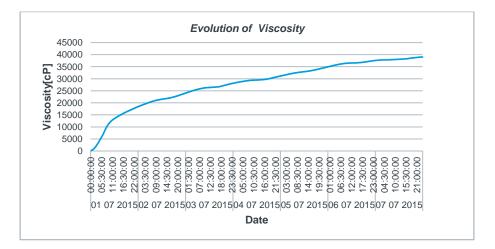


FIGURE 51 - EVOLUTION OF VISCOSITY WITH TIME IN SETTING 2 - SCENARIO 2

4.2 SENSITIVITY ANALYSIS

The sensitivity analysis (S.A) consisted in analysing and summarizing data obtained from the 48 simulations performed, excel and VBA were used to facilitate that task. A clear way to interpret the results is through a sensitivity index. The simple difference between the reference model output and the simulations was also computed and simple statistics presented for the first setting in order to compare these results with the ones from the forcing analysis and wind coefficient and spill location variations.

4.2.1 SETTING 1 - SCENARIO 1

The sensitivity analysis for the Portuguese coast in an upwelling event indicates that the model is most sensitive to changes in API gravity, which affected all the variables analysed. Table 12 shows the results for the sensitive index as for Table 13 shows the same result with a colour scale that indicates the degree of sensitivity of the model and also if the index is positive or negative. Changes of the order of 10% in the reference viscosity parameter also have a significant impact in the model results, mainly the mass of oil dispersed. The remaining perturbations performed did not affect the model results.

It's observed that a positive perturbation in the API gravity parameter has a negative sensitivity index for the following properties: mass oil, volume oil, volume, thickness, mass dispersed and density. This implies that this perturbation has a negative impact on the end result, this is a lower value is obtained when compared with the reference run. Moreover, the same perturbation in the API parameter also results in positive sensitivity index for the following properties: area, mass evaporated, mass water content, and viscosity. Hence, this perturbation has a positive effect in the model results, with higher end values when compared with the reference run.

Additionally, a negative perturbation of the API parameter results in a positive index for the following properties: mass oil, volume oil, volume, thickness, mass dispersed and density, which means a negative perturbation in the result, or a lower value compared with the reference simulation. However, it results in a negative index for the following properties: area, mass evaporated, mass water content, and viscosity. This stands for a positive perturbation in the end result of each property. Each index described before shows that the model is sensitive to a 10% perturbation in the API Gravity, apart from three properties viscosity, thickness and area; the first two are highly sensitive to +/-10% variations and the latter to -10% changes.

The perturbations in reference viscosity show that the model is highly sensitive regarding the mass dispersed and viscosity, indicating that a positive perturbation has a negative perturbation in the result, lower value compared with the reference run, and vice versa. For a negative perturbation properties, such as area, mass evaporated, water content and density were not affected by either of the perturbations on the reference viscosity. The remaining properties were affected positively by the positive variations of the parameter and negatively by negative variations of the parameter, however their sensitive index is very low and the model is found to be not sensitive.

	API g	ravity	Pour	Point	Refer Visco		Re: Con		Satu Con	irate tent	Aspha Con	
	+10%	-10%	+10%	- 10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
MassOil	-0.597	0.622	0	0	0.001	-0.002	0	0	0	0	0	0
VolumeOil	-0.379	0.390	0	0	0.001	-0.002	0	0	0	0	0	0
Volume	-0.379	0.390	0	0	0.001	-0.002	0	0	0	0	0	0
Area	0.832	-1.025	0	0	0	0	0	0	0	0	0	0
Thickness	-1.118	1.577	0	0	0.001	-0.002	0	0	0	0	0	0
MEvaporated	0.835	-0.874	0	0	0	0	0	0	0	0	0	0
MDispersed	-0.887	0.800	0	0	-1.726	2.322	0	0	0	0	0	0
MWaterContent	0.083	-0.085	0	0	0	0	0	0	0	0	0	0
Density	-0.026	0.026	0	0	0	0	0	0	0	0	0	0
Viscosity	3.683	-2.724	0	0	1.000	-1.000	0	0	0	0	0	0

TABLE 12 - SENSITIVITY INDEX FOR THE PORTUGUESE COAST IN AN UPWELLING SCENARIO

TABLE 13 – QUALITATIVE DESCRIPTION OF THE SENSITIVITY ANALYSIS FOR THE PORTUGUESE COAST IN AN UPWELLING SCENARIO (NO COLOUR – NOT SENSITIVE; GREEN – SENSITIVE MODEL; ORANGE – HIGHLY SENSITIVE MODEL | + – POSITIVE SENSITIVITY INDEX; - – NEGATIVE SENSITIVITY INDEX)

	API gr	avity	Pour l	Point	Refer Visco		Res Cont			urate ntent	Asphalt Conte	
	+10%	-10%	+10%	-10%	+10%	-10%	+10%	- 10%	+10 %	-10%	+10%	- 10%
MassOil	-	+			+	-						
VolumeOil	-	+			+	-						
Volume	-	+			+	-						
Area	+	-										
Thickness	-	+			+	-						
MEvaporated	+	-										
MDispersed	-	+			-	+						
MWaterContent	+	-										
Density	-	+										
Viscosity	+	-			+	-						

As observed in Table 14 most of the parameters did not affect the models results, namely variations in pour point, resin content, saturate and asphaltenes content. The parameters that affect the model behaviour are API gravity and reference viscosity, as seen in the sensitivity analysis. API gravity has an impact on all the variables and reference viscosity influenced oil mass, volume oil, volume, mass dispersed and viscosity.

The analysis of the evolution of the centre of mass shows very little impact on the trajectory of the spilled oil (Table 15), and only with the API variation. All other parameters did not affect the position of the centre of mass.

		∆M Oil	∆VOil	∆Vol	∆Area	∆Thick	∆M Evap	∆M Disp	∆MWC	∆Density	∆Viscosit y
API	Avg	-34184	-23.25	-82.35	29887	-0.19	20861	-46.83	0.01	-2.8	20732
+10%	Std Dev	3116	3.36	14.3	12015	0.06	3117	2.37	0	0.8	11251
API	Avg	34698	23.01	81.55	-36538	0.25	-20967	41.81	-0.01	2.91	-15325
-10%	Std Dev	3463	3.69	15.21	15103	0.07	3464	2.22	0	0.83	8177
PPoint	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
PPoint	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
RefVis	Avg	90	0.1	0.34	0	0	0	-89.97	0	0	6231
+10%	Std Dev	3	0	0.03	0	0	0	3.41	0	0	2874
RefVis	Avg	-121	-0.13	-0.46	0	0	0	120.96	0	0	-6231
-10%	Std Dev	5	0	0.04	0	0	0	4.58	0	0	2874
ResC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
ResC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
SatC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
SatC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
AsphC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
AsphC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0

TABLE 14 -STATISTICS FOR THE DIFFERENCES BETWEEN THE SIMULATIONS AND THE REFERENCE. UPWELLING SCENARIO

TABLE 15 - STATISTICS CONCERNING THE EVOLUTION OF CENTRE OF MASS, IN DEGREES. UPWELLING SCENARIO

		AF	P	Pour	Point	Refer Visco		Re: Con		Satu Cont		Aspha Con	
		+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
Ava	Lat	0	0	0.001	0.001	0	0	0	0	0	0	0	0
Avg	Long	0.001	0	0.001	0.001	0	0	0	0	0	0	0	0
Std	Lat	0	0	0.001	0.001	0	0	0	0	0	0	0	0
Dev	Long	0.001	0	0.001	0.001	0	0	0	0	0	0	0	0

4.2.2 SETTING 1 - SCENARIO 2

For a western wind scenario, it is observed that the API gravity parameter still has the higher impact on all of the models output analysed, changes in the reference viscosity also had impact but on fewer variables (Table 16 and Table 17). All other parameter variations showed no impact on the model results.

Positive variations of the API gravity resulted in a negative sensitivity index for oil mass, oil volume and total volume, thickness, mass dispersed and density, which means it had a negative impact on the model result. Slick area, mass evaporated, mass water content and viscosity showed a positive end result, given by a positive sensitivity index. Oil volume, total volume, thickness, mass dispersed and viscosity are highly sensitive, and mass oil, area and MWC are sensitive to this variation. A negative perturbation of the API gravity shows a sensitive model regarding oil mass, mass dispersed, oil volume, total volume, area and mass evaporated; viscosity was highly sensitive to this variation. A -10% variations resulted in a negative perturbation in the output for total volume and oil volume, area, mass evaporated, MWC and viscosity; mass oil, thickness, mass dispersed and density had a higher end value when compared with the reference run.

Changes in the reference viscosity had a much smaller impact, only the mass dispersed and viscosities where found to be highly sensitive to these variations, all other variables were not sensitive. The mass dispersed showed a negative sensitivity index for a positive parameter perturbation and a positive index for a negative perturbation. The opposite occurred for viscosity.

	API g	ravity	Pour	Point		rence osity		sin Itent		irate tent		altenes ntent
	10%	-10%	10%	-10%	10%	-10%	10%	-10%	10%	-10%	10%	-10%
MassOil	-0.577	0.587	0.00	0.00	0.001	-0.001	0.00	0.00	0.00	0.00	0.00	0.00
VolumeOil	-1.454	-0.870	0.00	0.00	0.001	-0.001	0.00	0.00	0.00	0.00	0.00	0.00
Volume	-1.454	-0.870	0.00	0.00	0.001	-0.001	0.00	0.00	0.00	0.00	0.00	0.00
Area	0.757	-0.922	0.00	0.00	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
Thickness	-2.055	0.057	0.00	0.00	0.000	-0.001	0.00	0.00	0.00	0.00	0.00	0.00
MEvaporated	0.837	-0.845	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MDispersed	-1.009	0.917	0.00	0.00	-1.730	2.327	0.00	0.00	0.00	0.00	0.00	0.00
MWaterContent	0.0808	-0.083	0.00	0.00	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
Density	-0.026	0.027	0.00	0.00	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
Viscosity	3.556	-2.586	0.00	0.00	1.000	-1.000	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 16 - SENSITIVITY INDEX FOR THE PORTUGUESE COAST IN A WESTERN WIND SCENARIO

Regarding the changes with the reference run, Table 18 confirms the analysis shown before, that the API parameter has impact on all analysed outputs and that the reference viscosity also changes some variables.

Table 19 shows the changes of evolution in the centre of mass with each variation, the changes analysed in this scenario had no significant impact on the trajectory of the oil spill.

 TABLE 17 - QUALITATIVE DESCRIPTION OF THE SENSITIVITY ANALYSIS FOR THE PORTUGUESE COAST IN AN WESTERN WIND SCENARIO

 (NO COLOUR - NOT SENSITIVE; GREEN - SENSITIVE MODEL; ORANGE - HIGHLY SENSITIVE MODEL | + - POSITIVE SENSITIVITY INDEX; - - NEGATIVE SENSITIVITY INDEX)

	API g	ravity	Pour	Point		rence cosity		sin Itent		urate Itent	-	altenes ntent
	10%	-10%	1 0 %	-10%	10%	-10%	10%	-10%	10%	-10%	10%	-10%
MassOil	-	+			+	-						
VolumeOil	-	-			+	-						
Volume	-	-			+	-						
Area	+	-										
Thickness	-	+			+	-						
MEvaporated	+	-										
MDispersed	-	+			-	+						
MWaterContent	+	-										
Density	-	+										
Viscosity	+	-			+	-						

TABLE 18 - STATISTICS FOR THE DIFFERENCES BETWEEN THE SIMULATIONS AND THE REFERENCE, WESTERN WIND SCENARIO

		∆M Oil	∆VOil	ΔVol	∆Area	∆Thick	∆M Evap	∆M Disp	∆MWC	∆Density	∆Viscosity
API	Avg	-33398	-17.92	-61.94	28441	-0.14	20058	-29.69	0.01	-2.97	17294
+10%	Std Dev	3073	8.88	32.75	10425	0.09	3073	1.83	0	1.03	10289
API	Avg	33765	13.49	46.24	-34433	0.17	-20020	26.94	-0.01	3.09	-12814
-10%	Std Dev	3302	11.49	41.16	12934	0.12	3302	1.73	0	1.08	7440
PPoint	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
PPoint	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
RefVis	Avg	50	0.04	0.13	0	0	0	-49.65	0	0	5392
+10%	Std Dev	2	0.02	0.07	0	0	0	2.31	0	0	2755
RefVis	Avg	-67	-0.05	-0.17	0	0	0	66.73	0	0	-5392
-10%	Std Dev	3	0.03	0.1	0	0	0	3.1	0	0	2755
ResC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
ResC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
SatC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
SatC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0
AsphC	Avg	0	0	0	0	0	0	0	0	0	0
+10%	Std Dev	0	0	0	0	0	0	0	0	0	0
AsphC	Avg	0	0	0	0	0	0	0	0	0	0
-10%	Std Dev	0	0	0	0	0	0	0	0	0	0

		Α	PI	Pour	Point	Refer Visco		-	sin Itent	Satu Con		Aspha Con	
		+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
Δνα	LAT	0	0	0	0	0	0	0	0	0	0	0	0
Avg	LONG	-0.001	-0.001	0	0	0	0	0	0	0	0	0	0
STD	LAT	0.001	0	0	0	0	0	0	0	0	0	0	0
DEV	LONG	0.001	0.001	0	0	0	0	0	0	0	0	0	0

TABLE 19 - STATISTICS CONCERNING THE EVOLUTION OF THE CENTRE OF MASS, IN DEGREES. WESTERN WIND SCENARIO

4.2.3 SETTING 2 - SCENARIO 1

A similar analysis was also carried out in the Tagus estuary and the results for the sensitivity index for scenario one and two are shown quantitatively in Table 20 and qualitatively in Table 21.

The sensitive analysis for the neap tide scenario shows that: the model is sensitive to a positive perturbation of the API gravity, namely for mass oil, area, thickness, mass evaporated; the model is highly sensitive for volume, oil volume, thickness, mass dispersed and viscosity. Mass dispersed and density (for API variations) and mass oil, mass evaporated, MWC and density (for reference viscosity variations) have shown a very small impact and therefore the model is found to be not sensitive for these variable.

A positive perturbation resulted in a negative sensitivity index, which meant that it had a negative effect on: mass oil, mass dispersed and density properties. On the other hand, it had a positive sensitive index for the following properties: volume, volume oil, area, thickness, mass evaporated, mass water content and viscosity. This means that for these properties the positive parameter perturbation had a positive end result.

When the API gravity was perturbed by -10% the following properties were not sensitive to the perturbation: area, water content, density. The model is sensitive to changes in the API gravity for the properties: mass oil, volume, volume oil, thickness, mass evaporated, mass dispersed and highly sensitive to viscosity. This negative perturbation results in a positive sensitivity index for the mass oil, volume oil and volume, area, mass dispersed and density, which results on a lower value then the reference run. The remaining properties have a negative sensitivity index, meaning a higher value when compared with the reference run.

The positive perturbation of the reference viscosity parameter showed a highly sensitive model for the volume oil, volume, thickness, mass dispersed and viscosity; all other properties apart from the area showed some perturbation, but in very small scales. A positive index was obtained for the mass of oil, volume, oil volume, thickness, mass evaporated, water content, density and viscosity. These results showed a higher end result when compared with the reference. The mass dispersed had a negative index, meaning lower results and the area showed no alteration.

A negative perturbation of the reference viscosity showed that the oil volume, volume, thickness, were extremely sensitive; MWC and viscosity were found to be highly sensitive; mass evaporated was sensitive. The remaining properties showed a very small impact by this variation so the model is not sensitive to ten percent variations, apart from the area which showed no impact. The oil mass, oil volume, volume and mass dispersed have a positive sensitivity index for a negative perturbation of the

parameter, which means they have a lower end value compared with the reference. The mass evaporated, water content, density and viscosity have a negative index value, which shows that the end result is higher than the reference run.

	API g	ravity	Pour	Point		rence osity	Re: Con		Satu Con		Aspha Con	
	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
MassOil	-0.476	0.455	0	0	0	0.031	0	0	0	0	0	0
VolumeOil	2.367	0.847	0	0	4.146	11.520	0	0	0	0	0	0
Volume	2.367	0.847	0	0	4.146	11.520	0	0	0	0	0	0
Area	0.579	0.007	0	0	0	0	0	0	0	0	0	0
Thickness	1.690	0.840	0	0	4.146	11.520	0	0	0	0	0	0
MEvaporated	0.928	-0.840	0	0	0	-0.104	0	0	0	0	0	0
MDispersed	-1.068	0.662	0	0	-1.717	2.316	0	0	0	0	0	0
MWaterContent	0.081	-0.085	0	0	0	0	0	0	0	0	0	0
Density	-0.028	0.030	0	0	0	-0.001	0	0	0	0	0	0
Viscosity	2.916	-2.048	0	0	1.000	-1.217	0	0	0	0	0	0

TABLE 20 - SENSITIVITY INDEX FOR THE TAGUS ESTUARY IN AN NEAP TIDE SCENARIO

 TABLE 21 - QUALITATIVE DESCRIPTION OF THE SENSITIVITY ANALYSIS FOR THE TAGUS ESTUARY IN AN NEAP TIDE SCENARIO (NO

 COLOUR - NOT SENSITIVE; GREEN - SENSITIVE MODEL; ORANGE - HIGHLY SENSITIVE MODEL; RED - EXTREMELY SENSITIVE MODEL | +

 POSITIVE SENSITIVITY INDEX; - NEGATIVE SENSITIVITY INDEX)

	API gr	avity	Pour	Point	Refer Visco		Res Con		Satu Con		Aspha Con	
	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
MassOil	-	+			+	+						
VolumeOil	+	+			+	+						
Volume	+	+			+	+						
Area	+	+										
Thickness	+	+			+	+						
MEvaporated	+	-			+	-						
MDispersed	-	+			-	+						
MWaterContent	+	-			+	-						
Density	-	+			+	-						
Viscosity	+	-			+	-						

4.2.4 SETTING 2 – SCENARIO 2

For the spring tides scenario, similar results were observed (Table 22 and Table 23). Positive variations in the API parameter resulted in negative sensitivity indexes for: mass oil, volume oil, volume, thickness, mass dispersed and density; and positive indexes for area, mass evaporated, water content and viscosity. The first set of properties have a negative end result, meaning lower value compared with the reference run and vice versa for the second set of properties. This model was found to be sensitive

in regards to the mass oil, volume, oil volume and mass dispersed; highly sensitive in regards to the area, thickness, mass evaporated and viscosity.

For negative perturbations of the API parameter a positive sensitivity index was obtained for the mass oil, volume oil, volume, thickness, mass dispersed and density and negative indexes for area, mass evaporated, water content and viscosity. And for mass oil, volume, oil volume, area and mass dispersed the model is sensitive; for thickness, mass evaporated and viscosity is highly sensitive. A positive index, means a negative perturbation in the result and a lower value compared with the reference run. As a negative perturbation index and a positive perturbation in the end result of the property and a higher value comparing with reference run.

Positive 10% variations in the reference viscosity resulted in positive sensitivity indexes for the volume, volume oil, thickness, mass evaporated, water content, density and viscosity that stand for a positive perturbation of the end results; and a negative sensitivity index for the mass oil and mass dispersed. The model was found to be highly sensitive with regards to volume oil and volume, thickness, mass dispersed and viscosity. The area did not change with these variations.

For negative variations of the reference viscosity the following properties resulted in a positive sensitivity index: volume, volume oil, thickness, mass evaporated, mass dispersed and density. And mass oil, water content and viscosity resulted in a negative sensitivity index. The model was found to be sensitive to viscosity and highly sensitive in volume and volume oil, thickness and mass dispersed

	API gi	ravity	Pour	Point	Refer Visco		Res Con		Satu Con		Aspha Con	
	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
MassOil	-0.526	0.485	0	0	-0.020	-0.016	0	0	0	0	0	0
VolumeOil	-0.144	0.587	0	0	1.959	2.132	0	0	0	0	0	0
Volume	-0.144	0.587	0	0	1.959	2.132	0	0	0	0	0	0
Area	1.213	-0.952	0	0	0	0	0	0	0	0	0	0
Thickness	-1.210	1.701	0	0	1.959	2.132	0	0	0	0	0	0
MEvaporated	1.210	-1.043	0	0	0.073	0.054	0	0	0	0	0	0
MDispersed	-0.801	0.576	0	0	-1.711	2.293	0	0	0	0	0	0
MWaterContent	0.081	-0.084	0	0	0	0	0	0	0	0	0	0
Density	-0.026	0.028	0	0	0.001	0.001	0	0	0	0	0	0
Viscosity	3.512	-2.268	0	0	1.178	-0.894	0	0	0	0	0	0

TABLE 22 - SENSITIVITY INDEX FOR THE TAGUS ESTUARY IN AN NEAP TIDE SCENARIO SPRING TIDES

TABLE 23 - QUALITATIVE DESCRIPTION OF THE SENSITIVITY ANALYSIS FOR THE TAGUS ESTUARY IN A SPRING TIDE SCENARIO (NO COLOUR – NOT SENSITIVE; GREEN – SENSITIVE MODEL; ORANGE – HIGHLY SENSITIVE MODEL | + – POSITIVE SENSITIVITY INDEX; - – NEGATIVE SENSITIVITY SENSITIVITY INDEX)

	API gr	avity	Pour	Point	Refer Visco		Res Con		Satu Cont		Aspha Con	
	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%	+10%	-10%
MassOil	-	+			-	-						
VolumeOil	-	+			+	+						
Volume	-	+			+	+						
Area	+	-										
Thickness	-	+			+	+						
MEvaporated	+	-			+	+						
MDispersed	-	+			-	+						
MWaterContent	+	-			+	-						
Density	-	+			+	+						
Viscosity	+	-			+	-						

4.3 WIND COEFFICIENT AND SPILL LOCATION

The following analysis was made to complement the Sensitivity Analysis performed previously; it consists of analysing two extra models inputs that may influence the model output, namely wind coefficient and spill location. The first was 0.3 in the reference run and was varied to 0.2 and 0.4, the variations in spill location were of 1km north, south, east and west. The difference between the model outputs presented earlier and the reference simulations was calculated in combination with simple statistics. The evolution of the centre of mass and the influence on the trajectory was also analysed.

In these simulations, the impact on the variables studied in the sensitivity analysis was also analysed. Table 24 shows that all the variations performed had an impact on the model results. Overall changes in the wind coefficient to 0.02 implies the most changes in the studied variable, being the most relevant variation for mass oil, volume, volume oil, area, mass evaporated, density and viscosity. Changes in spill location of 1km to the east were also significant, leading to the most changes in mass dispersed and mass water content, this may be due to changes in the circulation of the currents closer to shore.

Table 25 shows that wind coefficient is the model parameter that has a greater influence, with a coefficient of 0.02 resulting in average changes of around 0.232 degrees in latitude and 0.022 degrees in longitude. A coefficient of 0.04 results in changes of 0.221 degrees in latitude and 0.016 degrees in longitude. Other changes in the spill location also had an impact on the trajectory of the spilled oil but in smaller scales.

The graphs below (Figure 52 to Figure 55) show the evolution of the coordinates of the centre of mass for this scenario. They also confirm that the difference between the simulations where the wind coefficient was changed and the reference is greater than with the changes in discharge location.

		ΔM Oil	ΔVOil	ΔVol	ΔArea	ΔThick	∆M Evap	ΔM Disp	ΔMWC	ΔDens	ΔVisc
Wind C	Avg	157	0,16	0,46	185	0	-157	-0,21	0	-0,01	-205
0,02	Std Dev	466	0,47	1,77	432	0	466	0,16	0	0,02	481
Wind C	Avg	29	0,03	0,21	-5,47	0	-29,3	0,26	0	0,00	5,33
0,04	Std Dev	157	0,16	0,71	127	0	157	0,06	0	0,01	141
1Km	Avg	73,7	0,07	0,01	79,4	0	-71,6	-2,11	0	-0,01	-84,9
North	Std Dev	163	0,16	1,21	160	0	163	0,09	0	0,02	179
1Km	Avg	25,2	0,03	0,35	16,8	0	-27,3	2,10	0	0,00	-22,5
South	Std Dev	34,3	0,03	1,00	43,8	0	34,0	0,06	0	0,02	41,4
1Km	Avg	109	0,12	0,82	91,4	0	-112	2,99	0	0,00	-108
East	Std Dev	159	0,16	1,68	171	0	159	0,12	0	0,03	183
1Km	Avg	30,7	0,02	-0,30	43,3	0	-27,6	-3,15	0	-0,01	-42,1
West	Std Dev	95,2	0,09	1,75	93,0	0	95,2	0,10	0	0,03	99,4

TABLE 24 - STATISTICS FOR THE DIFFERENCES BETWEEN THE SIMULATIONS AND THE REFERENCE, WIND AND SPILL SITE

TABLE 25 - STATISTICS CONCERNING THE EVOLUTION OF THE CENTRE OF MASS, IN DEGREES.

		WindC 0,02	WindC 0,04	1km North	1km South	1km East	1km West
Ava	Lat	0.232	-0.221	0.007	-0.011	-0.006	0.007
Avg	Long	0.022	0.016	0.004	0.00	0.002	0.012
Std	Lat	-0.139	0.127	0.003	0.001	0.014	0.003
Deviation	Long	0.03	0.022	0.003	0.002	0.003	0.001

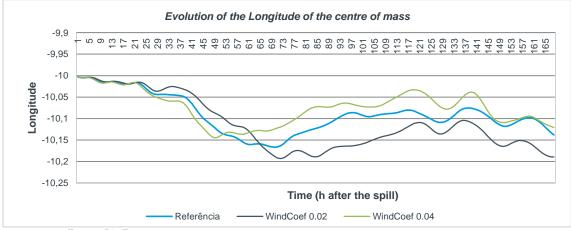


FIGURE 52- EVOLUTION OF THE CENTRE OF MASS LONGITUDE IN THE WIND COEFFICIENT ANALYSIS.

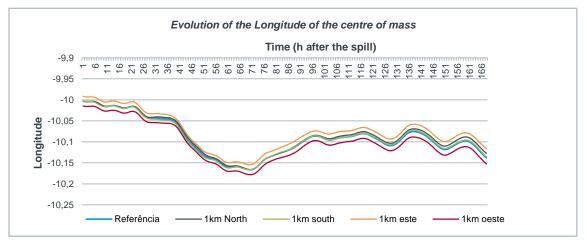


FIGURE 53 - EVOLUTION OF THE CENTRE OF MASS LONGITUDE IN THE SPILL SITE ANALYSIS.

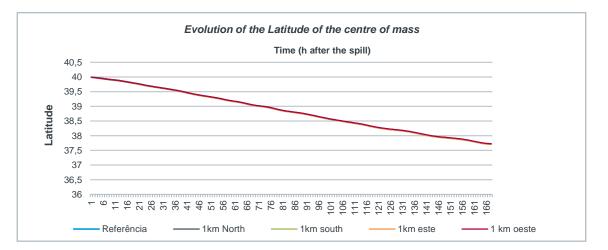


FIGURE 54 - EVOLUTION OF THE CENTRE OF MASS LATITUDE IN THE ANALYSIS TO SPILL SITE.

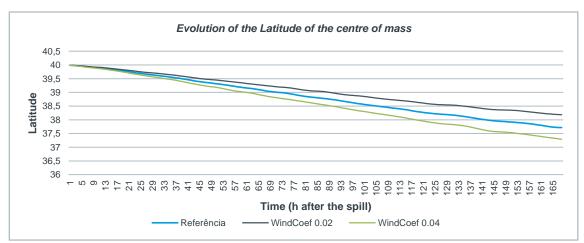


FIGURE 55 - EVOLUTION OF THE CENTRE OF MASS LATITUDE IN THE ANALYSIS TO WIND COEFFICIENT.

Figure 56 through Figure 58 show the evolution of the lagrangian tracers in three different instances, at the start of the simulation in the end and an intermediate time, comparing the different simulations performed for wind coefficient.

Figure 59 to Figure 61 show the results for the same time period but for changes in spill location. The results obtained by analysing the centre of mass are confirmed, showing that the wind coefficient has the most significant impact. Wind coefficient changed the result in a total distance travelled by oil around 180 km and 270 kilometres for wind coefficient equal to 0.02 and 0.04 respectively, a difference of around -10% and +35% from the reference. Changes in spill site resulted in smaller changes in the trajectory, in the last time presented the slicks are almost overlapped.

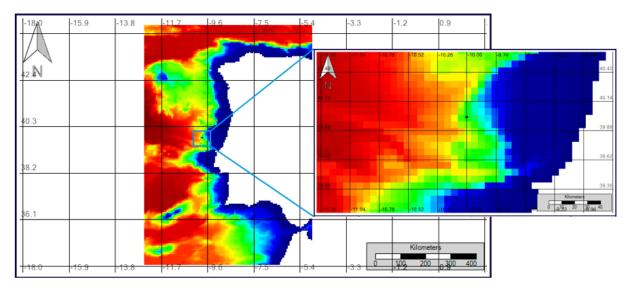


FIGURE 56 – OIL SLICK LOCATION FOR WIND COEFFICIENT ON THE 11TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WIND COEFFICIENT 0.02; BLACK – WIND COEFFICIENT 0.04)

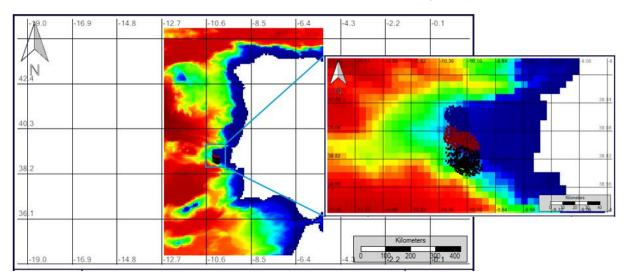


FIGURE 57 - OIL SLICK LOCATION FOR WIND COEFFICIENT ON THE 14TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WIND COEFFICIENT 0.02; BLACK – WIND COEFFICIENT 0.04)

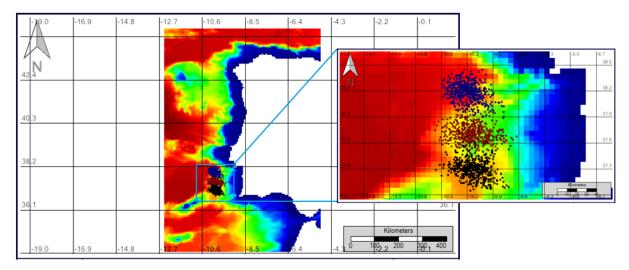


FIGURE 58 – OIL SLICK LOCATION FOR WIND COEFFICIENT ON THE 18TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WIND COEFFICIENT 0.02; BLACK – WIND COEFFICIENT 0.04)

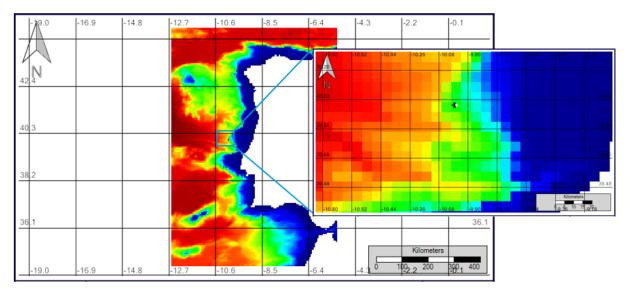


FIGURE 59 - OIL SLICK LOCATION FOR SPILL LOCATION ON THE 11TH JULY (BROWN – REFERENCE RUN; DARK BLUE –1KM NORTH; BLACK – 1 KM SOUTH; WHITE – 1 KM EAST; GREEN – 1 KM WEST)

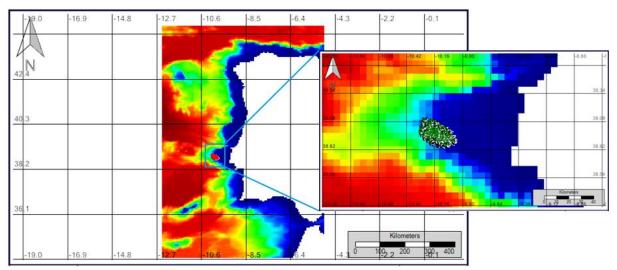


Figure 60 - Oil slick location for spill location on the 14th July (Brown – reference run; Dark blue –1km north; Black – 1 km south; White – 1 km east; Green – 1 km west)

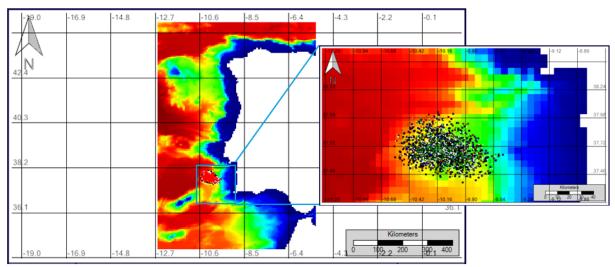


Figure 61 - Oil slick location for spill location on the 18^{TH} July (Brown – reference run; Dark blue –1km north; Black – 1 km south; White – 1 km east; Green – 1 km west)

4.4 FORCING ANALYSIS

An identical analysis as the one presented in the previous section was carried out for the changes in wind and wave forcing, namely on the x and y components of wind velocity and on wave height and period.

Changes in wind and wave forcing showed an impact on the outputs studied in the sensitivity analysis (Table 26), apart from negative perturbation of the wave height. The simulations that had the greatest impact were in the y component of the wind velocity, $\pm 20\%$ variations were the ones that changed the results the most, since in this scenario the wind is mainly from the north, apart from the mass dispersed that was influenced the most by negative variations of the y component of wind velocity and negative variations of wave period.

The centre of mass analysis (Table 27 and Table 28) shows that the y component of the wind velocity is the most significant one. When increased by 20% it has an average impact of -0.132 degrees in latitude, when it is varied by -20% it has an impact of 0.138 degrees. Wave forcing was found more significant with variations of wave height, resulting in -0.078 degrees' variations in latitude when varied +20% and 0.149 degrees in longitude.

Figure 62 through Figure 65 show the impact of wind and wave forcing in the longitude and latitude of the centre of mass, they confirm the results seen before, that both wind and wave forcing have a significant impact on the trajectory of the spill, mainly in the longitude. The impact is noted mainly in longitude as the prevailing wind is from the north, which also explains the greater significance of the y component of wind velocity.

Figure 66 to Figure 68 show the evolution of the lagrangian tracers in three different instances of the spill, at the start of the simulation (11th July) in the end (18th July) and an intermediate time (14th July), comparing the different simulations performed for the assessment of wind forcing. Figure 69 through Figure 71 shows the same results with regards to wave forcing. It can be observed that both wind and wave forcing had a significant impact on the slick, as stated by the statistics of the evolution of the centre of mass, wind forcing was found to be more relevant, namely the y component of wind velocity due to the importance of northern winds.

		ΔM Oil	ΔVOil	ΔVol	∆Area	ΔThick	∆M Evap	ΔM Disp	ΔMWC	ΔDens	∆Visc
Windx	Avg	-36.3	-0.03	-0.01	-30.7	0	35.7	0.61	0	0	32.4
+20%	Std Dev	30.4	0.03	0.46	31.2	0	30.5	0.02	0	0.01	35.3
Windx	Avg	32.0	0.03	0.01	27.6	0	-31.5	-0.50	0	0	-29.2
-20%	Std Dev	31.0	0.03	0.39	31.7	0	31.0	0.02	0	0.01	35.8
Windy	Avg	-5669	-5.34	-3.99	-417	0.02	5619	49.7	0	0.47	4521
+20%	Std Dev	1755	1.75	67.7	1850	0.06	1756	2.94	0.01	0.82	2235
Windy	Avg	6698	6.28	-2.40	5094	-0.02	-6565	-133	-0.01	-0.64	-5087
-20%	Std Dev	2362	2.36	93.4	2267	0.08	2363	4.25	0.02	1131	2512
Wave height	Avg	-200	-0.21	-0.69	-111	0	79.1	121	0	0.01	125
+20%	Std Dev	369	0.37	1.37	337	0	370	4.59	0	0.02	378
Wave height	Avg	0	0	0	0	0	0	0	0	0	0
-20%	Std Dev	0	0	0	0	0	0	0	0	0	0
Wave p.	Avg	210	0.22	0.75	130	0	-122	-87.30	0	-0.01	-144
+20%	Std Dev	304	0.31	1.11	295	0	304	3.31	0	0.02	328
Wave p.	Avg	-94.2	-0.10	-0.33	16.2	0	-36.8	131	0	0	-18.2
-20%	Std Dev	72.8	0.07	0.29	56.0	0	73.1	4.95	0	0	62.2

TABLE 26 – STATISTICS FOR THE DIFFERENCES BETWEEN THE SIMULATIONS AND THE REFERENCE, FORCING ANALYSIS

TABLE 27 - STATISTICS CONCERNING THE CENTRE OF MASS, DEGREES, WIND FORCING

	Windx +20 Latitude Longitude		Win	Windx-20		ly+20	Windy-20		
			Latitude	Longitude	Latitude	Longitude	Latitude	Longitude	
Avg	-0.002	0.010	-0.001	-0.001	-0.132	0.009	0.138	-0.003	
Std Dev	0.002	0.008	0.002	0.004	0.076	0.014	0.083	0.015	

TABLE 28 - STATISTICS CONCERNING THE CENTRE OF MASS, DEGREES, WAVE FORCING

		Wave height +20		Wave height -20		Peak p	eriod +20	Peak period -20		
_		Latitude	Longitude	Latitude	Longitude	Latitude	Longitude	Latitude	Longitude	
ĺ	Avg	-0.078	0.149	0.00011	-0.00002	0.025	-0.051	-0.041	0.081	
	Std Dev	0.053	0.105	0.00005	0.00003	0.014	0.033	0.026	0.056	

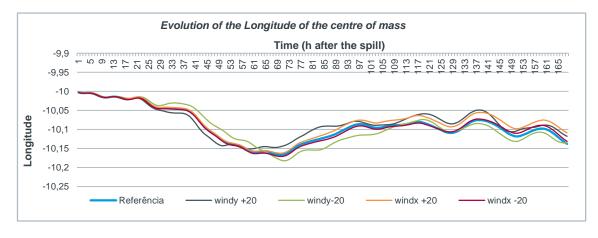


FIGURE 62 - EVOLUTION OF THE CENTRE OF MASS LONGITUDE IN THE WIND FORCING ANALYSIS.

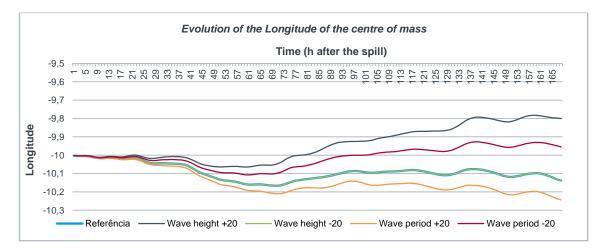


FIGURE 63 - EVOLUTION OF THE CENTRE OF MASS LONGITUDE IN THE WAVE FORCING ANALYSIS.

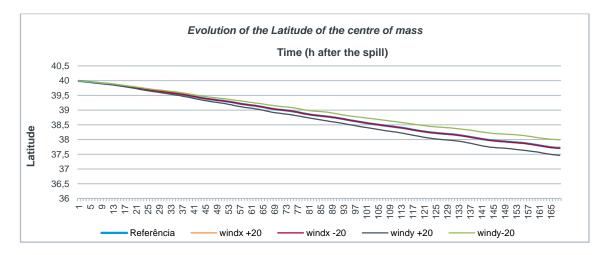


FIGURE 64- EVOLUTION OF THE CENTRE OF MASS LATITUDE IN THE WIND FORCING ANALYSIS.

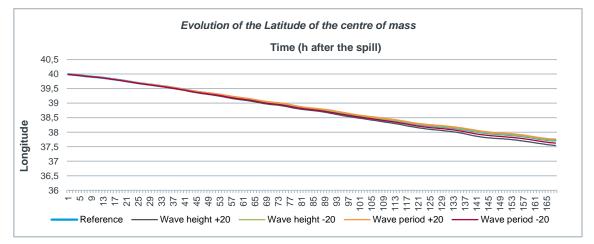


FIGURE 65 - EVOLUTION OF THE CENTRE OF MASS LATITUDE IN THE WAVE FORCING ANALYSIS.

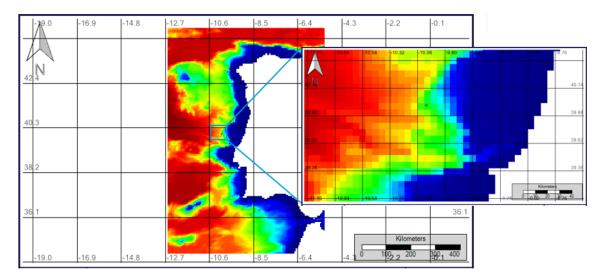


FIGURE 66 - OIL SICK LOCATION FOR WIND FORCING ANALYSIS ON THE 11TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WINDX +20; BLACK – WINDX -20; WHITE – WINDY +20; RED – WINDY -20)

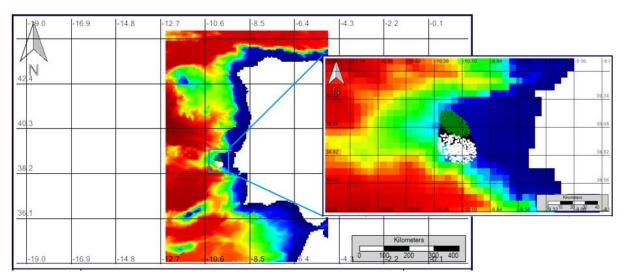


FIGURE 67 - OIL SICK LOCATION FOR WIND FORCING ANALYSIS ON THE 14[™] JULY (BROWN – REFERENCE RUN; DARK BLUE – WINDX +20; BLACK – WINDX -20; WHITE – WINDY +20; RED – WINDY -20)

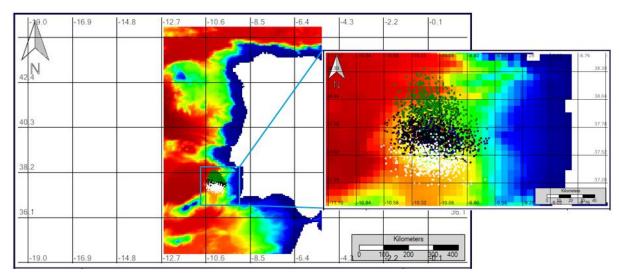


FIGURE 68 – OIL SICK LOCATION FOR WIND FORCING ANALYSIS ON THE 18TH JULY(BROWN – REFERENCE RUN; DARK BLUE – WINDX +20; BLACK – WINDX -20; WHITE – WINDY +20; RED – WINDY -20)

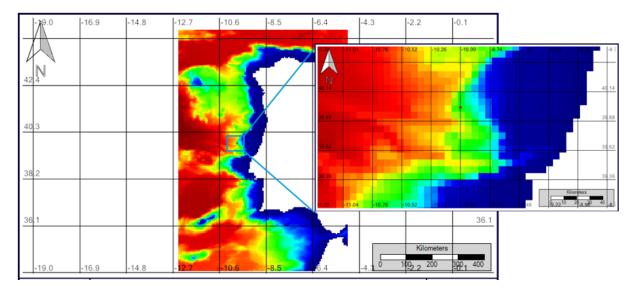


FIGURE 69 – OIL SICK LOCATION FOR THE WAVE FORCING ANALYSIS ON THE 11TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WAVE HEIGHT +20; BLACK – WAVE HEIGHT -20; WHITE – WAVE PERIOD +20; RED – WAVE PERIOD -20)

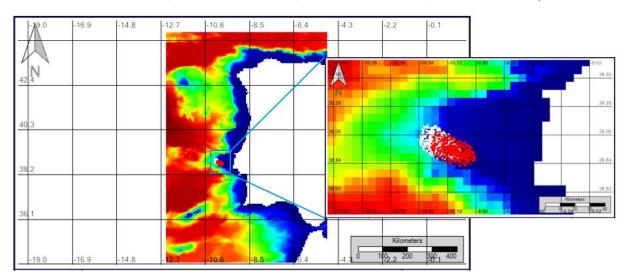


FIGURE 70 - OIL SICK LOCATION FOR THE WAVE FORCING ANALYSIS ON THE 14TH JULY (BROWN – REFERENCE RUN; DARK BLUE – WAVE HEIGHT +20; BLACK – WAVE HEIGHT -20; WHITE – WAVE PERIOD +20; RED – WAVE PERIOD -20)

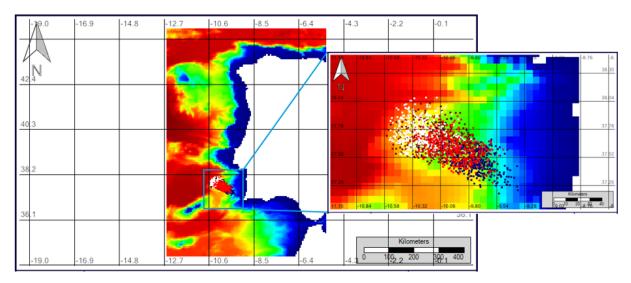


FIGURE 71 - OIL SICK LOCATION FOR THE WAVE FORCING ANALYSIS ON THE 18[™] JULY (BROWN – REFERENCE RUN; DARK BLUE – WAVE HEIGHT +20; BLACK – WAVE HEIGHT -20; WHITE – WAVE PERIOD +20; RED – WAVE PERIOD -20)

4.5 COMPARISON OF RESULTS

As mentioned before, the sensitivity index calculated in the Sensitivity Analysis cannot be computed for changes in spill site and forcing. That index is designed to measure the influence of changes in parameters in the model results, since variations of wind/wave forcing or spill site are not parameters an alternative was necessary, namely the difference between the simulations and the reference was calculated. However, in this case the sensitivity of the model is not calculated directly, and has the downside of not being normalized, so the conclusions must be drawn with caution, and comparisons in between output variables is not possible within each scenario.

The value of the difference was compared for each variable in between scenarios, in order to draw conclusions in this study, which is still adequate for the understanding on the parameters and variables that affect model behaviour, this being the main goal of this investigation.

Table 29 shows the average results (in absolute value) for all variables in each simulation, summarized from Table 14, Table 24 and Table 26, the top 4 average difference values where highlighted in red.

This table shows clearly what simulations had the most impact for each variable evaluated. For all the parameters, apart from the mass dispersed, the API gravity was one of the variations which contributed more significantly to changes in the model output. Wind forcing, namely the y component of the velocity, also plays a major role in modelling the fate of the spilled oil impacting all the outputs apart from viscosity, due to the fact that in this scenario the wind is mainly from the north. Wave forcing and reference viscosity in some cases also contributed significantly to the changes in the results.

Comparing Table 29 with results from the Sensitivity Analysis it can be concluded that the changes in all of the simulations did not significantly impact the mass water content or density, since the API parameter resulted in the largest change (Table 28) and the model was found to be not sensitive to changes in the API gravity (Table 12 and Table 13). For all other parameters, apart from area, thickness and viscosity, the model was found to be sensitive to the simulations performed so results are as expected, since for most cases the difference obtained in the other simulations are smaller conclusions cannot be made regarding the sensitivity of the model in such cases. For area and thickness the Sensitivity Analysis showed a highly sensitive model to changes in the API parameter, viscosity was found to be highly sensitive to changes in the API gravity and reference viscosity, explaining the results obtained in this section. For mass dispersed which was found to be highly sensitive to changes in the reference viscosity, with the results showing that wave height and period, with +20% and -20% variations respectively, had a larger difference value then the reference viscosity, which can imply that the model is at least highly sensitive to these changes in wave forcing.

	∆M Oil	∆VOil	∆Vol	∆Area	∆Thick	∆M Evap	∆M Disp	∆MWC	∆Dens	∆Visc
API +10%	34 184	23.3	82.4	29 887	0.19	20 861	46.8	0.01	2.80	20 732
API -10%	34 697	23.0	81.6	-36 538	0.25	-20 967	41.8	-0.01	2.91	-15 324
RefVis +10%	89.9	0.10	0.34	15 103	0.07	3 463	2.22	0	0.83	8 176
RefVis -10%	121	0.13	0.46	0	0	0	121	0	0	6 231
WindC 0,02	157	0.16	0.46	185	0	157	0.21	0	0.01	205
WindC 0,04	29.0	0.03	0.21	5.50	0	29.3	0.26	0	0	5.33
1Km N	73.7	0.07	0.01	79.4	0	71.6	2.12	0	0.01	84.9
1Km S	25.2	0.03	0.35	16.8	0	27.3	2.10	0	0	22.5
1Km E	109	0.12	0.82	91.4	0	112	2.99	0	0	108
1Km W	30.7	0.0	0.32	43.3	0	27.6	3.15	0	0.01	42.1
Windx +20%	36.3	0.0	0.01	30.7	0	35.7	0.61	0	0	32.4
Windx -20%	31.9	0.0	0.02	27.6	0	31.5	0.50	0	0	29.2
Windy +20%	5 668	5.34	3.99	4 172	0.02	5 618	49.7	0	0.47	4 521
Windy -20%	6 698	6.28	2.40	5 094	0.02	6 564	133	0.01	0.64	5 087
Wave h. +20%	200	0.21	0.69	111	0	79.1	121	0	0	125
Wave h20%	0	0.0	0	0	0	0	0	0	0	0
Wave p. +20%	210	0.22	0.75	130	0	122	87.3	0	0.01	144
Wave p20%	94.2	0.10	0.33	16.2	0	36.82	131	0	0	18.2

 TABLE 29 – COMPARISON OF RESULTS IN THE DIFFERENT SCENARIOS, RESULTS IN ABSOLUTE VALUE OBTAINED FROM TABLES 13,23

 AND 25, IN RED ARE HIGHLIGHTED THE TOP 5 VALUES FOR EACH VARIABLE STUDIED (COLUMNS)

5. DISCUSSION

Oil mass and volume, total volume, slick area and thickness, mass evaporated and dispersed, water content, density and viscosity were impacted by the simulations where model parameters were changed sequentially, then by changes in wind coefficient and spill site and lastly by wind and wave forcing.

In the Sensitivity Analysis it became clear that the most important parameters were the API gravity and reference viscosity, both influencing the model results in the Portuguese coast and Tagus estuary. For the first setting the API gravity resulted in a variation of more than 1% for most variables (oil mass, oil volume, total volume, area, mass evaporated and dispersed) and of more than 10% for viscosity. Reference viscosity on the other hand impacted a fewer number of variables but it had an impact of more then 10% change in the model output of mass dispersed and viscosity. In the Tagus estuary API is also relevant and its variations result in changes of more than 1% and more than 10% for all variables except for mass water content and density. As for reference viscosity in this setting the same impact as in the Portuguese coast was observed. In addition, the model was found to be highly sensitive with regards to oil volume and total volume, in some cases the model was even extremely sensitive (changes of more than 10%).

Comparing the difference between the reference simulation from the first scenario in the Portuguese coast with runs from the different analysis it may be concluded which parameter or forcing had the most impact on the model results. For oil mass, it was found that variations of the API gravity had the most influence, followed by negative variations of y component of wind velocity and positive variations of wave period. For both oil volume and total volume, it is noticeable a greater influence by changes in the y component of the wind velocity and API gravity. The slick area is affected the most by changes API gravity and wind forcing as well. Thickness, mass evaporated, MWC and density are more influenced by variations in API gravity and by the y component of the wind velocity. As for the dispersed mass, negative variations of reference viscosity, negative variations of the y component of wind velocity and velocity and velocity and changes in wave forcing altered the results more significantly. Viscosity was changed mainly by variations in the API gravity and reference viscosity performed for the sensitive analysis.

When comparing the results from the Sensitivity Analysis it became clear that no simulation impacted the mass water content or density of the slick significantly, since API impacted this result the most but by less than 1%. This result implies that the percentage of water in the slick due to emulsion and the slick density are not sensitive to the variations tested. For the mass dispersed the model was highly sensitive for changes in reference viscosity, since wave height and period showed a more significant impact on this results, it can be concluded that the model is at least highly sensitive to these changes.

For the other variables, since the model was sensitive to changes in API gravity but the results obtained from the difference between the simulations and reference were less significant it is not possible to assess the sensitivity.

The influence of the model parameters on the oil slick trajectory was also assessed and found to be insignificant, however other parameters, such as wind coefficient had a great impact on the trajectory of the oil tracers. Wind and wave forcing also showed a significant influence in the spilled oil trajectory.

The parameter that had the most effect on the spilled oil trajectory was the wind coefficient (when equal to 0.02), followed by changes in the spill site.

The methodology proposed was successful in identifying the most important parameters and forcing affecting oil spill modelling, for parameters it is able to classify the model as sensitive, highly sensitive and extremely sensitive, for forcing or spill site this classification is indirect and based on a comparison. This comparison has the disadvantage of not taking into account the variation of the parameter, in this case results from variations of 10% in the parameter were compared with results from 1km variations in spill site and 20% in wind forcing components. For a correct comparison the variations should be comparable, for instances in this case all variations are within the expected uncertainty for each parameter, forcing or spill site.

6. CONCLUSIONS

This work proposed analysing parameters that contribute to uncertainties that influence oil spill modelling as well as the influence of forcing in the model results. When uncertainty is unknown the confidence in numerical models such as MOHID decreases, hindering the response in the case of a spill. This study focuses on the shift of paradigm necessary in the evolution of oil spill modelling.

The sensitivity analysis showed that the API gravity and reference viscosity had the most impact on the model results, all other parameters did not change the outputs analysed. Ten percent variations of API parameter resulted in more than one percent change in the model results for several variables in all of the scenarios tested, and more than ten percent for slick properties in the scenarios tested.

Wind and wave forcing impacted both oil weathering and oil spreading, particularly wind forcing. The oil mass, volume, area, and masses weathered were significantly impacted by wind and wave. Which is important to know for the response in case of spill incidents.

In general the API gravity was found to be very relevant for most of the outputs studied as well as the y component of wind forcing, due to prevailing winds from the north. It is worth pointing out that the mass water content was not changed significantly, by any simulation and that mass dispersed is highly sensitive to variations performed in the API gravity and consequentially is also highly sensitive to changes in wave forcing. All other model outputs were changed by the simulations analysed but a conclusion on how sensitive was the model was not possible.

The evolution of the centre of mass is important to assess the impact of the simulations on the trajectory of the spilled oil.

The parameters evaluated on the sensitivity analysis had little to no impact on the trajectory of the oil slick, only the API gravity and Pour point showed some impact, but it was not significant. However, the influence in the trajectory of the slick by wind forcing had a significant impact, namely the y component of the wind velocity since wind was mainly from the north. Wave period had a smaller impact on the trajectory of the spill, but still more significant than the variations done in the sensitivity analysis. The other parameters tested, wind coefficient and spill site location had a significant impact on the centre of mass evolution. The wind coefficient was the simulation which had the most influence in this result, followed by spill site that as expected had a significant impact on the slick. Since the model domain used for this analysis had winds mainly from the north it was observed a larger impact of the simulations on the longitude of the centre of mass in all the simulations performed.

The methodology proposed was successful in comparing the impact of the different simulations on the diverse model results analysed, it has the advantage of being easy to implement, and special software is not required and provides results that are easy to interpret. The limitations relate with the impossibility of calculating an index for spill site and wind and wave forcing, which would indicate the sensitivity of the model, therefore it is necessary to compare the differences amongst scenarios with the index calculated for the sensitivity analysis to assess the model sensitivity for forcing and spill location. This work has contributed to, in the future, implement new concepts in spill modelling, namely probabilistic modelling, with uncertainty measures or confidence intervals associated with the results. Probability maps can also be generated; these maps identify areas of least regret making them useful for response teams.

7. References

- Abascal, A. J., S. Castanedo, R. Medina and M. Liste (2010). "Analysis of the reliability of a statistical oil spill response model." Marine Pollution Bulletin 60: 11.
- Afenyo, M., B. Veitch and F. Khan (2015). "A state-of-the-art review of fate and transport of oil spills in open and ice-covered water." Ocean Engineering.
- Bernabeu, A. M., S. Fernandez-Fernandez, F. Bouchette, D. Rey, A. Arcos, J. M. Bayona and J. Albaiges (2013). "Recurrent arrival of oil to Galician coast: the final step of the Prestige deep oil spill." J Hazard Mater 250-251: 82-90.
- Bi, H. and H. Si (2012). "Dynamic risk assessment of oil spill scenario for Three Gorges Reservoir in China based on numerical simulation." Safety Science(50): 1112-1118.
- Buchanan, I. and N. Hurford (1988). "Methods for predicting the physical changes in oil spilt at sea." Oil and Chemical Pollution 4(4): 311-328.
- Delvigne, G. A. L. and C. E. Sweeney (1988). "Natural dispersion of oil." Oil & Chemical Pollution 4(4): 281-310.
- Fay, J. A. (1969). "The spread of oil slicks on a calm sea." Oil on the Sea, Plenum Press: 53-63.
- Fernandes, R. (2001). Modelação de Derrames de Hidrocarbonetos. Licenciatura em Engenharia do Ambiente, Instituto Superior Técnico.
- Fernandes, R., F. Braunschweig, F. Lourenço and R. Neves (2016). "Combining operational models and data into a dynamic vessel risk assessment tool for coastal regions." Ocean Science 12: 285-317.
- Fingas, M. F., D. A. Kyle and E. J. Tennyson (1993). "Physical and Chemical Studies on Dispersants: The effect of Dispersant Amount and Energy." Environment Canada.
- Garcia-Martinez, R. F.-T., H. (1999). "Computer Modelling of oil Spill Trajectories with a high accuracy method." Spill Science & Technology Bulletin 6: 323-330.
- Hackett, B., Ø. Breivik and C. Wettre (2006). Forecasting the drift of objects and substances in the ocean. N. M. Institute.
- Huang, J. C. and F. C. Monastero (1982). "A REVIEW OF THE STATE-OF-THE-ART OF OIL SPILL FATE/BEHAVIOR MODELS." International Oil Spill Conference Proceedings 1983(1): 313-322. International Energy Agency, I. (2016). Key Oil Trends.
- ITOPF (2016). "Oil Tanker Spill Statistics 2015."
- Jolliff, J. K., T. A. Smith, S. Ladner and R. A. Arnone (2014). "Simulating surface oil transport during the Deepwater Horizon oil spill: Experiments with the BioCast system." Ocean Modelling 75: 84-99.
- Lehr, W. J. (2001). Review of modeling procedures for oil spill weathering behavior. Advances in Ecological Sciences. 9: 51-90.
- Mackay, D., A. Buistt, R. Mascarenhas and S. Paterson (1980). "Oil spill processes and models." Environment Canada Manuscript Report Nº EE-8.
- Mackay, D. and R. S. Matsugu (1973). "Evaporation rates of liquid hydrocarbon spills on land and water." The Canadian Journal of Chemical Engineering 51(4): 434-439.

- Mateus, M. and R. Fernandes (2008). Modelling Pollution: Oil spills and faecal contamination. I. Press: 89-102.
- Mateus, M., G. Riflet, P. Chambel, L. Fernandes, R. Fernandes, M. Juliano, F. Campuzano, H. de Pablo and R. Neves (2012). "An operational model for the West Iberian coast: products and services." Ocean Science 8(4): 713-732.
- Mishra, A. K. and G. S. Kumar (2015). "Weathering of Oil Spill: Modeling and Analysis." Aquatic Procedia 4: 435-442.
- Monteiro, C. E., R. Cesario, N. J. O'Driscoll, M. Nogueira, M. Valega, M. Caetano and J. Canario (2016). "Seasonal variation of methylmercury in sediment cores from the Tagus Estuary (Portugal)." Mar Pollut Bull 104(1-2): 162-170.
- Neves, R. (2007). Numerical models as decision support tools in coastal areas. Assessment of the Fate and Effects of Toxic Agents on Water Resources, Springer Netherlands: 171-195.
- Neves, R. (2013). The MOHID Concept. Ocean modelling for coastal management Case studies with MOHID R. Neves and M. Mateus, IST Press.
- NOAA (1994). ADIOS (Automated Data Inquiry for Oil Spills): User's Manual, NOAA.
- NOAA (2000). "ADIOS (Automated Data Inquiry for Oil Spills) version 2.0. Seattle: Hazardous Materials Response and Assessment Division."
- NOAA (2002). Trajectory Analysis Handbook. N. O. Service.
- Payne, J. R., B. E. Kirstein, G. D. McNabb, J. L. Lambach, R. Redding, R. E. Jordan, W. Hom, C. de Oliveira, G. S. Smith, D. M. Baxter and G. R. (1984). "Multivariate analysis of petroleum weathering in the marine environment." Sub arctic. Environment Assessment of the Alaska Continental Shelf 22.
- Rasmussen, D. (1985). "OIL SPILL MODELING—A TOOL FOR CLEANUP OPERATIONS." International Oil Spill Conference Proceedings 1985(1): 243-249.
- Rayson, M. D., E. S. Gross and O. B. Fringer (2015). "Modeling the tidal and sub-tidal hydrodynamics in a shallow, micro-tidal estuary." Ocean Modelling 89: 29-44.
- Reed, M. (1989). "The physical fates component of the natural resource damage assessment model system." Oil & Chemical Pollution 5: 99-123.
- Reed, M., i. Johansen, P. J. Brandvik, P. Daling, A. Lewis, R. Fiocco, D. MacKay and R. Prentki (1999).
 "Oil spill modeling towards the close of the 20th century: Overview of the state of the art." Spill Science and Technology Bulletin 5(1): 3-16.
- Sá Pereira, M. T. and A. R. Silveira Ramos (2014). "The port of Lisbon, Portugal: Maintenance dredging in a sensitive environment." Terra et Aqua 134.
- Sebastião, P. and C. G. Soares (2006). "Uncertainty in predictions of oil spill trajectories in a coastal zone." Journal of Marine Systems 63: 257-269.
- Stiver, W. and D. Mackay (1984). "Evaporation rate of spills of hydrocarbons and petroleum mixtures." Environmental Science & Tecnhology 18(11): 834-840.
- Stolzenbach, K. D., O. S. Madsen, E. E. Adams, A. M. Pollack and C. K. Cooper (1977). "REVIEW AND EVALUATION OF BASIC TECHNIQUES FOR PREDICTING THE BEHAVIOR OF SURFACE OIL SLICKS." MIT Sea Grant Program, Report No. 222.

Yang, W. C. and H. Wang (1977). "Modelling of Oil Evaporation in Aqueous Environment." Water Research 11: 879-887.