UNIVERSITY OF SÃO PAULO
ENGINEERING SCHOOL OF SÃO CARLOS
ENVIRONMENTAL ENGINEERING

LUCIANA DA COSTA FERREIRA

SIMULATION OF A THEORETICAL OIL SPILL IN THE CYPRUS BASIN (MEDITERRANEAN SEA) USING MEDSLIK AND COMPARISONS WITH THE BRAZILIAN MARGINS

São Carlos
2017

LUCIANA DA COSTA FERREIRA

SIMULATION OF A THEORETICAL OIL SPILL IN THE CYPRUS BASIN (MEDITERRANEAN SEA) USING MEDSLIK AND COMPARISONS WITH THE BRAZILIAN MARGINS

Undergraduate thesis presented to the Engineering School of São Carlos, University of São Paulo, in order to obtain the degree of Bachelor in Environmental Engineering.

Advisor: Tiago M. Alves – Cardiff University (Cardiff, UK)

Co-advisor: Valéria G. S. Rodrigues – Department of Geotechnical Engineering – São Carlos School of Engineering – University of São Paulo

São Carlos

2017

da Costa Ferreira, Luciana
D368s SIMULATION OF A THEORETICAL OIL SPILL IN THE CYPRUS BASIN (MEDITERRANEAN SEA) USING MEDSLIK AND COMPARISONS WITH THE BRAZILIAN MARGINS / Luciana da Costa Ferreira; orientador Tiago Alves ; coorientadora Profa. Dra. Valéria Guimarães Silvestre Rodrigues. São Carlos, 2017.

Monografia (Graduação em Engenharia Ambiental) -- Escola de Engenharia de São Carlos da Universidade de São Paulo, 2017.

1. Oil. 2. Spills. 3. Cyprus. 4. Medslik. 5. Brazilian Margins. I. Título.

FOLHA DE JULGAMENTO

Candidato(a): **Luciana da Costa Ferreira**

Data da Defesa: 30/10/2017

Comissão Julgadora: Resultado:

Valeria Guimarães Silvestre Rodrigues (Co-orientador(a)) Aprovada

Mariana Consiglio Kasemodel Aprovado

Isabela Monici Raimondi Aprovada

Prof. Dr. Marcelo Zaiat
Coordenador da Disciplina 1800091- Trabalho de Graduação

To my parents, as no building can ever stand
without a solid foundation.

ACKNOWLEDGEMENTS

My most sincere thanks to all the people who made the development of this thesis possible.

To my family, for believing in me for a whole life and giving me wings so my dreams could become a reality.

To my friends, for always being on my side during my graduation, making the good moments unforgettable and the bad ones tolerable.

To my boyfriend, to whom I will forever be thankful for all the patience, the love and the encouragement he continuously gives me when following my goals.

To my advisor and co-advisor, key parts from the beginning to the end of the development of this thesis.

To the professors and staff of the University of São Paulo, especially the ones directly related to the Environmental Engineering course of the Engineering School of São Carlos, who were a part of my everyday life for 5 years and undoubtedly helped to shape who I am today.

And to the University of São Paulo, for all the opportunities it gave me.

“A society grows great when old men plant trees whose shade they know they shall never sit in” - Greek proverb

RESUMO

FERREIRA, Luciana da Costa. **Simulação de um derramamento teórico de petróleo na bacia do Chipre (Mar Mediterrâneo) usando MEDSLIK e comparações com a costa brasileira.** 2017. 96 p. Trabalho de Graduação (Bacharelado em Engenharia Ambiental) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2017.

Este trabalho explora os resultados de um vazamento hipotético de petróleo no campo Afrodite, na costa do Chipre, país insular localizado no Mar Mediterrâneo, utilizando o software de previsão e simulação Medslik. Os potenciais negativos da presença de petróleo liberado incorretamente na natureza também são abordados na revisão bibliográfica através do estudo das características de contaminantes orgânicos, do petróleo bruto em si e dos procedimentos de contenção e mitigação de vazamentos mais comumente utilizados, apresentando os prós, contras e indicações de uso de cada um destes. De forma a tornar a simulação mais abrangente, foram considerados cenários de vazamentos com três diferentes tipos de petróleo ocorrendo durante o verão e o inverno na mesma região. Os resultados das simulações mostraram poucas variações na forma das manchas de diferentes tipos de petróleo em uma mesma condição climática, mas diferenças drásticas foram percebidas entre manchas ocorrendo no verão e no inverno. Também foram observadas diferenças entre os seis cenários estudados para parâmetros como viscosidade, área total da mancha e taxas de evaporação do óleo, entre outros. Por fim, comparações da área estudada com a costa brasileira também foram feitas através de extrapolação de resultados, com o intuito de fomentar e iniciar um estudo mais profundo deste local com relação a possíveis vazamentos futuros.

Palavras-chave: Danos Ambientais; Oceanos; Meio Ambiente.

ABSTRACT

FERREIRA, Luciana da Costa. **Simulation of a theoretical oil spill in the Cyprus basin (Mediterranean Sea) using MEDSLIK and comparisons with the Brazilian margins.** 2017. 96 p. Trabalho de Graduação (Bacharelado em Engenharia Ambiental) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2017.

This thesis explores the outcomes of an hypothetical oil spill in the Aphrodite field, offshore Cyprus, island country located in the Mediterranean Sea, using the oil spill prediction and simulation software Medslik. The negative potentials of the presence of oil incorrectly released in nature are also addressed through the study of the literature about the characteristics of organic contaminants, of crude oil itself and the containment and mitigation procedures most commonly used, presenting the pros, cons and the indications of use for each one of them. In order to make the simulation more comprehensive, scenarios involving spills of three different types of oil occurring during summer and winter in the same region were considered. The results of the simulations showed little variation in the shape of the slicks of different types of oil in the same climatic condition, but drastic differences were observed between slicks occurring in summer and winter. Differences were also observed between the six scenarios studied for parameters such as viscosity, total area of the slick and evaporation rates, among others. Finally, comparisons of the studied area with the Brazilian coast were also made through extrapolation, in order to encourage and initiate a deeper study of this area in relation to possible future spills.

Keywords: Environmental Damage; Oceans; Environment.

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ADIOS	Automated Data Inquiry for Oil Spills
API	American Petroleum Institute
BOD	Biochemical Oxygen Demand
CAFE	Chemical Aquatic Fate and Effects
CETESB	Environmental Company of the State of São Paulo
CONAMA	Environment National Council
CYBO	Cyprus Basin Oceanography
DNAPL	Dense Non-Aqueous Phase Liquid
EEZ	Exclusive Economic Zone
EPA	United States Environmental Protection Agency
GIS	Geographic Information System
GNOME	General NOAA Operational Modelling Environment
IBAMA	Brazilian Institute for the Environment and Renewable Natural Resources
ITOPF	International Tanker Owners Pollution Federation Limited
LNAPL	Light Non-Aqueous Phase Liquid
MMJ	Mid-Mediterranean Jet
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
OSCAR	Oil Spill Contingency and Response
OSIS	Oil Spill Information System
PAH	Polycyclic Aromatic Hydrocarbons
UNEP	United Nations Environment Programme
°C	Degrees Celsius
°F	Degrees Fahrenheit
ρ_r	Density of the oil relative to that of water at 15.6°C (or 60°F)
km	kilometres
km^2	square kilometres
m/s	meters per second
cs	centistokes

SUMMARY

1. INTRODUCTION

The oil business intrinsically presents a series of risks, from the exploitation itself to the refining activities. A large variety of workers in this business deal with toxic, flammable and/or explosive compounds on a daily basis, which, as prepared as the company may be, not only poses risks to the workers themselves, but also to adjacent communities, to the infrastructure of the industry and to the environment. In the years between 1945 and 1989, for example, oil refineries held the position as the chemical processes industry with the highest rate of fatal accidents in the world, presenting five or more deaths per year (SOUZA; FREITAS, 2002). Among the accidents that affect the environment, the ones that compromise the water resources, as oil spills, are considered to be the ones that need more attention, especially considering they can occur through all the parts of the production process (LEME; MARIN-MORALES, 2007).

Oil spill is a term describing any situation in which crude or refined oil is released into the water or land. According to the Cambridge Dictionary, an oil spill is "an accident in which oil has come out of a ship and caused pollution". The United States Environmental Protection Agency (EPA), on the other hand, describes it as "a discharge of oil into navigable waters or adjoining shorelines", and determines that should be reported any "discharges of oil in quantities that may be harmful to public health or the environment, including those that violate applicable water quality standards; cause a film or "sheen" upon, or discoloration of the surface of the water or adjoining shorelines; or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines". As mentioned by Annunciado, Sydenstricker and Amico (2005), they represent a global concern due to their impacts, both environmental and economical.

Small spills occur with great frequency and come from the various parts of the oil industry (from exploration to transport), being caused by a range of different reasons, as structural failures, human mistakes and even earthquakes, among many other reasons (FINGAS, 2011). Although natural sources, such as leakage from sea beads, are responsible by part of the spills that occur annually, human induced spills are considerably more frequent (KUBAT; HOLTE; MATWIN, 1998). The incidents of more public concern, though, are those that involve bigger amounts of oil, causing immediate damage on the local environment of the region in which the spill occurred and dragging huge attention from the media. Those, fortunately, are relatively rare events (FINGAS, 2011).

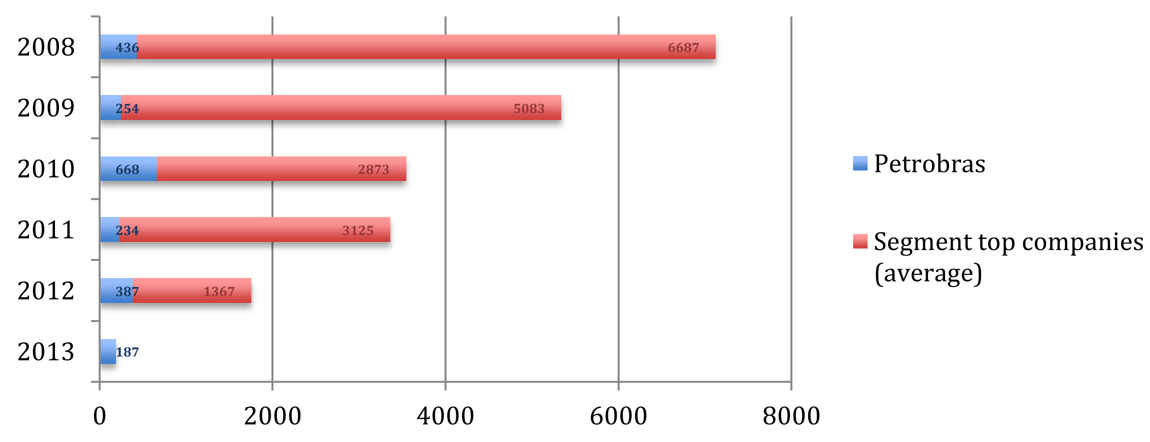
In Brazil, oil spills were reported in the last decades in various regions. In 2016, an oil spill was reported in a Petrobras facility in Cubatão, in the state of São Paulo, a city considered one of the most polluted in the world in the early 1980s (BROOKE, 1991). The spill directly affected Cubatão River, precisely the source that supplies water to the station responsible for providing almost half of the water produced in the region (G1 SANTOS, 2016). Another accident, widely reported by the media due to its proportion, happened in the Campos Basin, 120 km away from the Rio de Janeiro coast, in November of 2011. Involving the American company Chevron, the incident was responsible for the release of 3.700 barrels of oil in the ocean, caused by excessive pressure exerted during the drilling of wells, and generated incalculable losses to the biodiversity of the region (BRANCO, 2016).

According to the Joye Research Group from the University of Georgia, most of the largest oil spills reported worldwide is linked to tanker accidents, although those are less frequent than spills caused by pipeline breaks. This is confirmed by numbers: the US Department of the Interior Minerals Management Service reported in 2002 that, between 1971 and 2000, 45 percent of all the oil spilled in the United States waters came from accidents involving tankers and barges, while only 16 percent corresponded to pipelines leakages. The same source also provides a long list of significant oil spills in history and considers as the largest ones those of over 100,000 tons. The list includes accidents as the tanker explosion in 1991 in the coast of Angola, Africa, in which one person died and four were reported missing in the three-day fire generated; the Castillo de Bellver accident that happened off Table Bay, in South Africa, breaking the ship in two after an explosion and spilling approximately 1,848,000 barrels of light crude; and, of course, the more recent Deepwater Horizon oil spill, that during 87 days, released 4.9 million barrels of oil and gas that is equivalent of 1.5 to 2.9 barrels of oil into the deep waters of the Gulf of Mexico, which instigated research studies (ECHOLS et al., 2015; MUHLING et al., 2012; OMAR-ALI et al., 2015; SCHWING et al., 2015; WARNOCK; HAGEN; PASSERI, 2015), among others, documentaries and a large variety of news articles.

If not considered those and the intentional spillage related to the 1991 Gulf War - the largest oil spill in history, in which an estimated of 160 to 340 million gallons of Kuwait crude oil were discharged into the Gulf -, worldwide oil spillage rates have considerably decreased since 1970's (FINGAS, 2011; SAUER et al., 1993). Levine (2014) reported something similar regarding the U.S. waters, affirming that ''total petroleum industry spillage has decreased consistently over the last 40 years'' in the country. Cantagallo et al. (2007) also point out this decrease in oil spillage rates, attributing the reduction in accident occurrences to an increase in the public concern regarding environmental issues, which results in companies taking more precautions during all their operations involving oil exploitation, transport and storage.

Petrobras, the largest oil business company in Brazil, affirms that investing in systemic, comprehensive and continuous maintenance and safety methods is a part of their policy, which leads to increasingly good results in regards of spill incidents. Figure 1 shows the number of spills reported from Petrobras facilities from 2008 to 2013, in comparison to the average presented from other top companies of the segment.

Figure 1. Spills occurred in Petrobras facilities vs. average of spills occurred in top companies facilities from 2008 to 2013.



Source: Petrobras (2014).

It should also be pointed out that, in October of 2016, IBAMA (the Brazilian Institute for the Environment and Renewable Natural Resources) released a National Emergency Action Plan for Oil Impacted Fauna, an important and innovative resource for the country's public policies. The plan provides detailed instructions on how to deal with such occurrences in a way that reduces environmental impacts on the local biodiversity.

Oil spilled on land often reaches lakes, rivers and wetlands, causing damage to these environments (ENVIRONMENTAL PROTECTION AGENCY - EPA, 1999). Accidents involving major oil spills in waters are known for being a threat for both environmental and financial aspects of local communities (ALVES; KOKINOU; ZODIATIS, 2014), affecting not only organisms that live on or around the water surface but also impacting parts of the food chain (EPA, 1999). According to Peterson et al. (2003), it is estimated that 250 thousand seabirds perished in the days following the disaster involving the oil tanker Exxon Valdez, in 1989. Sea otters deaths were also documented during this period in Prince William Sound, Alaska, the place that was most affected by the accident. A frequent cause of death of marine animals and seabirds involving oil spills is by hypothermia, as oiling of fur or feathers results in loss of insulating capacity (NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION OF THE UNITED STATES DEPARTMENT OF COMMERC – NOAA, 2015; PETERSON et al., 2003). The NOAA (National Oceanic and Atmospheric Administration of the United States Department of Commerce) website also refers to the chemical constituents of oil as poisonous to organisms, affecting them from internal exposure (from ingestion or inhalation) or external, through eyes and skin irritation. Ingestion can easily occur when animals try to clean themselves after being covered by the oil released in the sea during an accident. If mixed into the water column, oil can also cause reduced growth, enlarged livers, changes in heart and respiration rates, fin erosion and reproduction impairment in local fish and shellfish, as well as affecting eggs and larval survival. Small spills, frequent from shipping operations – although less concerning to the media and public in general –, can also be a threat: a two-year study conducted in Germany from August 1983 to April 1984, for example, concluded that at least half of the 8750 dead seabirds found along West German beaches in this period died from oil pollution caused by minor spills (GOURLAY, 1988).

In Brazil, 4.000 square meters of mangrove areas were devastated in 1997 when a rupture occurred in an oil duct in Guanabara Bay, Rio de Janeiro, spilling 600 thousand litres of oil in the sea. Due to the richness of the biodiversity in these ecosystems, it was reported incalculable the losses in fauna and flora following the accident (GARCIA, 2000).

As for social-economic effects, the United Nations Environmental Programme (UNEP, 2015) website lists problems related to fisheries and aquaculture (affecting both the quality of the catches and the preservation of the equipment), tourism and recreation (related to the damage caused to the shoreline), industries that require clean water, as well as negative effects to human health (by contact with oil products through skin or inhalation, or when eating contaminated sea food). The sensitivity of the affected place is also decisive in the determination of the damage caused by the spill: 'a little oil in a sensitive area can do considerably more harm than a large quantity on a desolate rocky shore', as affirmed by the International Tanker Owners Pollution Federation (ITOPF, 1987). The same book also explores the already mentioned effects of oil spills on coasts, especially impacts on recreational activities (boating, bathing, angling, diving, etc.), mentioning the losses that can occur to hotel and restaurant owners of the region, the impacts on industries and also biological effects of spills.

The region covered in this study is the Mediterranean Sea, a sea divided into several sub basins (BIJU-DUVAL et al., 1974), connected with the Atlantic Ocean by the narrow and shallow Strait of Gibraltar and surrounded by the south coast of Europe, the north of Africa and a part of the west coast of Asia (SALAH; BOXER, 2017). The main focus is to analyse the probable responses of the Mediterranean system having occurred a spill and extrapolate these results in order to predict the responses of the Brazilian coastal system during a similar occurrence, as both ecosystems are visibly comparable on their climatic characteristics, although they still have their particularities. The Mediterranean region was chosen for this thesis as the focus area of study due to the highly advanced exploration of oil occurring in the region and its consolidated spill model developed specifically for the area.

Currently, the Mediterranean Sea is being vastly explored for oil and gas. It bears intense ship traffic, being a corridor for a quarter of the total oil transported annually (ALVES et al., 2016). An example of a notable hydrocarbon spot is the

Levantine basin, adjacent to countries such as Lebanon, Syria and Israel, where the Aphrodite, Leviathan and Dolphin fields are located, among others. Currently, close to 750,000 tonnes of oil are introduced annually as a result of minor near-coast spills and ship discharges (ALVES et al., 2016). Still according to the same article, the prospect of an increase in these numbers due to the opening of new exploration sites highlights even more the importance of studies in this area. Recently, for instance, the Israeli Delek Group and the American Noble Energy publicly announced that the Aphrodite gas field is commercially viable (DELEK, 2015). Similarly, the Brazilian coast is also increasingly getting the attention of oil and gas companies, especially after the discovery of the pre-salt, an offshore aggregation of rocks encompassing a large area, formed under an extensive layer of salt and with great potential to generate and accumulate oil (PETROBRAS, 2017). Although the status of both regions represent a good sign for the economies of the countries and companies involved, a larger number of fields also numerically implies in a possibly larger risk of accidents involving oil spills, thus being the modelling and prediction of a theoretical occurrence in areas presenting those common physical characteristics a particularly important prevention study.

2. OBJECTIVES

It is expected, as a result for this thesis, an analysis of the outputs of an oil spill simulation in the software MEDSLIK, considering data from the Cyprus coastal area.

The two specific aims of this thesis are as follow:

- To determine whether there are differences on the outcomes of oil spills occurring in the Mediterranean Sea during summer or winter climatic conditions, and involving different types of oil (heavy, medium and light);
- To perceive probable outcomes if an oil spill were to happen in the Brazilian oil exploration scenario, by comparing characteristics between the Brazilian and Mediterranean coasts. Hopefully, further discussions and studies regarding this matter will be fomented.

3. LITERATURE REVIEW

In this section, basic knowledge of the main topics explored in this thesis (characteristics of organic contaminants; geological, oceanographic and climatological settings of the studied area; characteristics of crude oil; containment and mitigation procedures for oil spills; and attributes of the software MEDSLIK) is provided, in order to facilitate the comprehension of the results presented in Section 5.

3.1. ORGANIC CONTAMINANTS

Before discussing the characteristics of the main compound discussed in this thesis (oil, a fossil fuel, also called “petroleum” in a broader approach), it is important to review organic contaminants in general and how they may be classified. In a more strict way, regarding all their properties, Bragato (2006) divides organic compounds in three main groups: organochlorides (or halogenated organic compounds) – derived mainly from solvents originated in industrial processes and pesticides –, nitrogenated compounds - derived especially from explosives, restricting the majority of sites contaminated with this type of organic contaminants to the proximities of arms industries or war grounds – and hydrocarbons, which includes crude oil and oil products.

It is not rare to find a study correlating contaminated areas or water bodies and organic compounds. Domestic wastewater and the waste resultant from industrial activities are some of the threats to ecosystems all over the world, being those partly constituted of organic matter (PEREIRA, 2004). A great amount of those studies are, still, dedicated to persistent organic pollutants, also known as POPs, highly stable organic compounds that, as their name suggest, tend to persist in the environment, resisting to chemical, photolytic and biologic degradation (OLIVEIRA, 2011). POPs are vastly studied due to their toxicity to living beings, as their lipophilic characteristic enable them to distribute in the interior of cell membranes and fat deposits, thus accumulating through food chains. Organisms that occupy high trophic levels in a determined food chain may present extremely high concentrations of pollutants, as those can be accumulating in said food chain since the lower trophic levels (OLIVEIRA, 2011). In soils, the threat this type of contaminant present lies in its capacity of forming pesticide residues that cannot be easily extracted from the area (OLIVEIRA, 2011). Negative effects for the environment caused by organic contaminants in general include changes in colour, turbidity and biochemical oxygen demand (BOD), hence affecting the local ecological balance (COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO - CETESB, 2009).

Despite the solubility of organic contaminants being insignificant in water, their concentration is normally found greater than the maximum safety limits for public health in contaminated areas (TRESSOLDI; CONSONI, 1998). It is also common, in characterization studies for contaminated areas, to classify those contaminants as LNAPLs and DNAPLs (TRESSOLDI; CONSONI, 1998). The first acronym refers to "Light Non-Aqueous Phase Liquid", i.e. contaminants that are lighter than water, thus floating in the surface of water tables or aquifers (gasoline, for example). For that reason, LNAPLs tend to flow in the capillary fringe and to separate in multiple phases: the contaminant itself, found in the water surface; the dissolved fraction and the vapour phase, found in the unsaturated zone. The second acronym, on the other hand, refers to "Dense Non-Aqueous Phase Liquid", i.e. contaminants that are heavier than water, concentrating at the bottom of aquifers (TRESSOLDI; CONSONI, 1998).

Oil is composed of a complex mixture of hydrocarbons, which accounts for 50 to 98% of its composition (NATIONAL RESEARCH COUNCIL - NRC, 1985; TONINI; REZENDE; GRATIVOL, 2010). Different processes that occurred during petroleum formation in various parts of the Earth resulted in a large variety of chemical compositions for crude oil (NRC, 1985). Hydrocarbons, according to the Cambridge Dictionary, are "a chemical combination of hydrogen and carbon", thus compounds containing only atoms of carbon and hydrogen. Arranged in different positions and proportions, those two elements create the great variety of hydrocarbons known: alkanes, alkenes, naphthenes (also known as cycloalkanes), aromatics and many others (ABHA; SINGH, 2012). Petroleum hydrocarbons are toxic to living beings, although not many are well characterized for their toxicity (ABHA; SINGH, 2012; VIEIRA, 2004). The impact caused in the human body from exposition to the highly toxic chemicals contained in crude oil includes damages to the nervous, respiratory, circulatory, immune, reproductive, sensory and endocrine systems, consequently being able to generate a wide range of diseases and disorders (ABHA; SINGH, 2012). In the environment, the toxicity of hydrocarbons when a certain area is affected results in the disruption of the balance of natural processes. Besides hydrocarbons, still according to NRC (1985), sulphur, oxygen and nitrogen can also be found as minor constituents, as well as trace metals (such as aluminium, copper and nickel).

Out of more than 17000 compounds that can be found in crude oil, a group that has been studied for its hazardous properties in water consists of polycyclic aromatic hydrocarbons (PAHs). PAHs are generated by natural products found in crude oil that have been chemically converted over time, resulting in compounds that comprehend two to eight conjugated ring systems (PAMPANIN; SYDNES, 2013). Those compounds are hydrophobic, which means they repel water, and their capacity to binding strongly to sediments makes them a threat to aquatic environments, as they can represent a long-term source of contaminants (LUTHY, 2004).

PAHs found in considerable concentrations in marine environments can be characterised as pyrogenic and petrogenic, the first referring to hydrocarbons formed by incomplete combustion of organic material and the second, to those that integrates crude oil and oil products, being this second group the focus in this study (PAMPANIN; SYDNES, 2013). PAHs represent a threat to people - especially the ones who are the most exposed to a PAH source in a daily basis - as they are associated with the occurrence of a variety of cancer forms (PEREIRA NETTO et al., 2000). Human exposition occurs mainly due to environment contamination, in which huge urban conglomerates have the most expressive contribution. Their lipophilic characteristic is the reason behind their quick distribution throughout an individual's body, while their absorption may happen via inhalation, ingestion or penetration through the skin (PEREIRA NETTO et al., 2000). Porto (2014) identified a high concentration of PAHs (above CETESB screening levels) in underground water extracted from wells located in a bus company's parking lot in Ribeirão Preto, São Paulo, including fluorene, phenanthrene, acenaphene and naphthalene, as a result from a spill occurred in 2013, caused by poor handling of a gas pump.

Monoaromatic hydrocarbons are also frequently associated with contamination caused by oil spills and represent as much of a public health issue as

PAHs. Also known as BTEX (an abbreviation for the group's compounds names: benzene, toluene, ethylbenzene and xylene isomers), these compounds are the most soluble and mobile fraction of oil derivatives, thus being the first to reach underground waters in soil contaminations. They are powerful central nervous system depressives, and present chronic toxicity even in small concentrations. The most toxic from all four compounds is benzene, being also a scientifically proven carcinogenic (BEZERRA, 2011). A study conducted in Lucaia River's basin, located in Salvador, Bahia, in 2011, consisted in the detection and quantification of BTEX compounds in underground waters from wells near gas stations (BEZERRA, 2011). Two of the spots analysed presented results far above the screening levels determined by the National Environmental Council in Brazil (*Conselho Nacional do Meio Ambiente* - CONAMA), indicating an urgent need of underground water monitoring in the affected areas, as well as efficient and broad spread of information to the local communities, in order to avoid the consumption of improper water extracted from wells. Fortunately, the studies conclusions showed that natural attenuation was very effective in the region for BTEX compounds, indicating a possible lack of necessity for human intervention in form of remediation processes (BEZERRA, 2011).

Another case study found PAH and BTEX compounds in 2008 in underground waters extracted from wells located in a gas station in São Sebastião, São Paulo, identifying free-phase contamination plumes in the area. A pump and treat system was installed in order to remediate the location, as concentrations of some of the analysed compounds were far above CETESB screening levels. The results of the treatment of choice were successful, as no concentration of pollutants was detected in the effluent from the process (FREIRE; TRANNIN; SIMÕES, 2014).

In the Cyprus area, an oil spill that happened on July 2013 was reported to "threaten the wildlife and tourism of a pristine coastline" in the north of the country. More than one containment method were used to contain the 7 km slick generated by an accident involving a tanker, responsible for releasing almost 40 tonnes of oil in the sea, as it was delivering fuel to a power station located in Turkey. The Karpasia peninsula, directly affected by the spill, is a nature reserve that serves as a breeding ground for rare turtles in July and August (YACKLEY, 2013).

As mentioned previously, water quality is increasingly getting more attention, especially in countries affected by hydrocarbon extraction (COLELLA; D'ORSOGNA, 2014). Sediments are frequently investigated in regions where it's suspected that contamination occurred in the past and/or is still occurring, as they act as "chemical archives" and geo-chronometers of contaminant deposition in the environment (COLELLA; D'ORSOGNA, 2014). However, the heterogeneity of sediment across the globe poses a challenge for scientists and environmental engineers as, although anthropogenic contaminants can be detected even in small concentrations in water, the understanding of the binding and release processes that occur between those compounds and the soil is still considered inadequate and insufficient. This fact results in poor or, at least, incomplete conclusions regarding how sediments concentrations relate to water quality, biological availability and toxicological effects of those contaminants (LUTHY, 2004).

3.2. GEOLOGICAL, OCEANOGRAPHIC AND CLIMATOLOGICAL SETTINGS: CYPRUS BASIN

Understanding the region in which the spill occurred (or may occur) is primordial to any containment or mitigation procedure to take place efficiently in the affected area.

In the next 3 sections (3.2.1, 3.2.2 and 3.2.3), the geological, oceanographic and climatological settings of the area studied in this thesis are described.

3.2.1. GEOLOGICAL SETTINGS

The areas of main focus in this revision are the southern margins offshore Cyprus, an island country located in the eastern Mediterranean Sea. Similarly to the previously mentioned country, this sea in general presents a turbulent history, but regarding its geological settings. Formed as a result of the separation and drifting of the Pangea continent, it was initially called Tethys by the Greeks (Figure 2). Over millions of years, the movement of the continents surrounding it changed its shape and size constantly, eventually making it stuck between the African and Eurasian plates, causing it to gradually dry up, turning into a huge salt desert. The later incursion of water from the Strait of Gibraltar filled it up again, resulting in what is seen today (OCA, 2000). It is of interest to also point out that the whole Mediterranean is considered to be a concentration basin, as evaporation exceeds precipitation and runoff (HECHT; PINARDI; ROBINSON, 1988). The collision of the Gondwana continents (Africa – Arabia) with Eurasia also was responsible for the formation of the most impressive mountain ranges in the world, such as the Alps and the Himalayas (VAN DER VOO, 1993). The geological history of the Tethys Sea is discussed in a series of books and articles (e.g. BIJU-DUVAL; LETOUZEY; MONTADERT, 2007; DIXON; ROBERTSON, 1984; VAN DER VOO, 1993; ZIEGLER, 1999), among others, making it possible to analyse the changes that happened in the area over time and shaped the Mediterranean Sea (Figure 3). There is, however, some contradictions regarding the composition of the sea floor: some authors define it as oceanic, while others believe it to be composed of a transitional type of crust and finally, others even propose that the entire area is composed of continental crust (MAKRIS; STOBBE, 1984).

Figure 2. Location of the Tethys Sea after the drifting of the Pangea continent, in the Triassic.

Source: University of Guelph (2017).

Figure 3. The Mediterranean Sea now; Inside the circle, the location of Cyprus.

Source: Encyclopaedia Britannica (2017).

Montadert (2010) relates that changes in the relative movement of the African, Arabian, Anatolian Aegean and Eurasian plates were dominant in the shaping of the offshore seabed of the eastern Mediterranean. The Levantine and Herodotus Basins, contained within the region, were formed in a period of rifting from the Triassic to the mid-Jurassic followed by spreading during the upper Jurassic and the lower Cretaceous. The former is filled essentially with deep-water sediments and probably some oceanic crust, while the latter contains a very thick sedimentary section (of about 12 to 15 km) and an oceanic crust. During the period of the late Miocene to the early Pliocene, anticlines were formed in the Levantine Basin along with the deposition of very thick Messinian evaporites in the Levantine and Herodotus basins, increasing the petroleum potential of both areas.

Still according to Montadert (2010), from the Upper Cretaceous to the Eocene, compression movements in the whole Tethyan area formed the Cyprus arc and caused subduction of the northern Levantine basin below it. Finally, in the beginning of the late Eocene to the early Oligocene, a change in the tectonic regime connected with the beginning of the separation of Arabia from Africa had structural and sedimentary consequences offshore Cyprus, including a tectonic climax in the latest Miocene – early Pliocene. The Cyprus arc was also affected by tectonic deformation during the latest Miocene. According to Alves et al. (2016), Miocene reef, limestones and shales, part of the Pakhna Formation, are the oldest units found on the southern coast of Cyprus. To the south of Cyprus, two notable features of elevated topography are the Hecateus and Eratosthenes Seamounts (ÖZSOY; HECHT; ÜNLUATA, 1989).

3.2.2. OCEANOGRAPHIC SETTINGS

According to Maheras et al. (2001) and Zodiatis, Drakopoilos and Brenner (2005), a complicated and energetic flow marks the general circulation of the Levantine basin, a region well known for frequent cyclone formation, affected by moving depressions generated in the Atlantic Ocean (or, alternatively, in northwestern Europe). A counter-clockwise circulation is generated by this cyclonic atmosphere, passing through the Aegean Sea and arriving later in the Levantine Basin (Alves et al., 2016). It presents strong currents and is dominated to the west by the sub-basin multilobe cyclonic Rhodes gyre, surrounded by the Asia Minor current to the north and the Mid-Mediterranean Jet to the south. Also in the southeastern Levantine Basin, the anticyclonic Shikmona gyre can be considered important as it consists of three eddies (being the Cyprus one the most well pronounced) (ZODIATIS et al., 2012). The Levantine Intermediate Water is an important water mass that affects the entire Mediterranean and even the Atlantic Ocean, and it is suggested that it conveys from a multiplicity of sources within the Levantine Basin and its formation process may be linked to the evaporative losses of heat and buoyancy and mixing in the northern Levantine Basin. As it is imaginable, the Atlantic Water entering through the Strait of Gibraltar also represents an important water mass in the Eastern Mediterranean, balancing the mass deficit of this sea, as pointed out by Özsoy, Hecht and Ünluata (1989). More details about those water masses can be found in their work, as they will not be deeply discussed in this study. Regarding circulation, the same authors affirm that 'very few long term current measurements have been made in the Levantine Basin', but it has been established that a basin-wide cyclonic mean circulation – following the mainland coasts of the Levant – is the dominant system of the region, and the intensity of the gyres diminish with depth. Zodiatis et al. (2012) indicates that, according to data sets obtained in the Levantine from 1995 to 2011, the main flow features in the mesoscale variability of the circulation in the southeastern Levantine are the Cyprus warm eddy, which undertakes strong spatial and temporal variability, and the Mid-Mediterranean Jet (MMJ).

The Cyprus warm eddy (or simply Cyprus eddy, as called by Benner (1991)) is reported to have been active and quite persistent south of Cyprus in the late 80s, being shown to be the northernmost lobe of the Shikmona gyre during the POEM project time (1985 – 1987). Experiments carried out in the frame of the CYBO (Cyprus Basin Oceanography) project, in the late 90s, revealed that this eddy is recurrent and persistent for long periods, controlling the direction of the MMJ south of Cyprus as well as its bifurcation southwest of the island. Its influence extends to depths of about 400m and includes current velocities up to 30-35 cm/s, according to Benner (1991), although surface currents faster than 1 m/s have been acknowledged in measurements developed in April 2014. It presents an interesting cycle of the mixed layer and thermocline at its core, consisting of a single deep mixed layer in the winter, extending from the surface up to almost 400m deep, and a seasonal thermocline replacing the upper half of the mixed layer during the summer (BENNER et al., 1991). According to the same author, analysis of data collected in cruises during the POEM programme showed, among other parameters, that the temperature in the core of the eddy stays around 16˚C, generally varying in a range of less than 1˚C along the year. In a more recent study, undertaken in 2001 and 2002, the eddy still appeared as a large and intense anticyclonic flow feature south of Cyprus, having just slightly changed position compared to its location in the 80s and 90s in the beginning of the study (ZODIATIS; DRAKOPOULOS, BRENNER, 2005).

According to Robinson et al. (2009), the Mid-Mediterranean Jet (MMJ) is believed to be fed by the Atlantic Waters meandering through the interior of the Ionian Sea. The MMJ then bifurcates in the Levantine Basin, one branch flowing towards Cyprus in a northward direction to feed the Asia Minor Current, and the other flowing eastward, turning southward later. The ‘’Ionian stream’’, then called Mid-Mediterranean Jet, intensifies between the Rhodes and Mersa-Matruh Gyres (ROUSSENOV et al., 1995).

3.2.3. CLIMATOLOGICAL SETTINGS

Despite its enclosed shape, the Mediterranean Sea has a very specific and active water circulation both at surface level and deeper down (OCA, 2000). It is a very salty sea as a result of strong winds and arid climate, responsible for causing intense evaporation, and known to be a product of a tormented geological history (LEJEUSNE et al., 2010; OCA, 2000). On average, it is 1500m deep and is located in a region presenting hot, dry summers and relatively temperate, wet winters, with the exception of some areas characterised by arid climate (OCA, 2000).

Extreme variability characterizes the meteorology of the Levantine region: during summer and autumn, wind systems are dominated by Westerlies (reinforced by the northerly Etesians, resulting in west-northwesterly winds), Etesians and coastal sea breeze cells, in contrast with local wind regimes and frequent extra tropical cyclones during winter and spring, usually arriving from the Ionian Sea or northern Africa.

In the Cyprus area, dominant winds are from the northwest to the southwest (ALVES et al., 2016). Also, studies have shown that the frequency of thunderstorms increases during spring and October (MICHALOPOLOU; JACOVIDES, 1987). During storm events, northwesterly to southwesterly wind flows are more felt and oil spill dispersion is expected to be quicker (ALVES et al., 2016). As the country belongs in the Mediterranean climate zone, it experiences mild winters with average temperatures between 12 to 15˚C and hot dry summers, with an average maximum temperate of 32˚C in coastal regions. The highest precipitation in the region occur between December and February, but the wet season extends from November to March, this factor being associated with the movement of moist maritime flows to the North (GIANNAKOPOULOS et al., 2010).

3.3. GEOLOGICAL, OCEANOGRAPHIC AND CLIMATOLOGICAL SETTINGS: BRAZILIAN MARGINS

To allow comparisons between the Mediterranean Sea and the Brazilian margins and extrapolate the simulation results to the latter, it is important to understand the geological, oceanographic and climatological settings of both regions beforehand.

In the next 3 sections (3.3.1, 3.3.2 and 3.3.3), these settings are described for the Brazilian margins.

3.3.1. GEOLOGICAL SETTINGS

Brazil is a country with one of the world's largest continental margins in extension (BIZZI et al., 2003), encompassing a variety of geological differences between distinct regions. Generated by the rifting of the Gondwana continent, over 120 million years ago, the Brazilian coastal system comprises a large quantity of different sedimentary basins: Pelotas, Santos, Campos, Espírito Santo/Mucuri, Cumuruxatiba, Jequitinhonha Camamu – Almada Jacuípe, Sergipe/Alagoas, Pernambuco/Paraíba, Potiguar, Ceará, Barreirinhas, Pará – Maranhão, Foz do Amazonas, Tacutu, Cassiporé, Marajó, Bragança – São Luiz, Jacaúnas, Potiguar, Jatobá, Tucano, Recôncavo, Barra São João and Taubaté (BIZZI et al., 2003).

In the east and southeast margins, especially in the segment between the Santos and Espírito Santos basins, fold belts separating pre-Cambrian cratonic masses are characterized by NE-SW structures. In the northeast of the country, the east-west alignment of the Pernambuco/Paraíba basin exerts a fundamental role in the tectonic control of the region. In the northern margin, the highlight is the Transbrazilian lineament, a NE-SW structure that separates the extension of the Ceará basin from the transpression segments of the Piauí-Camocim basin (BIZZI et al., 2003).

The main pre-rift rocks among Brazilian coastal basins are volcanic rocks of the inferior Cretaceous (being found in the Santos, Campos and Espírito Santo/Mucuri basins), and Palaeozoic/Mesozoic sediments (in the Pelotas, Cumuruxatiba, Jequitinhonha Camamu – Almada Jacuípe, Sergipe/Alagoas, Pernambuco/Paraíba, Potiguar, Ceará, Barreirinhas, Pará – Maranhão, Foz do Amazonas, Jatobá, Tucano and Recôncavo basins). Jurassic volcanic rocks, Mesozoic rocks, Mesozoic volcanic rocks and Pre-Cambrian rocks can also be found as a main structure in a smaller amount of basins (BIZZI et al., 2003).

3.3.2. OCEANOGRAPHIC SETTINGS

Being of great importance for oil spills, oceanographic characteristics (such as currents and water masses) are especially relevant for the prediction of the scattering patterns, direction and velocity of oil slicks in the seas.

Moving from east to west near the Equator line, the South Equatorial Current bifurcates when it reaches the northeast coast of the country, generating the Guiana Current and the Brazil Current (MENDES; SOARES-GOMES, 2007).

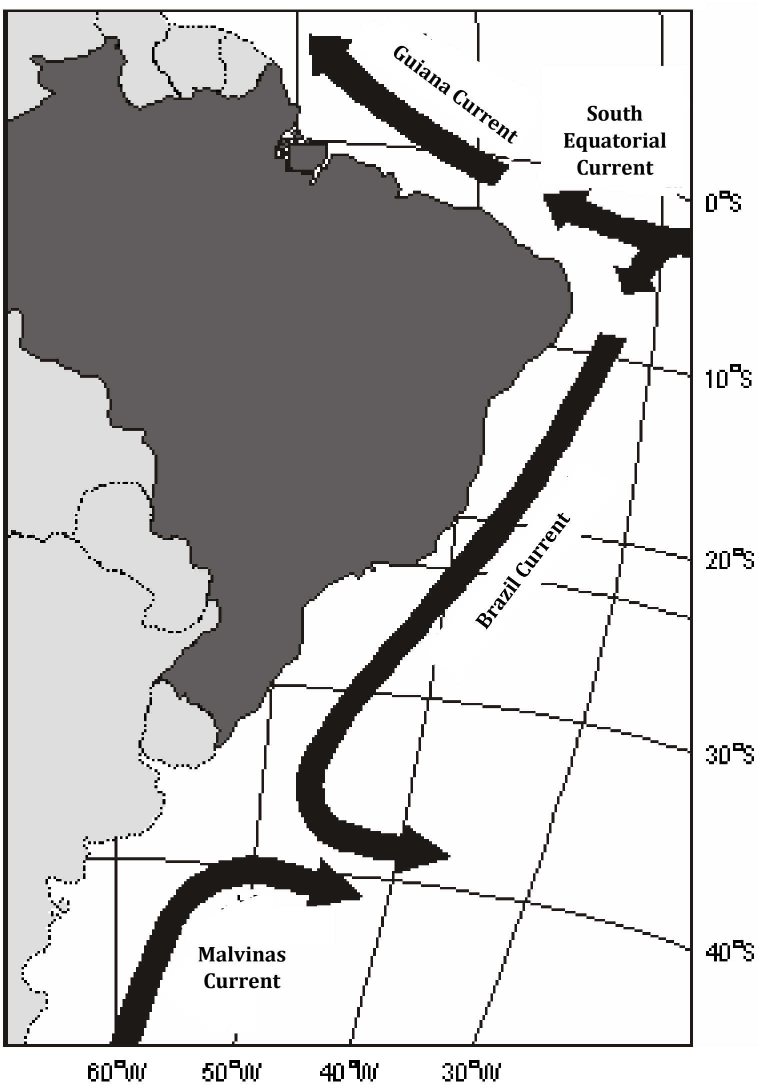
The Guiana Current is responsible for moving the waters from the Amazon River to the Amapá coast, reaching the French Guiana, where it separates from the coast (GYORY; MARIANO; RYAN, 2013; MENDES; SOARES-GOMES, 2007). Strong and persistent, the Guiana Current has its highest velocities occurring along the edge of the continental shelf, with the maximum speed registered in April-May and a mean speed of 41,6 cm/s (GYORY; MARIANO; RYAN, 2013)

The Brazil Current, a weak western boundary current that runs from about 9°S to about 38°S, carries warm subtropical waters, presenting a temperature of around 18 to 28°C (BISCHOF et al., 2004). It is originated in the region where the South Equatorial Current bifurcates, also generating the North Brazil Current (CAMPOS et al., 1995; SILVEIRA et al., 2000). It then borders the continent until it reaches the region of the Subtropical Convergence, where it gets separated from the coast. Although western currents are normally expected to bear intense and narrow water flows, the Brazil Current presents a relatively weak flow if compared to the Gulf Stream, the western current of the North Atlantic (SILVEIRA et al., 2000). It is pointed out, however, that it is energetically comparable to its North Atlantic counterpart, especially on its southernmost part, the region of confluence with the Malvinas Current (CAMPOS et al., 1995). The Brazil Current region is composed by the superposition of various water masses, including a surface mass known as Tropical Water, characterized by temperatures over 20˚C and high salinity, results of intense radiation and excess evaporation (EMÍLSSON, 1961; SILVEIRA et al., 2000). It appears as a layer of maximum salinity at depths between the surface and 100m in the area east of the

Bahia coast (EMÍLSSON, 1961). In general, velocities tend to increase as the current heads south, starting with $4x10^6$ m^3/s after the South Equatorial Current bifurcation and reaching around $18x10^6$ m^3/s around 31˚S, with all values obtained up to 1600m of depth, although some of the highest velocities calculated are restrict to the first 500 or 200m (SILVEIRA et al., 2000). It remains small, for more than 1000 km, showing values of $5x10^6$ m^3/s or less, while being confined to the upper continental slope and shelf edge (CAMPOS et al., 1995). It is also mentioned by Silveira et al. (2000) that the current moves away from the coast when it reaches 15˚S, due to the enlargement of the continental platform in the area. Moreover, seasonal wind-driven upwelling of cold, nutrient-rich waters are known to occur inshore from the northern Brazil Current, especially in the Cabo Frio area. Campos et al. (1995) mentions a counter-circulation on the shelf in the Santos Bight inshore of the current, possibly the northern end of a cold and fresh shelf current that originates on the Argentine shelf, but not much is known about it, although it could represent a major conduit for exchange of heat and salt. Little is known about eddies regularly spawned in the poleward extension of the Brazil Current, as well, other that some can be up to 300-400 km across, which can be considered large; and that they carry heat and salt to the northern realm of the Antarctic Circumpolar Current, possibly representing an important transfer mechanism. Near the Abrolhos region, in the south of the State of Bahia, large eddies are also formed, according to data collected by the Brazilian Navy, which in this case may be a consequence of the irregular bottom topography of the area. The same data shows that the Current becomes more regular from the Cabo Sao Tome area, 22˚S, reaching its highest velocities over the edge of the continental shelf (EMÍLSSON, 1961). Silveira et al. (2004) also references the Brazil Current between 20˚S and 28˚S as shallow, warm, salty and with an adjacent flow to the Brazilian coastline.

Figure 4 shows the simplified trajectory of the Brazil Current, the Guiana Current and the point where the South Equatorial Current bifurcates.

Figure 4. Trajectory of the South Equatorial, Guiana, Brazil and Malvinas Currents.



Source: Unisanta (2017).

3.3.3. CLIMATOLOGICAL SETTINGS

The Brazilian coast present similar climate characteristics to the Mediterranean region, although those tend to be more spatially varied and defined: in the northeast coast, the climate is hot (with an average of more than 18°C in every month of the year) and dry, turning wetter as one goes along the coast towards the south. From around 20-25°S, the average climate is reasonably colder, having a yearly temperature of around 10 to 16˚C (NIMER, 1989). Differently from the Mediterranean Sea due to its hemispherical position, the cooler temperatures are experienced around August-September, while the warmer are observed in February (BISCHOF et al., 2004).

In the east coast of South America, extra tropical cyclones are important meteorological systems during the whole year, but have a special relevance during the winter, when cold air masses create more substantial horizontal temperature and pressure gradients (FUENTES; BITENCOURT; FUENTES, 2013). Winds are also more intense in higher latitudes (FUENTES; BITENCOURT; FUENTES, 2013), which translates to regions towards the south of Brazil.

3.4. OIL SPILLS: CAUSES AND CONSEQUENCES

Discharging of oil into the sea or land may happen for a number of reasons, depending on factors as the place in which the oil is located, how frequently (and for how long) it is normally handled by workers and climatological conditions around it, among others.

Common causes of oil spills are human failures (which include, but are not restricted to, lack of knowledge, lack of attention, tiredness and negligence), equipment failures (that may happen especially when the equipment chosen to handle the oil is too outdated, not regularly checked or mishandled), due to cracks on the seabed caused by excessive pressure exerted in the extracting process (consequently letting oil escape from its basin) and, of course, explosions and ruptures on wells, oil pipes and oil tankers (ALVES; ALVES; MARTINS, 2013). The rupture of the tanker Castillo de Bellver, described in Section 1, is a great example of the latter.

An example of an oil spill caused by a pipeline leak was the discharge of around 176 thousand gallons of crude oil into Dakota Creek, in the United States of America. The accident happened in December of 2016 and had also as causes, besides the pipeline rupture itself, human and equipment failures to quickly identify and contain the leak (DICHRISTOPHER, 2016).

As already mentioned in items 1 (Introduction) and 2.1 (Organic Contaminants), regardless the causes, the presence of oil in ecosystems can cause a variety of environmental and public health problems, negatively affecting living beings (directly, by exposure; or indirectly, by causing disturbances on food webs and on habitats) and the natural balance of a region.

3.5 CHARACTERISTICS OF CRUDE OIL

One of the most common classifications to crude oil is based on its density and makes use of an international index of quality, known as API gravity, given by Equation 1, in which ρ_r represents the density of the oil relative to that of water at 15.6°C (or 60°F). Water, consequently, has an API gravity of 10 degrees (JONES, 2010).

$$\text{Degrees API} = 141.5/\rho_r - 131.5$$

[Equation 1]

This quality index was established by the American Petroleum Institute, an organization created in 1924 with the purpose of “establishing and maintaining standards for the worldwide oil and natural gas industry”, according to their own official website. It is still affirmed that their standards enhance the quality of products and safety in the petroleum industry, while minimizing waste, costs and confusions regarding said products. API Hydrometers, based on the scale used to describe crude oils in “degrees API”, have been in the market since 1921.

The fact that the index of quality of crude oils is based on density can be easily explained by the market preference for lighter crudes, as those are richer in the lowest boiling distillate, gasoline, and generally present a greater yield of light fractions by distillation (JONES, 2010; YASIN et al., 2013). The lighter the oil is, the higher API gravity it has and, commonly, the higher its prices are (YASIN et al., 2013). The intervals for each classification are shown in Table 1.

Table 1. Classification of crude oil based on its API gravity.

Classification	**API gravity**
Light Crude	> 31.1 degrees
Medium Crude	22.3 – 31.1 degrees
Heavy Crude	< 22.3 degrees

Source: GOODSON (2017).

According to GOODSON (2017) and Santos et al. (2014), the conventional oil reserves exploited in the present consist of light and medium oil, as those two types, as implied before, require less processing at a refinery to procure a more valuable mix of products. Due to the constant decline of the availability of those “conventional” reservoirs, however, Santos et al. (2014) pointed out that the development of new technologies capable of the commercial exploitation of unconventional resources (such as heavy oil and extra-heavy oil reserves) might be necessary in the near future.

Aside from API gravity degrees, a frequently used method that estimates relative crude oil values is also based on the sulphur content of a sample. Sulphur, as a common impurity, must be removed from the majority of transportation fuels to meet air quality requirements (BACON; TORDO, 2005). Thus, higher quality crudes contain lower levels of sulphur, being those called “sweet” crudes, in contrast to the so-called “sour” crudes (crude oils containing higher levels of sulphur). As it happens regarding the API gravity of a certain crude, the lowest its sulphur level (hence the higher its quality), the highest its prices tend to be, reflecting the complexity of the processing needed (BACON; TORDO, 2005).

The previously mentioned method consists of a comparison between price differentials and differences in API gravity degrees and sulphur contents regarding two crudes in analysis. Another frequently used method, adopted mainly by refiners, is based on the crude's properties and their relation to product specifications, granting and discounting values to each distillation fraction, hence reflecting the difference between the quality of said fraction and the specifications required from the final product (BACON; TORDO, 2005).

Another commonly employed characterisation of crude oil is the analysis of hydrocarbon group types, in which major structural classes of hydrocarbons found in crude oil are studied and separated (ASKE; KALLEVIK; SJÖBLOM, 2002). An example of this classification method is the SARA-separation, described as the separation of crude oils in four main chemical classes: saturates (S), aromatics (A), resins (R) and asphaltenes (A) (ASKE; KALLEVIK; SJÖBLOM, 2002). Knowledge of the chemical composition of crude oils, even though important, is not enough to completely explain crude oil behaviour regarding emulsion stability, asphaltene deposition, among other characteristics. The knowledge of the structure of the crude oil, resultant of the interactions between the continuums of its chemical constituents, is equally important as the analysis of its chemical composition (ASKE; KALLEVIK; SJÖBLOM, 2002).

The term "structure" concerns the stabilisation of asphaltene in crude oil. Asphaltenes, according to Aske, Kallevik and Sjöblom (2002), are believed to be particles of approximately 3nm, thus being considered microcolloids in suspension. There are more than one model to describe the interactions between aromatic sheets of asphaltene monomers and other particles dissolved in oil, as resins, and their detailed descriptions do not fit the purpose of this thesis. It can be affirmed, however, that a considerable proportion of the problems encountered in the processing and refining phases of the oil industries (among others, equipment plugging, catalyst deactivation and formation damage) relates to the broad tendency of asphaltenes to self-aggregate (ASKE; KALLEVIK; SJÖBLOM, 2002).

3.6. REVIEW OF MITIGATION AND CONTAINMENT PROCEDURES

Mitigation and containment procedures are methods in which the main goal is to lessen the gravity of the effects of a spill in an environment, or, at least, contain its spread to other locations.

Every procedure presented below is associated with pros and cons of choice to mitigate and/or contain a spill and the situations in which each of them are the most indicated for.

3.6.1. BOOMS

In simple terms, a boom is a floating mechanical barrier consisting of four main components: a means of flotation, a skirt, a freeboard member and one or more tension members supporting the entire boom, in some cases with added weight (FINGAS; DUVAL; STEVENSON, 1979). As a containment method, it is generally the first equipment adopted at a spill and used as a way to prevent the oil to spread to certain locations considered to contain biologically and/or socially important or vulnerable resources (such as fish farms, for example) or, still, specific areas such as entrances to harbours and rivers (ALVES et al., 2016); to divert it to another area, where it can be treated or recovered; or, finally, to concentrate the oil in order to facilitate its recovery or burning. They resemble a vertical curtain with portions extending above and below the waterline, and can be classified in three basic commercially available types – fence, curtain or shoreline seal booms – and the particular type of location they should be used – offshore, inshore, harbour or rivers -, the usefulness of each of those types depending on the specific situation analysed (FINGAS, 2012; FINGAS; DUVAL; STEVENSON, 1979; ITOPF, 1987; NOAA, 2015).

The skirt has a particular importance in a boom, as the component that provides the basic barrier to the spread of oil. The design and depth of a skirt determines the efficiency of the boom in preventing the escape of oil and also the load exerted on the entire system. Different materials can be used in the construction of a skirt, the most common ones being fabric coated with nylon, polyester or fibreglass, and some can be reinforced with metal cloth. Expanded plastic foams as polyethylene or polyurethane and gases such as air or carbon dioxide are generally used as means of floatation, as well as natural floating materials as cork or wood. Floatation is necessary in order to keep the boom at the water surface and it is known that the greater amount of floatation material in a boom, the greater its ability to ride on the surface of waves. The freeboard member is positioned on top of the floating material to prevent the oil from washing over the top of the boom. Finally, tension members running along the bottom of the boom reinforce it against the horizontal load imposed by waves and currents, and ballast or weights are sometimes used to maintain the bottom in an upright position (FINGAS, 2012; FINGAS; DUVAL; STEVENSON, 1979).

According to Oil Spill Solutions (2015a), the weather conditions in the area of the spill are one of the main factors to determine which type of boom is going to be used as a response to the accident. In calm and quiet waters, fence booms are highly indicated, as they are more able to resist abrasion and are very reliable. In the presence of strong winds and currents, though, they are known to present low stability, besides having a slight flexibility for towing and low efficiency in waves, being then not indicated for these areas. The best solution in these cases is to employ curtain booms. They are generally air filled (although the means of flotation can also be solid for this type) and very good for towing and for use in rolling seas. Curtain booms have the advantage of being efficient, easily stored (as air filled booms are relatively compact when empty), easily handled and cleaned, having good wave-following capabilities and moderate escape velocities (ITOPF, 1987). Their disadvantages involve low resistance to abrasion and the risk of puncturing if mishandled (solid flotation booms, although more resistant, are bulky in storage). Finally, shore seal booms are used in the intertidal section of the shoreline and knowledge of the position of the low and high tide lines in the region is necessary. It is also notable the existence of options such as fence booms with external floats (mentioned as being bulky in storage and difficult to clean by the ITOPF book) and models that can act both as fence and curtain booms for different waters and situations (OIL SPILL SOLUTIONS, 2015a).

Another possible type classification for those materials divides them in hard, sorbent and fire booms. The former consists on the ones already described in this section. Sorbent booms are specialized devices used to absorb the moving oil slick in a porous material, such as straw (FINGAS; DUVAL; STEVENSON, 1979). Fire booms resemble metal plates with a floating cylinder at the top and thin metal plates, replacing the skirt present in hard booms, and are ideal to contain oil long enough that it can be burned up (NOAA, 2015).

Booms are a relatively simple and quick first step in dealing with an oil spill, protecting sensitive areas and making the cleaning process easier and less expensive as it deflects and/or concentrates the oil in a smaller area. Despite these advantages, it is necessary to point out that booms are subject to a variety of failures, which can make it less efficient in containing the spill. Winds, water currents and waves are often factors that can negatively affect a boom system, leading to loss of oil. For booms riding perpendicular to the current, there is a critical velocity that should not be exceeded. Regions presenting more turbulent waters (as most rivers and estuaries) generally offer more complications in the use of booms and sometimes, in those cases, deflection is the only way containment can be achieved, with more than one boom system being employed if necessary (FINGAS, 2012) and positioned at various angles to the current, in a cascading pattern (FINGAS, 2011).

The most common arrangement used is a U configuration, but it is also possible to find booms arranged in a V or J configuration. The U configuration is generally achieved by towing the boom behind two vessels and allowing the current to push against the centre of the boom, always being careful to notice the velocity of the current, which cannot exceed 0.5 m/s (or 1 knot), the critical velocity. Allowing the entire boom to move down current is also a way to achieve this configuration. The J configuration is a variation of the U configuration, also used to contain oil as well as to deflect it to the containment area. Lastly, the V configuration is commonly achieved by attaching two booms to boats in order to direct the oil slick towards a skimmer (boats and other devices that can remove oil from the sea surface) situated at the apex of the system (FINGAS, 2011; NOAA, 2015). When used with the purpose of protecting areas from an oil spill or enclosing areas where oil is frequently loaded or unloaded, special long-lasting booms may be employed as fixed systems attached to docks, piers, harbour walls or other permanent structures with sliding-type connectors that allow the boom to move up and down with the tide variations and waves (FINGAS, 2011).

It is notable the existence, yet, of permanent booms being offered in the market for areas where round the clock protection is required. They need to be robust and durable for long-term installations (CLEAN-UP OIL, 2015).

3.6.2. BURNING

Burning is, on the other hand, a treatment procedure – other than a containment one – that involves the controlled ignition and burning of the oil at or near the spill site on the surface of the water or in a marsh (MULLIN; CHAMP, 2003). It has specific requirements to work properly: for example, the thickness of the oil layer must be enough to continually support combustion without getting affected by the coolness of the water below it (at least 2 – 3mm, as indicated by Oil Spill Solutions (2015b)), being a decisive factor on the application of in situ burning. A common approach to solve this matter consists of moving booms around the spill in order to concentrate the slick. The combustion must also be supplied with enough oxygen (FINGAS; DUVAL; STEVENSON, 1979). According to the NOAA website, this technique works best in regions presenting relatively calm weather and still fresh oil. It is, for example, one of the main responses to spills in the USA Mexican Gulf since 1994, according to the Oil Spill Solutions website (2015b).

Mullin and Champ (2003) point out that it is still a controversial method due to the consequent release of resulting gases in the atmosphere, but it has been shown to be an appropriate, versatile, efficient and non-complex oil spill countermeasure if applied in the right circumstances. According still to the same authors, ‘’In situ burning offers a logistically simple, rapid, inexpensive and if controlled a relatively safe means for reducing the environmental impacts of an oil spill’’. It changes the oil into water and carbon dioxide, primary combustion products, and diminishes the volume of the oil, reducing the need for techniques of collection and disposal of recovered material, a considerable matter in a great amount of environmental aiding processes. Also, large quantities may be burnt at a time, and if this method is applied early in a spill, removal efficiencies for thick slicks can exceed 95%. Buist (2003) mentions that oil removal efficiency is a function not only of the initial thickness of the slick, but also of the thickness of the residue remaining after extinction and the areal coverage of the flame. It requires minimal, but some specialized equipment (i.e. fire booms, to avoid the fire to affect other ships and properties), and it is an excellent method to remove spilled oil from ice covered waters and snow (MULLIN; CHAMP, 2003).

The main disadvantage of this method is the very limited window-of-opportunity involved in applying these operations. For the treatment to be successful, the oil (or part of it) must not have already emulsified to a point where it’s not ignitable anymore, normally this point being when the oil presents around 25% of water content, a stable emulsion that starts to form as soon as the oil is spilled. Even if it still burns, emulsions are more difficult to ignite and once ignited display reduced flame spreading, despite being more sensible to wind and waves. The window-of-opportunity in each case is defined by the type of oil spilled, prevailing meteorological and oceanographic conditions and the time it takes for the oil to emulsify (MULLIN; CHAMP, 2003). Another disadvantage is also one of the most common factors against widespread acceptance of this procedure: if applied in an area poor in oxygen, the incomplete combustion of the oil generates atmospheric emissions – as indicated by large volumes of black, particle-laden smoke -, containing particulates, combustion gases, unburned hydrocarbons and residue (AURELL; GULLETT, 2010; MULLIN; CHAMP, 2003). Human health is the primary concern regarding these emissions, which led to the establishment of extensive research on the matter. Smaller or respirable particles are some of the most hazardous components of the smoke, and studies showed that ground level concentrations could exceed regulated health values. Polyaromatic hydrocarbons are also a concern in the emissions from burning processes, as all crude oils contain a certain amount of PAHs, but more recent studies have shown that gaseous PAHs emissions are negligible and PAHs in the soot and residue have a smaller concentration than in the crude oil (MULLIN; CHAMP, 2003). Overall, more PAHs are destroyed by the fires than are created (FINGAS, 1999). Gaseous products in the smoke, including carbon dioxide, also did not appear as a major concern for the environment or human health in the conducted studies, which indicates that airborne emissions should not the considered a serious threat to human health nor the environment, given the results of the already concluded studies on the subject, especially if considered that the greatest portion of population the closest to the burning is generally located several miles away from its spot (FINGAS, 1999; MULLIN; CHAMP, 2003). Still, a remaining concern lies on the possibility of the existence of any ‘’hidden’’ components that may be produced and present unwanted effects when released in the atmosphere (FINGAS, 1999). The resultant residue, although does not present any detectable acutely toxic compounds, should always be collected from the surface of the water before sinking (MULLIN; CHAMP, 2003).

Compounds sometimes are used as burning agents (such as gasoline and light crude oils), in an attempt to ignite and sustain the combustion, and others as wicking agents (such as straw, wood chips, glass beads, etc.), to increase oxygen availability and insulate the burning oil from water (FINGAS; DUVAL; STEVENSON, 1979).

It is also essential to consider if there are any communities near the place of the burning and if there is a risk of secondary fires; for that, weather forecasting is extremely important to inform if the wind will not shift and threat to push the fire to an unwanted direction (OIL SPILL SOLUTIONS, 2015b).

3.6.3. THE USE OF BOOMS AND BURNING TREATMENTS IN THE MEDITERRANEAN SEA

Remarkable beaches and cities with ancient buildings mark the coast of Cyprus, especially towards the south (e.g. Coral Bay, Paphos; Nissi Beach, Ayia Napa, etc.). Depending on the wind regime established by then, oil spilled anywhere near the island could end up being washed inland, reflecting in environmental and economic issues to the coastal areas of the country, as tourism would be seriously compromised. In the case of an accident, the employment of booms could represent a temporary protection to these areas. Despite this fact, it is important to point out that careful analysis regarding the precise type and location of possible booms would be indispensable, due to the energetic circulation and high climatic variability observable in the area. Frequent extra tropical cyclones in the region during winter and spring, mentioned by Michalopolou and Jacovides (1987), represent a considerable threat to the efficiency of booms, as winds are a main failure factor for those systems. It is also in the spring period that an increase in thunderstorms is frequently observed, which indicates that booms possibly present a bigger tendency to fail if an accident occurs in the area between the months of March and June.

Given that the circumstances of the accident are favourable for this technique, in-situ burning of spilled oil would also be viable in the Mediterranean. As pointed out by the NOAA website and mentioned in the previous section, areas with calm weather tend to facilitate burning procedures, so as it happens with the use of booms, thunderstorms and extra tropical cyclones could also be an issue.

3.6.4. SKIMMERS

Skimmers are mechanical devices designed to remove and recover oil from the water surface, maintaining the physical and chemical properties of spilt oil (FINGAS; DUVAL; STEVENSON, 1979; ITOPF, 2014). They are all composed by an oil recovery element, a flotation means or support arrangement and a pump, used to transfer collected material to storage (ITOPF, 1987). According to the ITOPF (2014), the ultimate aim of any recovery operation is to collect as much oil as is reasonably and economically possible, overcoming interrelated problems. Fingas, Duval and Stevenson (1979) divide skimmers into five generic categories, following their basic principles of operation: weir-type devices (1); suction devices (2); centrifugal devices (3); submersion devices (4) and sorbent surface devices (5). The descriptions of the systems below are based on Fingas, Duval and Stevenson (1979) and on ASTM (2016).

1. Weir skimmers, the first generic category above mentioned, consists of a weir or dam system with a holding tank and an attachment connected to an external pumping equipment that collects oil. As it may be noticed, the principle of this model is to use gravity to drain oil off the water surface. Complex versions of these

skimmers include features for self-levelling and adjustable skimming depth. Some models allow adjustment to prevent massive amounts of water to enter the weir; in case this feature is not present, it can be of interest to consider including oil/water separators in the system. Weir skimmers have been proven a successful way to recover a range of low viscosity oils, however, their efficiency can be reduced by the presence of litter or any other debris and they are very susceptible to wave action.

2. Suction systems sit on the water surface and consist simply of a suction hose with an enlarged end. They require little to no adjustment and are able to recover a great range of different viscosity oils. They present, though, the same problems as weir skimmers: debris and waves threat the efficiency of the system, being then more commonly used in shallow and calm waters. Also, they may plane over the top of the water surface if the currents are faster than 0.6 knots in the area.

3. Centrifugal skimmers create a water vortex (or whirlpool) in which oil and water are drawn into a collection area, where they are pumped towards an oil-water separator and the oil is recovered. As debris screens can be utilized without affecting oil recovery, this system deals more efficiently with this problem, although it still presents limitations regarding waves and currents.

4. Submersion skimmers use a slightly more complex system consisting of a moving belt partly submerged, being kept at an angle to the surface. This belt is responsible to force the oil downward toward the mouth of a collection well. These systems are normally mounted on or incorporated within a powered vessel, and normally present a high efficiency with low viscosity oils and relatively thin slicks. However, it should be carefully operated as oil may miss the collection well is the skimmer moves too quickly, which makes it excellent with low specific gravity oils, that are more buoyant. Debris and waves do not represent an issue as big as for the previous discussed systems, although waves can slightly decrease the collection efficiency of submersion skimmers.

5. Sorbent (or ‘’oleophilic’’) surface skimmers involve the use of a surface to which oil can adhere and later be removed by a wiper blade or pressure roller, then deposited into an on-board container or pumped to storage facilities on a barge or the shore. Sorbent surfaces can be shaped into a drum, disc, brush, belt or rope that is continuously moved through the oil film. The oil is then removed by scrapers. They are more efficient with medium viscosity oil (although some skimmers, as those with

toothed discs, were specifically designed for the recovery of heavy oils) and can operate considerably well with thin oil slicks, since they do not pick up large quantities of water. Of all types mentioned, this is the least affected by waves, but debris can negatively affect oil recovery and even damage some of the system's parts.

Fingas, Duval and Stevenson (1979) also affirm that different skimmers present a huge variation in recovery efficiency, capacity and forms, and that a number of factors can influence the effectiveness of the process: the type and viscosity of oil spilled; the thickness of the slick (as already mentioned to be important); the dimensions of the spill; the presence of debris either in the oil or water (the capability of handling debris depends hugely on the generic type of skimmer – some will stop as soon as branches, seaweed or debris are picked up); meteorological and oceanographic conditions (winds can move the slick away from the skimmer or towards it, and currents presenting velocities over 0.7 knots may cause the oil to be swept under the skimmer); the environments that may be affected; the calmness of the water in the site and its depth (the effect of waves on the efficiency depends majorly on the type of skimmer that is being used) and even the location of the spill, especially regarding access. The intake of air by certain types of skimmers can also represent problems in the recovery of oil. ITOPF (2014) proposes three different characterisations for skimmers, being them self-propelled, dynamic or stationary. While the latter, as the name suggests, is put still in the location bearing the highest concentration of oil, the two first types are moved, respectively with joysticks (or levers) or positioned on the bow or on side of a vessel. The same website also suggests that other factors such as the skill of the operator, storage capacity of the skimmer and degree of emulsification by the time of the procedure also affects the efficiency of the whole process.

Other types of skimmers are mentioned by the ASTM (2016), but they could generally be included in one (or more) of the groups already mentioned. Suction systems tend to collect large amounts of water with the oil, sometimes reaching values as high as 90% of water in the whole collected material, which then has to be separated using gravity. This fact can be considered an advantage when dealing with high viscosity oils, as the excess water helps maintaining the flow and prevent the blockage of hoses and pipework, but can represent a problem if the system is not equipped with adequate storage facilities (ITOPF, 1987).

3.6.5. CHEMICAL DISPERSANTS

The addition of some specific chemical agents in a spill region can facilitate oil removal, however, it is largely discouraged in most cases and even prohibited in others, being often used as a last resort, when containment and recovery is impractical (FINGAS; DUVAL; STEVENSON, 1979; ITOPF, 1987). In general, chemicals are only used in oil spill clean-up programs when the potential damage (to biological and physical resources) could be even greater if not used. One of the most common chemical treatments adopted is the use of dispersants. Those contain chemicals that in simple terms are responsible to accelerate the emulsion forming process by reducing the surface tension between oil and water, resulting in the breakup and dispersal of the slick. They are also used to prevent oil from adhering to solid surfaces (e.g. piers) (FINGAS; DUVAL; STEVENSON, 1979). A surface-active agent (surfactant) is the key component of a dispersant; having a molecular structure such that one part of the molecule has an affinity for oil (oleophile) while the other has an affinity for water (hydrophile). It is argued that dispersion of the slick increases the opportunity for oxidation, biodegradation and weathering processes, also reducing immediate damage to wildlife and the local environment (FINGAS; DUVAL; STEVENSON, 1979). In the past, hydrocarbon-based solvents were included in the formula of dispersants which used to increase the volume of hydrocarbon pollutants present in the water; over time, those solvents were substituted for organic solvents such as alcohols and glycols, making dispersants less toxic. However, additives included to increase their dispersing abilities threat natural waters (FINGAS; DUVAL; STEVENSON, 1979).

When spraying dispersants in the oil slick, it is necessary to agitate the water to facilitate formation of oil-in-water emulsions, even in the presence of waves, as their natural action, together with winds, are often not sufficient. Dispersants are generally most efficient in unweathered oil slick in relatively warm water (FINGAS, DUVAL & STEVENSON, 1979). Also, dispersants tend to be ineffective in very viscous oil slicks since they run off into the water before the solvent can penetrate the oil (ITOPF, 1987). Fingas, Duval and Stevenson (1979) point as advantages of the use of dispersants the increased rate of oil degradation; less tendency for the oil to form tarry residues and water-in-oil emulsions (which represent a threat to coastlines and seabirds); less contamination of beaches and decreased impact of the oil on waterfowl. They also affirm that disadvantages include potential toxic effects, increased exposure of organisms to toxic hydrocarbons in the dispersed oil and lack of knowledge on the fate of the resulting products.

Application methods depend on the type of dispersant, the size and location of the spill, and the availability of vessels or aircraft for spraying the dispersant. Even when using vessels (of all sizes), an aircraft overhead may be needed to direct the boat in case the oil moves away from the source of the spill (ITOPF, 1987).

3.7. MEDSLIK

The software chosen for the predictions in this work was MEDSLIK, an oil spill and trajectory 3D model developed and implemented by the Oceanography Centre of the University of Cyprus, in the Eastern Mediterranean. MEDSLIK was created specifically for predictions in the Mediterranean, the Black and the Baltic seas, having been successfully used for real oil spills incidents in the area (such as the Lebanese oil pollution crisis during the summer of 2006) and through EMSA warning reports and satellite images, besides risk assessments from the offshore planning of the exploration of the Eastern Mediterranean Levantine basin.

It gathers and uses a great variety of information to generate a prediction of the dispersion of the oil slick in water, the possibility of its adhesion to near coastal areas, its evaporation, its emulsification and its viscosity changes. The information taken into account to make it possible includes the location, date and time of the spill (and the characteristics of the area in those circumstances, such as winds, currents, waves, temperature, etc.); the duration of integration, the volume or rate of oil spilled at sea and the nature and characteristics of the oil spilled (using either the REM-PEC database with 240 oil type characteristics or its API number).

Other commonly used softwares for oil slick fate in waters are:

- ADIOS (Automated Data Inquiry for Oil Spills): Developed by the NOAA, this oil weathering model uses a database of more than a thousand different types of crude oil and refined products, offering as an output the expected characteristics and behaviour of spilled oil, focusing on their changes once the oil has been released. The information required by the software, besides the characteristics of the oil spilled, comprehends other data on the spill itself, environmental conditions and the planned clean up strategy. According to NOAA's website, the program was designed to run on as little information as possible, making predictions quicker and more practical as the type of information required can be obtained on the field or, at least, easily estimated (such as winds speeds, water temperature and wave heights). It also predicts the effects of common clean up techniques (e.g. skimming, burning or chemically dispersing the oil) and environmental processes (e.g. sedimentation), offering predictions for a maximum of five days. Despite the latter statement, ADIOS works in a way that is generally very similar to MEDSLIK.

- GNOME (General NOAA Operational Modelling Environment): Another software designed by NOAA, in this case specifically to predict the possible trajectory a pollutant might follow in or on a body of water. Although developed for dispersion of pollutants in general, the model is commonly applied to oil spills, being able to "predict how wind, currents and other processes might move and spread oil spilled on the water; learn how these predictions of where and how oil might move are affected by uncertainty in observations and forecasts for ocean currents and wind; and see how spilled oil is expected to change chemically and physically, known as weathering, during the time that it remains on the water surface", according to NOAA's website. It also estimates the amount of oil that is still floating, that was beached and that was evaporated after a certain period of time. The software's latest version was released on September of 2014.

- CAFE database (Chemical Aquatic Fate and Effects): This program, also developed by NOAA, enable users to estimate the fate and effects of a large variety of chemicals, oils and dispersants, assessing environmental impacts that may be caused by their presence in an aquatic environment. It allows responders to choose between four different spill scenarios: chemical, oil only, dispersant only and dispersants mixed with oil.

- OSCAR (Oil Spill Contingency and Response): Developed by SINTEF (an independent research organisation in Scandinavia), OSCAR is a model and simulation tool that accounts for weathering and the physical, biological and chemical processes that affect oil at sea. According to SINTEF's website, it is successfully used "for planning, hind casting and forecasting of accidental releases in locations such as the Northern and Baltic Sea, Gulf of Mexico and the Mediterranean Sea". The software also supports statistical and stochastic modelling, thus being able to predict scenarios under a wide range of weather or seasonal conditions.

- OSIS (Oil Spill Information System): Developed jointly by BMT and AEA Technology plc., this model simulates the fate and dispersion of surface oil slicks, representing them as a collection of free moving particles. It combines parameters such as weathering algorithms (determining physical chances in a slick as time passes), transport processes acting on the oil (currents, winds, waves, diffusion and buoyancy in the ocean surface layer), changes due to evaporation, emulsification and natural dispersion of oils and changes in physical properties (density, viscosity and flash point) to provide the fate of oil at sea as an outcome (ENERGEAN OIL & GAS, 2016).

- OILMAP: Developed by RPS ASA, global science and technology solutions company (member of the RPS Group), this software is also an oil spill response tool that predicts the movement of spilled oil, tracking various hydrocarbon components on the water surface, in the water column, and in the air. According to the developers' website, it has a broad range of applications, including emergency response decision support, spill drill exercises, oil spill response training, risk and impact assessment, contingency planning and hindcasts. The same website also states that OILMAP features an integrated GIS, a comprehensive oil database with complete oil properties information and easy access to online web maps and met-ocean data services, among others.

Despite the possibility of use of many of those software described and others not mentioned, MEDSLIK was chosen to make the predictions shown in this thesis due to its specificity and practical usage towards the studied area, the Levantine Basin in the Mediterranean Sea. It features data on the characteristics of a broad range of oil types, allowing the comparison made between three different oil types in the same scenario. Finally, the software and its needed data had easy access in the laboratory where this thesis was mainly developed, making the research process simpler and faster.

4. MATERIALS AND METHODS

MEDSLIK, software developed and implemented at the Oceanography Centre of the University of Cyprus (OC-UCY), was chosen to run the simulation intended in this thesis. It can be obtained online after registration in the software's website.

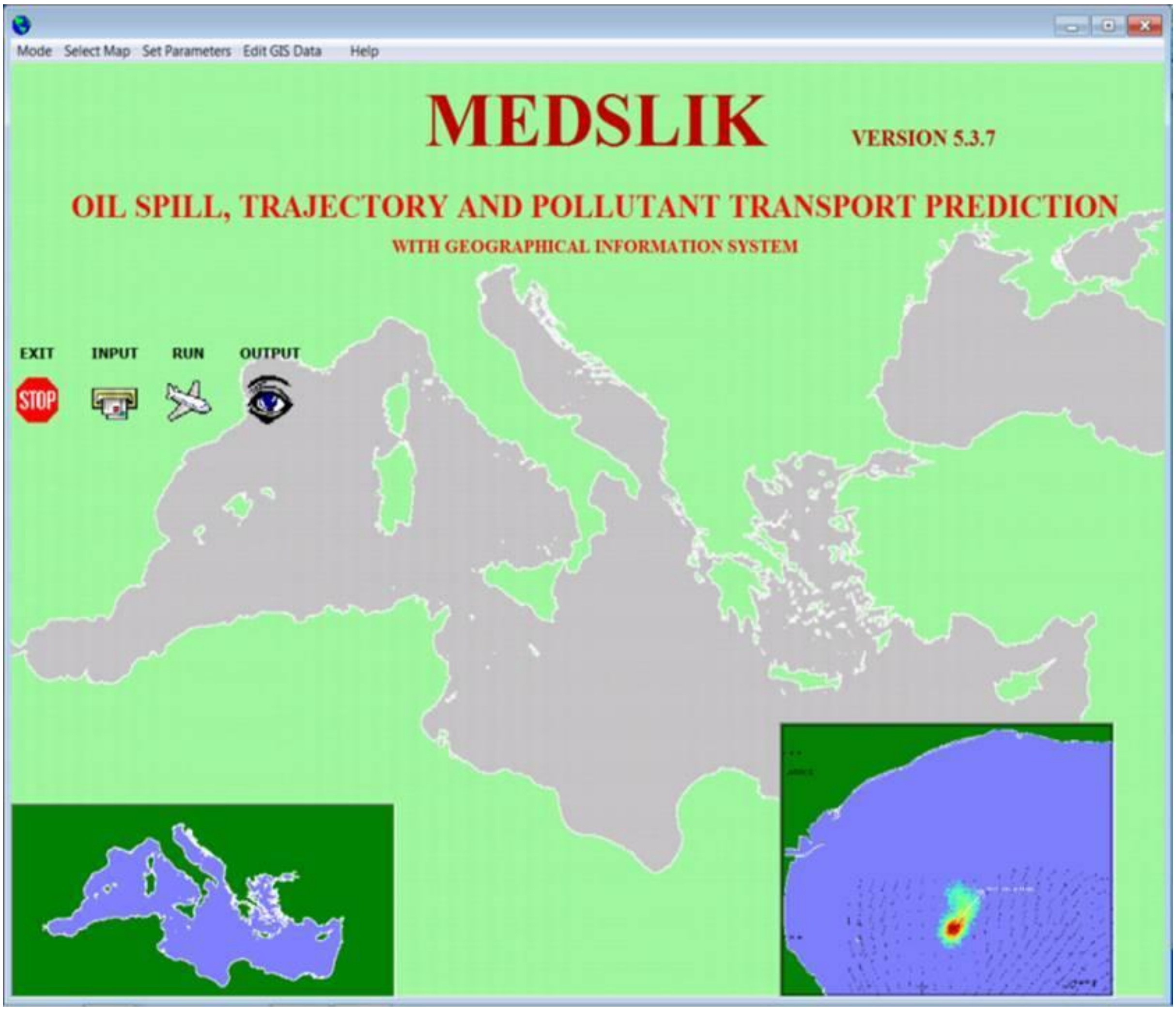
For the simulation to run, it is required by MEDSLIK for the user to enter forecast data for the studied region. Those can be downloaded from the CYCOPOS (Cyprus Coastal Ocean Forecasting and Observing System) website - http://www.oceanography.ucy.ac.cy/cycofos/browse.php, which also require previous registration. Various database options are provided by the website, giving the user the opportunity to choose whichever fits best their study.

Next, the user should enter the date of the spill (MEDSLIK matches the date entered with the forecast data), the time of the day in which the spill happens and its duration (in hours), the length of the simulation (counting from the time the spill happens), the location of the spill, sea surface temperature and type of oil (from a vast list already provided by the software's library). It is also important to set the specifics of the output, as the depth interval considered, its pixel size (in meters) and the time interval for the simulation (always confronting the quality and precision of the output and the time needed for the computer to run the simulation). The simulation is ready to be run and analysed after this step, only requiring the user to click the "run" button in the main screen and the "output" button to see the results.

The theoretical area studied comprises the Aphrodite field, offshore southern Cyprus, located at the exploratory drilling block 12 in the country's maritime EEZ (Exclusive Economic Zone). As already mentioned, to facilitate a broad view of possibilities and compare the outcomes of different possible accidents, the simulation was run for three different types of oil (Arabian Heavy, Arabian Medium and Arabian Light) and two very distinct climatic conditions through the choice of an incident day in the middle of the summer (5th of August, 2014) and a day in the middle of the winter (5th of February, 2015). That way, the influence of these differences could be noticed in the resulting damage of an oil spill in the area.

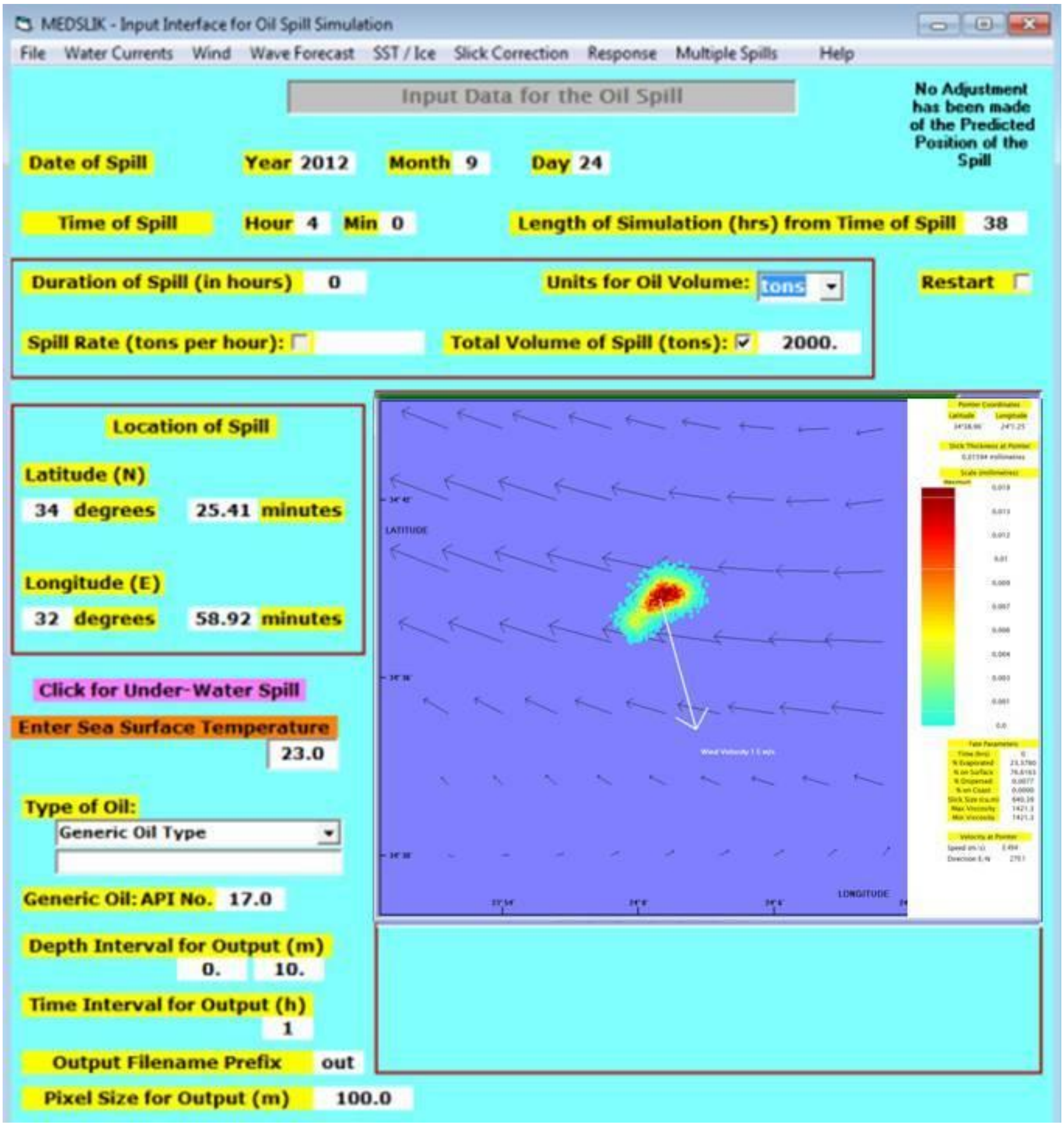
Figure 5 shows MEDSLIK's home screen (where the "Exit", "Input", "Run" and "Output" buttons are located) and Figure 6 shows the input screen.

Figure 5. MEDSLIK's home screen.



Source: MEDESS-4MS (2017).

Figure 6. MEDSLIK's input screen.



Source: MEDESS-4MS (2017).

The data input for this thesis were as follows:

<u>Date</u>

Year: 2014; Month: 08; Day: 05 (summer scenario)

Year: 2015; Month: 02; Day: 05 (winter scenario)

Time

08h00

Simulation length

120 hours (5 days)

Duration (hours) of spill:

15,4

Spill rate (tons per hour)

4000 (61600 tons of oil spilled in total)

Latitude (N)

33 degrees, 5 minutes

Longitude (E)

32 degrees, 59 minutes

Sea surface temperature

23.0 (default)

Type of oil

Three scenarios: Arabian light; Arabian medium; Arabian heavy

Depth interval

0 to 300m

Time interval

Hourly (1h)

Pixel size

100.0m

5. MODEL RESULTS

Analysing the results, it was not possible to distinguish a visible change in size, shape and direction of slicks when running the simulation with different types of oil. Considering the exact same dates and times (and, consequently, the same climatic circumstances) for all three different types of oil, it is noticeable a constant visual similarity in the outcomes, both for summer and winter cases, as exemplified in Figures 7 and 8.

Similar conclusions cannot be achieved when we consider the outcomes for one specific type of oil if spilled in the summer or in the winter. The change in climatic conditions - currents, waves, sea surface temperature and winds, mainly - result in drastic changes in the fate of the spilled oil.

The main results presented in this section will be summarized in Table 2, as a way to facilitate visualization and comparisons between oil types and climatic conditions.

In the prediction of a theoretical spill during the middle of the **summer of 2014** (Figure 9), all types of oil suffered a migration of approximately 95 km to the northeast, first by spreading in this direction and then moving, carried by currents and wind. From around the 75^{th} hour after the accident onwards, the oil appears to be occupying the largest areas during the period of the prediction, staying between 58 to 66 square kilometres in all three cases. This can be considered an expected result, as a liquid generally tend to gradually spread in a surface as time passes. For the dates considered, the fastest winds were mainly occurring on the first day of the spill (reaching 7 m/s in the 7^{th} hour), which may have accelerated the initial spreading, and during the whole period the wind was generally directed towards the northeast. The evaporation process occur during the first 26 hours for the Arabian Heavy oil, the first 33 hours for the Arabian Medium oil and the first 72 hours for the Arabian Light oil, staying constant through the rest of the simulation after that. This fact represents one of the main contrasts between the types of oil analysed: the lighter oil evaporates for a longer period and way more than the heavier oil, having 46.72% of its original volume evaporated after the 72th hour, while the heavier oil only presents 30.38% of its volume evaporated after the 26th hour, when the process stops. The Arabian Medium oil had 40.28% of its initial amount evaporated. The maximum concentration of oil in the slick is reached after 3 hours for the Arabian Heavy oil and corresponds to 22.46 tons per km^2; this maximum is reached after 2 hours for the Arabian Medium oil and corresponds to 24.60 tons per km^2 and after 21 hours for the Arabian Light oil, corresponding to 29.30 tons per km^2. Only 2.09% of the spilled Arabian Heavy oil has become mixed in the water column and was classified as dispersed oil; for the Arabian Medium predictions, 2.01% of the oil was dispersed in the same period of time, while the Arabian Light prediction presented a bigger percentage than the others, 2.34% (Figure 10 shows the visual outcomes for dispersed oil). Also, every spot of dispersed oil 120 hours after the spill showed more than 1000 tons of oil per km^2.

Climatic conditions during the middle of the **winter of 2015** (Figure 11) proportioned a different scenario in the result of the predictions: winds blowing towards the southwest caused the surface spill to move out of the Cyprus basin, starting in the 12th hour after the spill and completely disappearing from the area around the 28th hour. After that, for all three types of oil, it is only possible to start to see part of the slick in the basin 74 hours after the spill, perhaps mostly due to a change in the direction of the wind, now blowing towards the north-northeast. The narrow and long (approximately 93 km wide, being its west end almost in the same location where the spill occurred) final shape of the slick for the three predictions is completely different than the summer scenario, which is visible if comparing the three pictures in Figure 7 with those in Figure 8. The fact that only the oil located in the Cyprus basin is considered in these predictions make area comparisons between summer and winter conditions difficult as not all the oil spilled during the winter may be included in some of the numbers depending on the time considered. Despite that, it is possible to compare the outcomes for the different types of oil: regarding evaporation, the same pattern was noticed for this scenario – the lighter the oil, the greater evaporation it suffers during the same period of time. The Arabian Heavy oil type ceased evaporation after only 22 hours following the spill, reaching 30.40% of the initial amount evaporated; the Arabian Medium had 40.28% of the original spill evaporated after being 29 hours in the water surface, whereas the Arabian Light had 46.72% of the original spill evaporated in the 59 hours following the accident. 5.98% of oil was dispersed by the end of the simulation using Arabian Heavy oil, falling to 4.71% in the Arabian Medium prediction and to 5.36% in the Arabian Light (with every spot presenting more than 1000 tons of oil per km^2, in all three types), number bigger than twice the values for the summer predictions (Figure 12 depicts the outcomes for dispersed oil). Finally, it is interesting to point out that the maximum amount of oil observed in the winter slicks after 120 hours were around 8248.29 tons per km^2 for the Arabian Heavy type; 6494.70 for the Arabian Medium type and 5364.60 for the Arabian Light, but it is not possible to reach conclusions about those values, as the slick goes out of the basin (thus adding uncertainty to the values corresponding to the area of the slick and invalidating comparisons between summer and winter scenarios regarding this parameter).

Both for summer and winter predictions (for all oil types), no amount of oil reached the coast. Summer predictions were the ones that got closer to the coast of Lebanon and Israel, but still several kilometres far.

Comparing the results as far as it is possible, it is interesting to notice that the percentage that evaporates of the same types of oil is almost identical for summer and winter predictions, which suggests that climatic conditions may not have as much influence in this process as in the definition of the shape and direction of spreading of the slick, for instance. It is a fact, though, that during the winter, all oil types evaporated faster than in the summer, an unexpected outcome as the water surface tends to be warmer in the summer, theoretically increasing evaporation rates. The difference between the percentages of oil dispersion in the summer and winter may be somehow related to differences in wind velocities: while the maximum velocity registered during the summer period was only 7 m/s and the minimum 2.8 m/s, winds during the winter specifically in the Cyprus basin reached 13.7 m/s by the end of the prediction, being the minimum value of 3.6 m/s.

It may be also interesting to point out the differences regarding the maximum viscosity of the slick reached in each case. For both summer and winter predictions, the Arabian Medium type was the one that showed the highest end values for viscosity, if compared with the other two types of oil. For summer conditions, this value corresponds to 3060.7 cs, contrasting with 2794.2 cs for the Arabian Heavy and 1972.6 cs for the Arabian Light; as for winter conditions, the maximum viscosity reached by the Arabian Medium was 5068.9 cs, an even higher value than for summer predictions (which may be explained by the fact that, according to ITOPF (2014), ''all oils become more viscous as the temperature falls'') contrasting with 4628.4 cs for the Arabian Heavy and 3266.8 cs for the Arabian Light. Those highest values were also the fastest ones to be reached in each climatic condition: 49 hours after the spill for the summer and 29 hours for the winter; while the Arabian Heavy took 74 hours to reach its maximum viscosity in the summer and 32 hours in the winter, and the Arabian Light took 56 hours in the summer and 42 hours in the winter. In all cases, the maximum values escalated quickly, then gradually lowering the rate of increase as the minimum values started to rise and eventually caught up with the maximum values. This happened after 101 hours for the Arabian Heavy oil in the summer and after 53 hours in the winter; after 78 hours for the Arabian Medium in the summer and 49 hours in the winter; and, finally, after 75 hours for the Arabian Light in the summer and 59 hours in the winter. Higher viscosities can represent a problem to the use of dispersants, as they are increasingly less effective as the viscosity rises (ITOPF, 2014). Changes in viscosity also modifies the type of skimmers and pumps that are most indicated for the treatment of the area, being then an important factor to be considered when preparing a plan to clean-up the spill (ITOPF, 2014).

Figure 7. Final shape of the oil slick (120 hours after the spill) predicted by MEDSLIK during summer conditions. From top to bottom, oil types considered in the simulation are respectively: Arabian Heavy, Arabian Medium and Arabian Light.

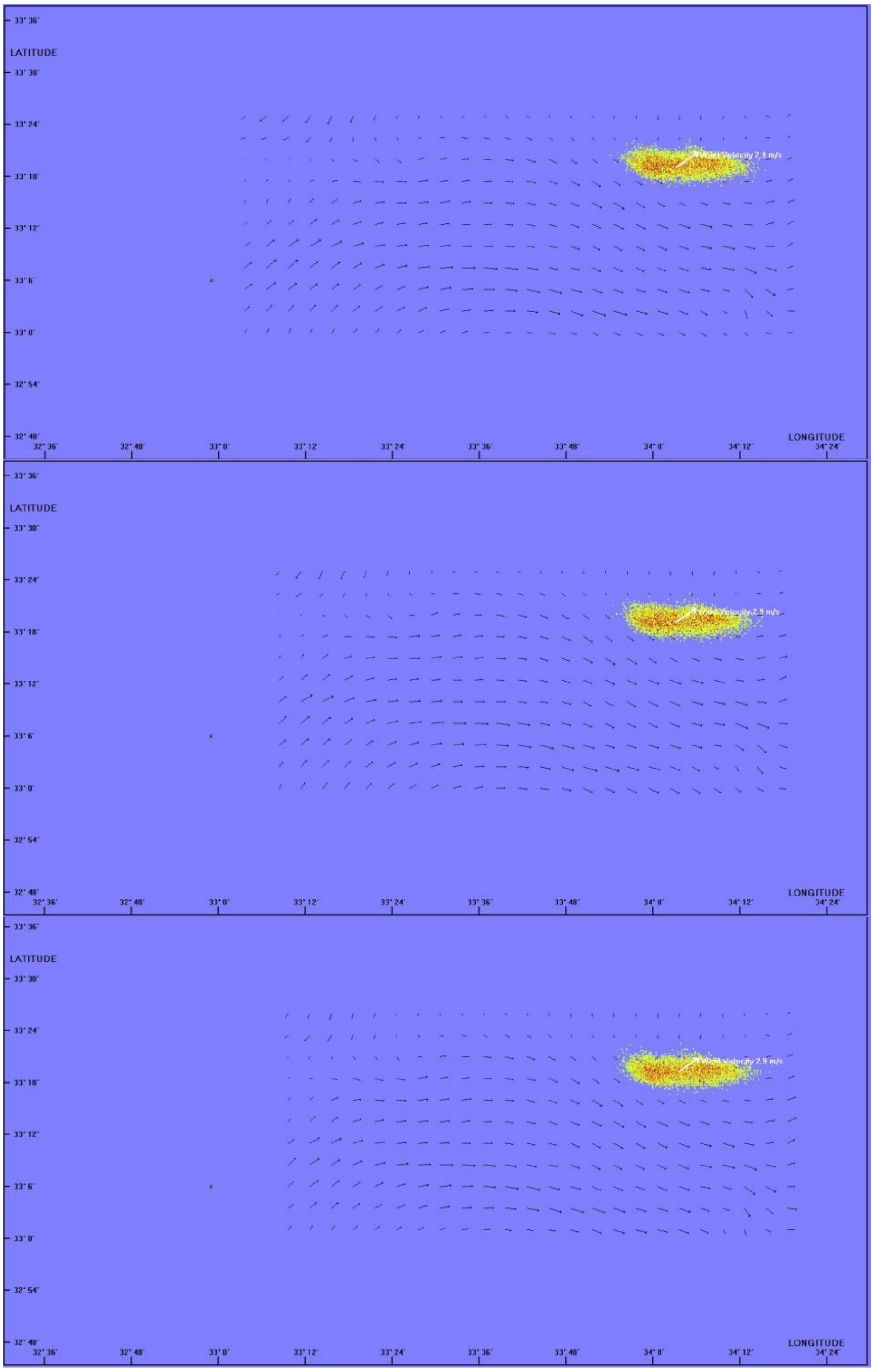


Figure 8. Final shape of the oil slick (120 hours after the spill) predicted by MEDSLIK during winter conditions. Again, from top to bottom, oil types considered in the simulation are respectively: Arabian Heavy, Arabian Medium and Arabian Light.

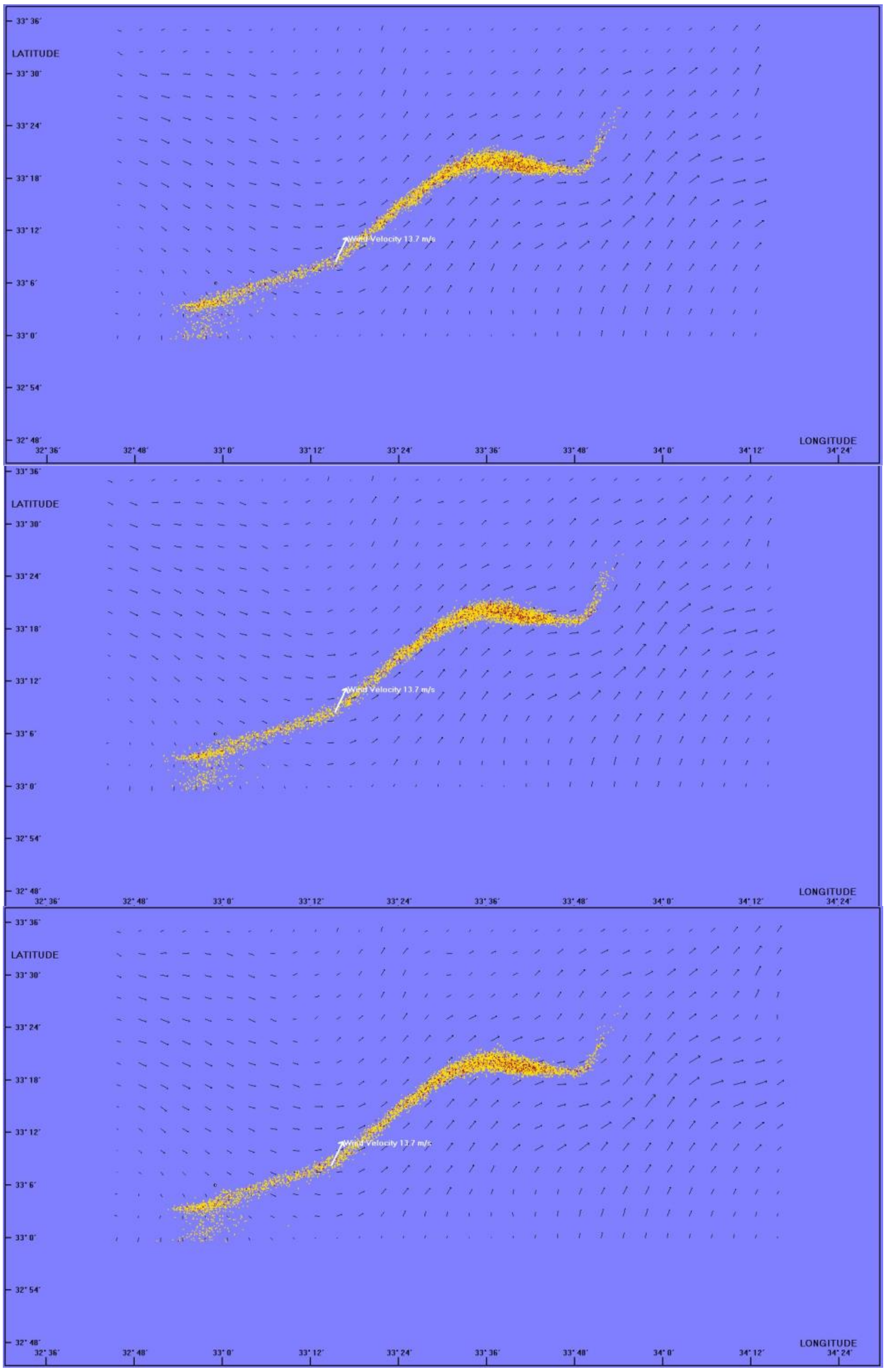


Figure 9. Predictions of the evolution in the position and shape of the oil slick through time during the summer, counted in hours after the accident (0, 40, 80 and 120), indicated in the bottom right corner of each image. Sequence marked 'A' represents Arabian Heavy oil predictions, 'B' represents Arabian Medium oil and 'C' represents Arabian Light oil.

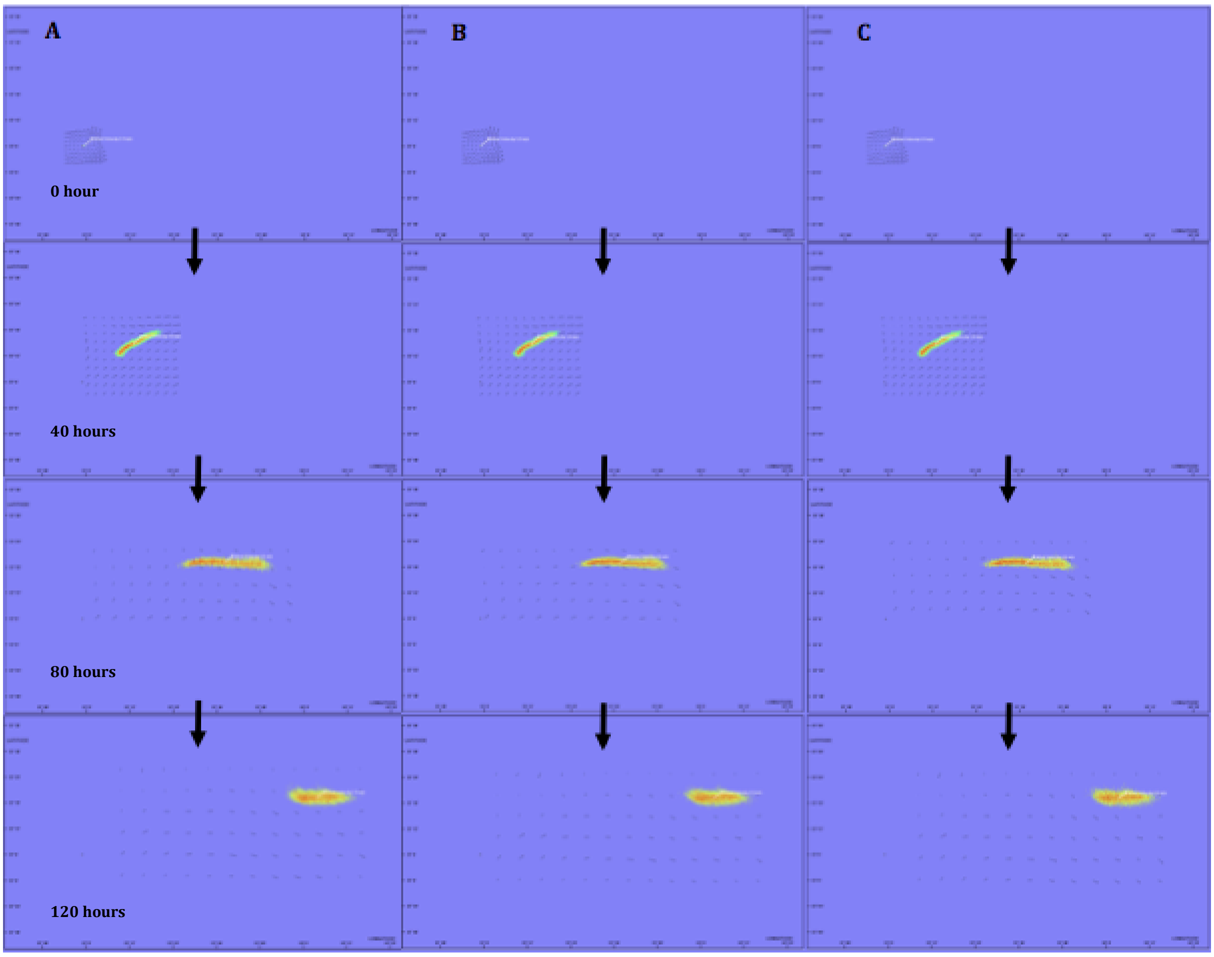


Figure 10. Dispersed oil distribution 120 hours after the spill, during the summer. From left to right, predictions correspond to Arabian Heavy, Arabian Medium and Arabian Light oil. Although the colours of the pixels (representing the amount of tons of oil per km^2) differ, the correspondent values are similar between all three types (around 1200 tons per km^2), being the cause of this difference a simple representation change made by the software.

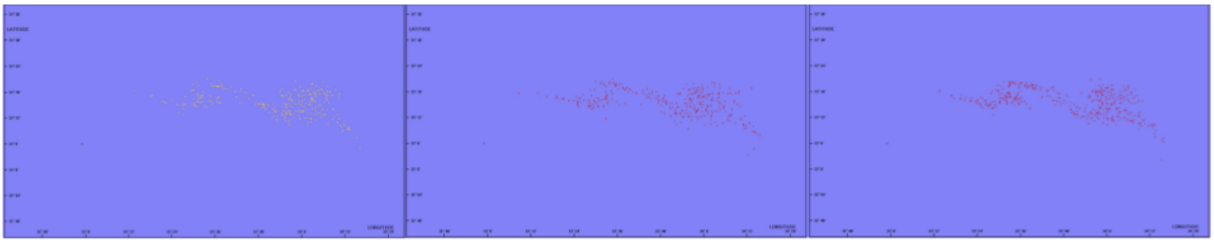


Figure 11. Predictions of the evolution in the position and shape of the oil slick through time during the winter, counted in hours after the accident (0, 40, 80 and 120), indicated in the bottom right corner of each image. Again, sequence marked 'A' represents Arabian Heavy oil predictions; 'B' represents Arabian Medium oil and 'C', Arabian Light oil.

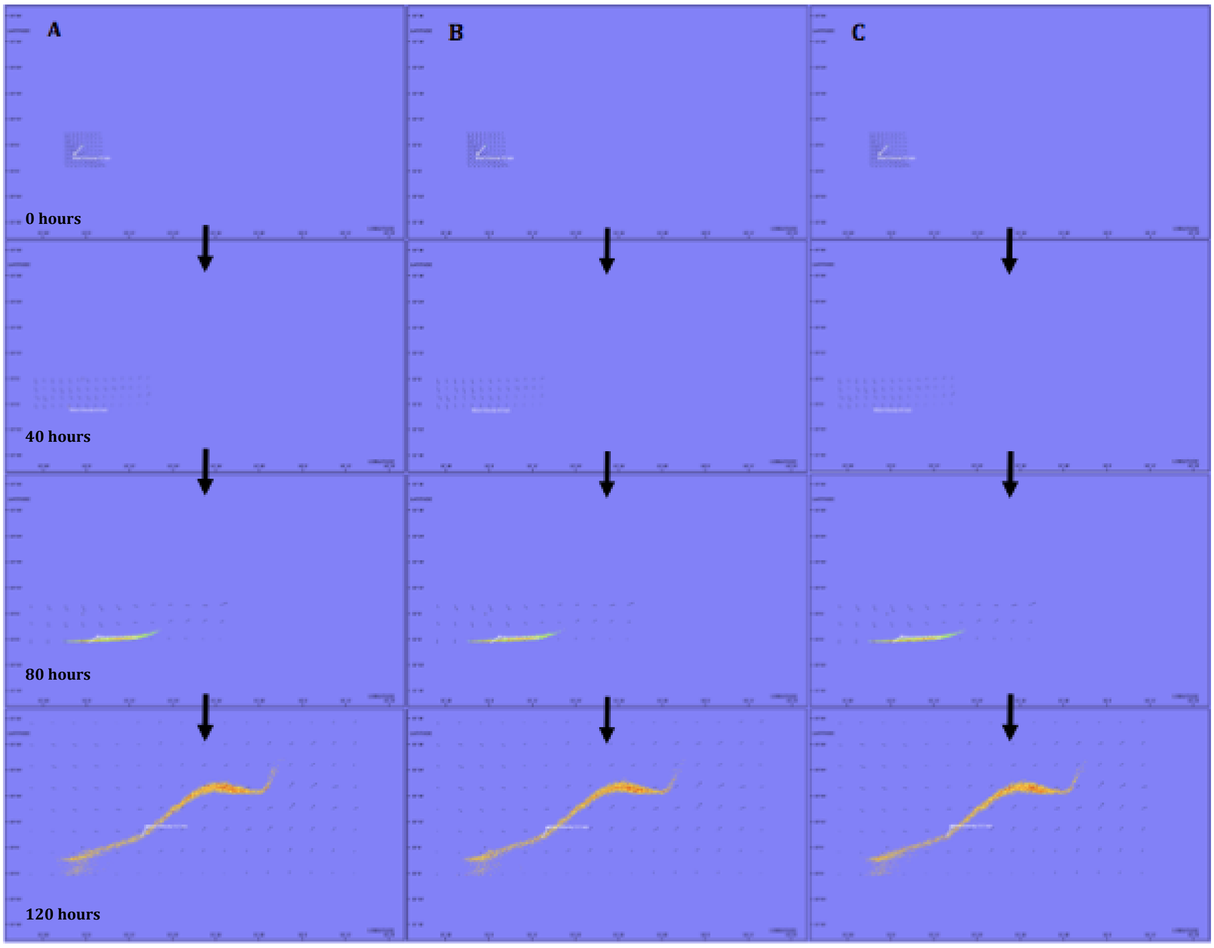


Figure 12. Dispersed oil distribution 120 hours after the spill, during the winter. Again, from left to right, predictions for oil types Arabian Heavy, Arabian Medium and Arabian Light, respectively. The reasons behind colour differences and the amount of tons per km^2 for these predictions are similar to summer conditions.

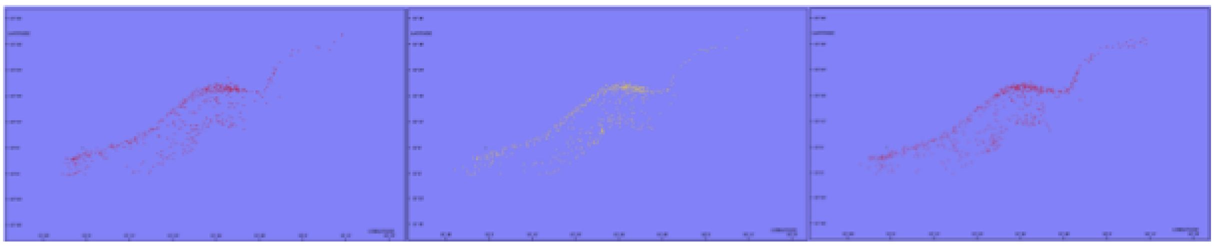


Table 2. Summary of the MEDSLIK simulation outputs.

	Summer			Winter		
	A. Light	A. Medium	A. Heavy	A. Light	A. Medium	A. Heavy
Evaporation Process (Hours)	72	33	26	59	29	22
Evaporated Volume (%)	46,72	40,28	30,38	46,72	40,28	30,40
Dispersed Oil (%)	2,34	2,01	2,09	5,36	4,71	5,98
Slick Viscosity (cs)	1972,6	3060,7	2794,2	3266,8	5068,9	4628,4
Highest viscosity reached after… (Hours)	56	49	74	42	29	32
Balance (max = min) reached after… (Hours)	75	78	101	59	49	53
Max Wind Velocity (m/s)		7,0			13,7	
Min Wind Velocity (m/s)		2,8			3,6	

6. COMPARISONS BETWEEN THE EASTERN MEDITERRANEAN SEA AND BRAZILIAN MARGINS

It is possible to notice similarities in both regions studied (the Mediterranean area and the Brazilian coast) especially regarding oceanographic settings and climate, as their geological formations differ from their origins. Studies analysed in literature revealed that, both in the Mediterranean and in Brazil, extra tropical cyclones are particularly relevant during the winter, strongly influencing wind systems. Climate during the summer in the Mediterranean is described as “hot and dry”, as well as the climate during the whole year in the northeast coast of Brazil and during the summer in other parts of the coast; winters are also mild in both regions.

As average climatic characteristics of the Brazilian coast are generally similar to the Mediterranean climate, it is possible to affirm that, in case of an accident in a Brazilian oil field, a similar response regarding the rate of evaporation for all three oil types and both seasons would be likely to take place. It is important, though, to take in consideration regional differences, as the closer to the north the region is, the closer to the Equator it gets, which causes the northernmost regions of the coast to be warmer, turning increasingly colder towards the south. This fact could cause possible spills in northern areas to present similar outcomes to summer results in the prediction for the most part of the year, and not only in actual summer periods.

The shape of the slick and the velocity it would travel is highly dependent on currents, therefore requiring a more careful analysis. As velocity values previously presented were measured in different and not comparable units (m^3/s for the Brazil Current and m/s for the Cyprus Eddy), and are the only numerical measurements obtained, it is difficult to predict if an oil slick in the Brazilian coast would possibly travel a longer or shorter area than the one showed in the MEDSLIK predictions for the Mediterranean. However, the fact that the water flow for the Levantine Basin was in general described as ‘’complicated’’ and ‘’energetic’’, presenting a large number of eddies and gyres, while the Brazil Current was pointed out as relatively ‘’weak’’ gives one the idea that the spreading and moving of a slick in the Levantine area would occur more rapidly and efficiently than what could be expected for the Brazilian coast south from the Equator. North from the Equator, the Guiana Current, presented by the literature as a considerably fast water mass (having a mean velocity of 14,6 cm/s), in the other hand, could generate results regarding the spread and displacement of the slick more similar to the ones predicted by MEDSLIK. The presence of storms and winds also seem to have made a considerable difference in the MEDSLIK predictions, especially in the winter results. According to Bitencourt et al. (2011), cyclones occur in all seasons in the eastern South America coast, but a larger frequency can be observed in the winter, which may indicate that a faster and more significant spreading of a potential slick could also happen in the region during this period, as much as it was predicted in the Mediterranean for the same weather conditions. Also, as most of the oil produced in Brazil is the heavy type (PIRES, 2008), there is a bigger likelihood for spills of this type of oil in the area, which can mean more difficulties in treatment processes as the predictions showed it is the oil type that evaporates the less and in a slower rate, persisting on the water surface.

Despite the considerable annual oil production in Brazil – in 2017, the country joined the list of the 10 top oil producers in the world, behind well-known leaders such as the United States of America and Saudi Arabia, and figured as the biggest producer in Latin America, with 918,7 million gallons produced in 2016 (PORTAL BRASIL, 2017) -, there is still much to be improved in the country's oil spill modelling and prediction resources. Besides models developed by universities focusing in a particular study (FREIRE; LIMA, 2002; MELO; FREIRE; LIMA, 2017) and "generalist" models that may be used for different locations – SPILLCALC (TETRA TECH, 2017) and OILMAP, for example -, no software specifically developed for the Brazilian coast (or, at least, for South American margins in general) was found during the research conducted for this thesis, thus the necessity for the extrapolation presented. However, considering the continuous investing in oil and gas exploration in Brazil, it is imperative the development of models designed specifically for the regions needs and particularities, as MEDSLIK was for the Mediterranean area, which would represent a great step towards more safety and preparedness regarding the oil business in the country.

7. FINAL CONSIDERATIONS

One of the main conclusions that can be achieved by analysing the outcomes of the software is that while weather conditions and currents are mainly responsible for determining the position and shape of the oil slick through time, the type of oil spilled are mostly related to other factors as the rate of evaporation and viscosity of the slick, not having much influence on its transport or spreading. The lighter oil (Arabian Light) proved in both weather conditions to be the one that evaporates the most and for longer time comparing to the other two types, indicating, then, a likelihood that lighter types of oil would not represent as much of a threat to the environment as the heavier ones when spilled, as they are not as persistent in the form of a surface slick. Regarding viscosity, the results showed that higher viscosity values are reached by the spilt Arabian Medium oil comparing to the other two types, and as already explained in the correspondent section, high rates of increasing viscosity may have effects on the determination of the best type of skimmer to be use, as well as representing a problem to the use of dispersants.

A higher intensity of winds was apparently one of the main reasons for the establishment of the wide final shape of the slick during winter conditions. As mentioned in section 3, the efficiency of a skimmer is broadly related with the thickness of the slick, which consequently relates to the concentration of oil in the area. Burning treatments also require, among other factors, a certain thickness of the oil layer to allow the high temperatures to be held, without the unwanted interference of lower temperatures of the sea water below the slick. For those reasons, it would be reasonable to conclude that a more active wind regime and the occurrence of storms in the area affected (and aimed for the treatment) would make clean-up strategies more difficult and, most possibly, also more costly. Taking the simulation outcomes as a model, it is imaginable that conducting a treatment using skimmers, for instance, would be way more complicated in the winter scenario than in the summer, due to the fact that in the first case, the slick experienced much more movement and spreading, which would require more effort in the process of concentrating the slick (more booms and/or vessels, etc). Along with that, it is also interesting to point out that the percentages of dispersed oil for all oil types were more than twice the values in the winter comparing to summer results, which also may have occurred due to the influence of stronger winds. For this parameter, the difference between oil types did not seem to exert a considerable influence in the outcomes, considering the similarity of the values.

The containment and treatment options considered in this study (the use of booms, burning, chemical dispersants and skimmers) can be considered adequate for both locations mentioned (Mediterranean Sea and Brazilian coast), depending on the circumstances of the accident, especially regarding the weather conditions of the area of the spill and the type of oil spilled. As most of the oil produced in Brazil belongs to the heavy type, and using the software model as a base for conclusions, it is predictable that the evaporation rates for a spill in the region would not be very high; however, it should also be considered that northernmost areas of the Brazilian coast tend to present hotter weathers than the majority of the Mediterranean areas, which undoubtedly influences this factor as well. Furthermore, it should also be mentioned that, although seasons have a major role in determining the occurrence of a storm and the temperature experienced in a certain location, weather conditions could be unpredictable, especially for long periods.

Finally, it should be suggested that more studies regarding oceanic circulation and characteristics should be conducted for the Brazilian coastal system, in order to make specific and more accurate studies possible for this large area, which recently has gained an increasing economic importance.

8. CONCLUSIONS

The first observable differences between the outcomes of the simulation are regarding the shape of the slicks that would be formed in accidents theoretically happening during the summer or the winter in the Mediterranean area. Not only the spreading of the oil was different, but also the direction and velocity in which the slicks travelled since the beginning of the simulation, highlighting the effects the faster winds of the winter scenario had on the surface of the water.

Although comparisons between oil types in the same scenario (summer or winter) are not as intuitive in the simulation (especially when observing only the visual outcomes), differences in evaporation, dispersion and viscosity of the slick were perceived and, in general, followed the patterns and expectations provided by the literature.

Comparisons with the Brazilian coast were valid in regards of the analysis of the climatic and oceanographic characteristics of the region and their similarities with the Mediterranean, which made possible the envisioning of the response the Brazilian coast would have in a hypothetical spill. However, further studies on the matter are indispensable for more precise predictions in the future, guaranteeing faster and more effective reactions by Brazilian authorities, consequently ensuring fewer risks to the environment and the public health.

REFERENCES

ABHA, S.; SINGH, C. S. Hydrocarbon pollution: effects on living organisms, remediation of contaminated environments, and effects on heavy metals co-contamination on bioremediation. In: ROMERO-ZERÓN, L. **Introduction to enhanced oil recovery (EOR) processes and bioremediation for oil-contaminated sites.** RIJEKA: InTech, 2012. cap. 7, p.185-206.

ALVES, A.K.; ALVES, B.; MARTINS, L. O petróleo e os impactos de seu derramamento no ecossistema de uma região. **Revista Bolsista de Valor**, v.3, p.81-86, Instituto Federal de Educação, Ciência e Tecnologia Fluminense, 2013.

ALVES, T. et al. Hindcast, GIS and susceptibility modelling to assist oil spill clean-up and mitigation on the southern coast of Cyprus (Eastern Mediterranean). **Deep Sea Research Part II: Tropical Studies in Oceanography,** v. 133, p.159-175, Elsevier, 2016.

ALVES, T. M.; KOKINOU, E.; ZODIATIS, G. A three-step model to access shoreline and offshore susceptibility to oil spills: The south Aegean (Crete) as analogue for confined marine basins. **Marine Pollution Bulletin,** v. 86, issues 1-2, p.443-457, Elsevier, 2014.

ANNUNCIADO, T.R.; SYDENSTRICKER, T. H. D.; AMICO, S. C. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. **Marine Pollution Bulletin,** v. 50, issue 11, p.1340-1346, Elsevier, 2005.

ASKE, N.; KALLEVIK, H.; SJÖBLOM, J. Water-in-crude oil emulsion stability studied by critical electric field measurements. Correlation to physicochemical parameters and near-infrared spectroscopy. **Journal of Petroleum Science and Engineering,** v. 36, issues 1-2, p.1-17, Elsevier, 2002.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). **Standard Guide for Selection of Skimmers for Oil-Spill Response**. 2016. Available at: <http://compass.astm.org/EDIT/html_annot.cgi?F1778+97\(2008\)>. Access on 22th July 2015.

AURELL, J.; GULLET, B. K. Aerostat sampling of PCDD/PCDF emissions from the Gulf oil spill in situ burns. **Environmental Sciences Technology,** v. 44. p.9431-9437, ACS Publications, 2010.

BACON, R.; TORDO, S. **Crude oil price differentials and differences in oil qualities: a statistical analysis.** ESMAP Technical Paper 081. Energy Sector Management Assistance Program (ESMAP). WASHINGTON: 2005.

BENNER, S. et al. The mixed-layer/thermocline cycle of a persistent warm core eddy in the eastern Mediterranean. **Dynamics of Atmospheres and Oceans,** v.15, issues 3-5. p.457-476, Elsevier, 1991.

BEZERRA, P. G. **Contaminação de águas subterrâneas por BTEX na bacia do rio Lucaia, Salvador, Bahia.** PhD Thesis (Geochemistry: Petroleum and Environment), Federal University of Bahia, Salvador, 2011.

BIJU-DUVAL, B. et al. Geology of the Mediterranean Sea Basins. In: **The Geology of continental Margins.** Drake and Burk Edit. NEW YORK: 1974. p.695-721.

BIJU-DUVAL, B.; LETOUZEY, J.; MONTADERT, L. **Structure and evolution of the Mediterranean Basins.** Deep Sea Drilling Project Reports and Publications. 2007. Available at: <http://www.deepseadrilling.org/42_1/volume/dsdp42pt1_50.pdf>. Access on 3rd July 2015.

BISCHOF, B. et al. **The Brazil current.** Surface currents in the Atlantic Ocean. Ocean Surface Currents, 2004. Available at: <http://oceancurrents.rsmas.miami.edu/atlantic/brazil.html>. Access on: 2nd September 2017.

BITENCOURT, D.P. et al. Relating winds along the Southern Brazilian coast to extratropical cyclones. **Meteorological applications**, v.18, p.223-229, Wiley, 2011.

BIZZI, L.A. et al. **Geologia, tectônica e recursos minerais do Brasil.** CPRM. Brasília: 2003.

BRAGATO, M. **Tratamento in-situ de solo contaminado por derivado de petróleo e metais.** PhD Thesis (Materials and Metallurgical Engineering), University of São Paulo, São Paulo, 2006.

BRANCO, M. Gigante americana Chevron provoca vazamento de óleo na Bacia de Campos. **O Globo.** 11 November 2016. Available at: <http://acervo.oglobo.globo.com/em-destaque/gigante-americana-chevron-provoca-vazamento-de-oleo-na-bacia-de-campos-20427385>. Access on 17th September 2017.

BROOKE, J. Cubatao Journal; Signs of life in Brazil's industrial Valley of Death. **NY Times.** 15 June 1991. Available at: http://www.nytimes.com/1991/06/15/world/cubatao-journal-signs-of-life-in-brazil-s-industrial-valley-of-death.html. Access on 15th November 2017.

BUIST, I. Window-of-Opportunity for In Situ Burning. **Spill Science & Technology Bulletin**, v.8, issue 4. p.341-346, Elsevier, 2003.

CETESB. **Significado ambiental e sanitaria das variáveis de qualidade das águas e dos sedimentos e metodologias analíticas e de amostragem.** Qualidade das águas interiores no estado de São Paulo – Série Relatórios – Apêndice A. SÃO PAULO: Secretaria do Meio Ambiente, 2009. Available at: <http://cetesb.sp.gov.br/aguas-interiores/wp-content/uploads/sites/32/2013/11/variaveis.pdf>. Access on 2nd September 2017

CANTAGALLO, C. et al. Limpeza de ambientes costeiros brasileiros contaminados por petroleo: uma revisão. **Pan-American Journal of Aquatic Sciences,** v. 2, issue 1, p.1-12, 2007.

CAMBRIDGE DICTIONARY. **Oil Spill.** Available at: <dictionary.cambridge.org/pt/dicionario/ingles/oil-spill>. Access on 1st October 2017.

CAMPOS, E. J. D et al. Physical Oceanography of the Southwest Atlantic Ocean. **The Oceanography Society**, v.8, no.3. p.87-91, 1995.

CLEAN-UP OIL. **Oil spill equipment glossary.** c2015. Available at: <http://cleanupoil.com/oil-spill-equipment/>. Access on 2nd September 2017.

COLELLA, A.; D'ORSOGNA, M. R. **Hydrocarbon contamination in waters and sediments of the Pertusillo freshwater reservoir, Val d'Agri, Southern Italy.** California State University Northridge, 2014. Available at: <https://www.csun.edu/~dorsogna/mwebsite/papers/GER-1col.pdf>. Access on 2nd September 2017.

DICHRISTOPHER, T. Pipeline spills 176,000 gallons of crude into creek about 150 miles from Dakota Access protest camp. **CNBC**, 12 December 2016. Available at: < https://www.cnbc.com/2016/12/12/pipeline-spills-176000-gallons-of-crude-into-creek-about-150-miles-from-dakota-access-protest-camp.html>. Access on 9th October 2017.

DIXON, J.E.; ROBERTSON, H.F. The Geological Evolution of Eastern Mediterranean. **Geological Society Special Publication**, n.17. Department of Geology and Geophysics, University of Edinburgh, 1984

ECHOLS et. al. Acute aquatic toxicity studies of Gulf of Mexico water samples collected following the Deepwater Horizon incident (May 12, 2010 to December 11, 2010). **Chemospere**, v.120. p.131-137, Elsevier, 2015.

ENCYCLOPAEDIA BRITANNICA. **Mediterranean Sea: depth contours and submarine features.** Available at: <https://www.britannica.com/place/Mediterranean-Sea>. Access on 9th October 2017.

ENERGEAN. c2016. Available at: <https://www.energean.com/>. Access on 2nd September 2017.

EMÍLSSON, I. The shelf and coastal waters off southern Brazil. **Boletim Instituto Oceanográfico.** São Paulo, Instituto Oceanográfico da Universidade de São Paulo, v.11(2), pp.101-112, 1961.

EPA. c2017. Available at: <www.epa.gov>. Access on 17th September 2017.

______. **Understanding oil spills and oil spill response:** understanding oil spills in freshwater environments. Oil Program Center. 1999. Available at: <https://www7.nau.edu/itep/main/HazSubMap/docs/OilSpill/EPAUnderstandingOilSpillsAndOilSpillResponse1999.pdf>. Access on 2nd September 2017.

FINGAS, M.F.; DUVAL, W.S. & STEVENSON, G.B. **The Basics of Oil Spill Cleanup with Particular Reference to Southern Canada.** 1979. Hull: Minister of Supply and Services Canada.

FINGAS, M.F. **In Situ Burning of oil spills: a historical perspective.** NIST Special Publication 935. 1999. Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg.

______. **Oil Spill Science and Technology.** OXFORD: Elsevier, 2011.

______. **The basics of oil spill cleanup.** 2012. 3rd edition. BOCA RATÓN: CRC Press.

FREIRE, J. P. F. C; LIMA, E. A. O. **Desenvolvimento de uma ferramenta em VRML para visualização científica e seu uso na visualização da simulação de acidentes de derramamento de petróleo em águas litorâneas.** Unicap. Pernambuco, 2002. Available at: http://www.unicap.br/eal/JoaoPaulopetroleo.pdf. Access on 19th November 2017.

FREIRE, P.A.C.; TRANNIN, I.C.B.; SIMÕES, S.J.C. **Bombeamento e tratamento da fase livre em Aquífero Litorâneo.** Revista Engenharia Sanitária e Ambiental, v.19, n.4, p.461-470, AIDIS, 2014.

FUENTES, E. V.; BITENCOURT, D. P.; FUENTES, M. V. Análise da velocidade do vento e altura de onda em incidentes de naufrágio na costa brasileira entre os estados do Sergipe e do Rio Grande do Sul. **Revista Brasileira de Meteorologia**, v.28, n.3, p. 257-266, Sociedade Brasileira de Meteorologia, 2013.

G1 SANTOS. Vazamento de petróleo atinge rio Cubatão; produção de água é reduzida. **G1**. Santos, 23 March 2016. Available at: <http://g1.globo.com/sp/santos-regiao/noticia/2016/03/vazamento-de-petroleo-atinge-rio-cubatao-producao-de-agua-e-reduzida.html>. Access on 17th September 2017.

GARCIA, C. Vazamento em 97 foi de 600 mil litros. **Folha de São Paulo.** São Paulo, 20 January 2000. Available at: <www1.folha.uol.com.br/fsp/cotidian/ff2001200007.htm>. Access on 1st October 2017.

GIANNAKOPOULOS C et al. Precipitation and temperature regime over Cyprus as a result of global climate change. **Advances in Geosciences. EGU, 2010.**

GOODSON, S. **About API Gravity.** Energy API. c2017. Available at: <http://mycommittees.api.org/standards/copm/Shared%20Documents/Miscellaneous/API%20Gravity.pdf>. Access on: 2nd September 2017.

GOURLAY, K.A. **Poisoners of the Seas.** LONDON: Zed Books Ltd, 1988.

GYORY, J.; MARIANO, A. J.; RYAN, E. H. **Surface currents in the Atlantic ocean.** Rosenstiel School. c2013. Available at:

http://oceancurrents.rsmas.miami.edu/atlantic/guiana.html. Access on 18 November 2017.

HECHT, A.; PINARDI, N.; ROBINSON, A.R. Currents, water masses, eddies and jets in the Mediterranean Levantine Basin. **Journal of Physical Oceanography,** vol.18, pp.1320-1353, AMS, 1988.

IBAMA. **Plano Nacional de Ação de Emergência para Fauna Impactada por Óleo.** 2016. Available at: <www.ibama.gov.br/phocadownload/emergenciasambientais/paefauna2016_plano.pdf>. Access on 1st October 2017.

ITOPF. **Response to marine oil spills.** LONDON: Witherby & Co. Ltd, 1987.

______. **Fate of marine oil spills.** 2014. Available at: <http://www.itopf.com/knowledge-resources/documents-guides/document/tip-2-fate-of-marine-oil-spills/>. Access on 5th August 2015.

JONES, J.C. **Hydrocarbons - Physical properties and their relevance to utilisation.** J.C. Jones & Ventus Publishing ApS, 2010. Available at: <https://kosalmath.files.wordpress.com/2010/08/hydrocarbons.pdf>. Access on 21st February 2017.

JOYE, S. B. **Oil spills and industry history.** Joye Research Group. University of Georgia, Department of Marine Sciences. c2000-2013. Available at: <http://www.joyeresearchgroup.uga.edu/public-outreach/marine-oil-spills/history>. Access on 2nd September 2017.

KUBAT, M.; HOLTE, R. C.; MATWIN, S. Machine learning for the detection of oil spills in satellite radar images. **Machine Learning,** v. 30, issue 2-3. p.195-215, Springer, 1998.

LEJEUSNE et al. Climate changes effects on a miniature ocean: the highly diverse, highly impacted Mediterranean Sea. **Trends in Ecology & Evolution,** v. 25(4), p.250-260, Elsevier, 2010.

LEME, D. M; MARIN-MORALES M. A. **Avaliação da qualidade de águas impactadas por petróleo por meio de sistema-teste biológico *(Allium cepa)* – Um estudo de caso.** CAMPINAS: 4° PDPETRO, 2007.

LEVINE, S. et al. **Understanding crude oil and product markets.** 2014. Prepared for The Brattle Group of the American Petroleum Institute (API). Available at: <http://www.api.org/~/media/Files/Oil-and-Natural-Gas/Crude-Oil-Product-Markets/Crude-Oil-Primer/Understanding-Crude-Oil-and-Product-Markets-Primer-Low.pdf>. Access on: 2nd September 2017.

LUTHY, R. G. **Organic contaminants in the environment: Challenges for the water/environmental engineering community.** WASHINGTON (DC): National Academies Press (US), 2004.

MAHERAS, P. et al. A 40 year objective climatology of surface cyclones in the Mediterranean region: spatial and temporal distribution. **International Journal of Climatology.** Wiley, 2001. Vol.21. p.109-130.

MAKRIS, J.; STOBBE, C. Physical properties and state of the crust and upper mantle of the Eastern Mediterranean Sea deduced from geophysical data. **Marine Geology.** Elsevier, 1984. Vol.55, issues 3-4. p.347-363.

MEDESS-4MS. **Oil spill models.** c2017. Available at: http://www.medess4ms.eu/oil-spill-models. Access on 18th November 2017.

MELO, G. G. M.; FREIRE, J. P. F; LIMA, E. A. O. **Software para simulação computacional de modelos de impacto ambiental causados pelo petróleo em meio aquoso.** 2016. Available at: http://abricom.org.br/wp-content/uploads/2016/08/CBRN2005_085.pdf. Access on 19th November 2017.

MENDES, C. L. T.; SOARES-GOMES, A. **Circulação nos oceanos: correntes oceânicas e massas d'água.** Department of Marine Biology, Federal Fluminense University, Niterói, 2007.
MICHALOPOLOU, H.; JACOVIDES, C. **Instability indices for the Cyprus area. Meteorology and Atmospheric Physics.** Springer: 1987. Vol. 37, Issue 3. p.153-158.

MONTADERT, L. et al. (2010). **Petroleum Systems Offshore Cyprus. AAPG Datapages – Search and Discovery.** AAPG, 2010. Available at: <http://www.searchanddiscovery.com/documents/2010/10279montadert/poster01.pdf>. Access on 3rd July 2015.

MUHLING et al. Overlap between Atlantic Bluefin tuna spawning grounds and observed Deepwater Horizon surface oil in the northern Gulf of Mexico. **Marine Pollution Bulletin.** Elsevier, 2012.

MULLIN, J.V.; CHAMP, M.A. Introduction/Overview to In Situ Burning of Oil Spills. **Spill Science & Technology Bulletin.** Elsevier, 2003. Vol. 8, Issue 4. p.323-330.

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION (NOAA). **Office of Response and Restoration: Spill Containment Methods.** 2017. Available at: <http://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/spill-containment-methods.html>. Access on 2nd September 2017.

NETTO, A. D. P. et al. Avaliação da contaminação humana por hidrocarbonetos policíclicos aromáticos (HPAs) e seus derivados nitrados (NHPAs): uma revisão metodológica. **Química Nova.** SBQ, 2000. Vol. 23(6).

NIMER, E. **Climatologia do Brasil.** RIO DE JANEIRO: IBGE, Departamento de Recursos Naturais e Estudos Ambientais, 1989. 2a. ed.

NATIONAL RESEARCH COUNCIL (NRC). **Oil in the sea: inputs, fates and effects.** WASHINGTON (DC): The National Academies Press, 1985.

DELEK ANNOUNCES commercial viability of Aphrodite natural gas field off Cyprus. **Offshore Technology.** 9 jun. 2015. Available at: <http://www.offshore-technology.com/news/newsdelek-announces-commercial-viability-aphrodite-natural-gas-field-off-cyprus-4596520>. Access on 30th July 2015.

OIL SPILL SOLUTIONS. **Booms.** 2015a. Available at: <http://www.oilspillsolutions.org/booms.htm>. Access on 14th July 2015.

______. **Controlled burning.** 2015b. Available at: <http://www.oilspillsolutions.org/controlledburning.htm>. Access on 14th July 2015

OLIVEIRA, J. P. R. **Estudo dos poluentes orgânicos persistentes (POP's) em regioes industriais da grande São Paulo – via cromatografia à gás acoplada a espectografia de massas (GC-MS) e captura de elétrons (GC-ECD).** 2011. Masters Degree Thesis (Nuclear Technology Sciences) – IPEN, São Paulo, 2011.

OMAR-ALI, A. et. al. Tissue PAH, blood cell and tissue changes following exposure to water accommodated fractions of crude oil in alligator gar, Atractosteus spatula. **Marine Environmental Research**, vol. 108. p.33-44, Elsevier, 2015

ÖZSOY, E.; HECHT, A.; ÜNLUATA, Ü. Circulation and hydrography of the Levantine Basin. Results of POEM coordinated experiments 1985-1986. **Progress in Oceanography**, v. 22, issue 2. p.125-170, 1989.

PAMPANIN, D. M.; SYDNES, M. O. Polycyclic aromatic hydrocarbons a constituent of petroleum: presence and influence in the aquatic environment. In: KUTCHEROV, V. **Hydrocarbon.** InTech, 2013. Available at: <http://www.intechopen.com/books/hydrocarbon/polycyclic-aromatic-hydrocarbons-a-constituent-of-petroleum-presence-and-influence-in-the-aquatic-en>. Access on 2nd September 2017.

PEREIRA, R.S. Identificação e caracterização das fonts de poluição em sistemas hídricos. **Revista Eletrônica de Recursos Hídricos, IPH-UFRGS**, v. 1, n. 1, p.20-36, 2004.

PETERSON, C.H. et al. Long-term ecosystem response to the Exxon Valdez oil spill. **Science**, v. 302, p.2082–2086, 2003.

PETROBRAS. **Índice de vazamentos: respostas à Reuters.** 2014. Available at: <www.petrobras.com.br/fatos-e-dados/indice-de-vazamentos-respostas-a-reuters.htm>. Access on 1st October 2017.

______. **Pré-Sal.** c2017. Available at: <http://www.petrobras.com.br/pt/nossas-atividades/areas-de-atuacao/exploracao-e-producao-de-petroleo-e-gas/pre-sal/>. Access on 2nd September 2017.

PIRES, A. In: GUIMARÃES, L. Entenda a diferença entre os tipos de petróleo. **G1**, São Paulo, 30 May 2008. Available at: <http://g1.globo.com/Noticias/Economia_Negocios/0,,MUL583646-9356,00-

ENTENDA+A+DIFERENCA+ENTRE+OS+TIPOS+DE+PETROLEO.html>. Access on 2nd September 2017.

PORTAL BRASIL. **Brasil se torna o maior produtor de petróleo da América Latina.** Portal Brasil. 7th August 2017. Available at: http://www.brasil.gov.br/economia-e-emprego/2017/07/brasil-se-torna-maior-produtor-de-petroleo-da-america-latina. Access on 19th November 2017.

PORTO, D.C. **Investigação da contaminação do solo e das águas subterrâneas por óleo combustível: Estudo de caso em Ribeirão Preto (SP) – Empresa Viação Garcia.** Undergraduate Thesis (Environmental Engineering), Federal Technology University of Paraná (UTFPR), Londrina, 2014.

ROBINSON, A.R. et al. Mediterranean Sea Circulation. In: Steele, J.H.; Thorpe, S.A.; Turekian, K.K. **Ocean Currents.** Oxford: Elsevier, p.283-298, 2009.

ROUSSENOV, V. et al. A seasonal model of the Mediterranean Sea general circulation. **Journal of Geophysical Research.** v.100, p.13,515-13,538, 1995.

SALAH, M.; BOXER, B. **Mediterranean Sea.** Encyclopedia Britannica. c2017. Available at: <http://www.britannica.com/place/Mediterranean-Sea>. Access on 2nd September 2017.

SANTOS et. al. An overview of heavy oil properties and its recovery and transportation methods. **Brazilian Journal of Chemical Engineering,** v. 31, n. 03, p.571-590, July - September 2014.

SAUER, T.C. et al. ROPME sea oil spill nearshore geochemical processes study. Volume 2 - Hydrocarbon chemistry analytical results for year 1 1992. **Marine Spill Response Corporation**, Washington, D.C. MSRC Technical Report Series 93-002.2. Washington (DC), USA, 1993.

SCHWING, P. T. et al. A decline in benthic foraminifera following the Deepwater Horizon Event in the Northeastern Gulf of Mexico. **PLOS ONE**, v.10(5), 2015.

SILVEIRA, I.C.A. et al. A Corrente do Brasil ao Largo da Costa Leste Brasileira. **Revista Brasileira de Oceanografia,** São Paulo, Instituto Oceanográfico da Universidade de São Paulo, v.48(2), pp.171-183, 2000.

______. On the baroclinic structure of the Brazil Current-Intermediate Western Boundary Current system at 22°S - 23°S. **Geophysical Research Letters,** v. 31, Wiley, 2004.

SOUZA, C. A. V.; FREITAS, C. M. Perfil dos acidentes de trabalho em refinaria de petróleo. **Revista de Saúde Pública**, v. 36, n. 5, São Paulo, October 2002.

OCA. The Mediterranean Sea. **The Geonauts inquire into the oceans.** Nice: OCA/CNES (Observatoire de la Côte d'Azur), 2000. CD-ROOM.

TETRA TECH. **SPILLCALC Oil and contaminant spill model.** c2017. Available at: http://www.tetratech.com/en/projects/spillcalc-oil-and-contaminant-spill-model. Access on 19th November 2017.

TONINI, R. M. C. W.; REZENDE, C. E.; GRATIVOL, A. D. Degradação e biorremediação de compostos do petróleo por bactérias: revisão. **Oecologia Australis**, v. 14, n. 4, 2010

TRESSOLDI, M.; CONSONI, A. J. Disposição de Resíduos. In: OLIVEIRA, A. M. S.; BRITO, S. N. A. (Eds.). **Geologia de Engenharia.** São Paulo: Associação Brasileira de Geologia de Engenharia (ABGE), cap 21, p. 343-360, 1998.

UNEP. Effects of marine oil pollution on economy and human health. **Global Marine Oil Pollution Information Gateway.** c2015. Available at: <http://oils.gpa.unep.org/facts/economy-health.htm>. Access on 2nd July 2015.

UNISANTA. **Correntes oceânicas e massas de água.** c2017. Available at: http://cursos.unisanta.br/oceanografia/correntes_marinhas.htm. Access on 19th November 2017.

UNIVERSITY OF GUELPH. **Tethys Sea.** c2017. Available at: <http://www.uoguelph.ca/geology/geol2250/glossary/HTML%20files/tethyssea.html>. Access on 9th October 2017.

VAN DER VOO, R. **Paleomagnetism of the Atlantic, Tethys and Iapetus oceans.** Cambridge, Cambridge University Press, 1993.

VIEIRA, F. C. S. **Toxicidade de hidrocarbonetos monoaromáticos do petróleo sobre *Metamysidopsis elongate atlantica* (Crustacea: Mysidacea).** PhD Thesis (Environmental Engineering), Universidade Federal de Santa Catarina, Florianópolis, 2004.

WARNOCK, A. M.; HAGEN, S. C.; PASSERI, D. L. Marine Tar Residues: a Review. **Water Air and Soil Pollution**, v. 226:68, 2015.

YACKLEY, A. J. **Oil spill in northern Cyprus threatens wildlife, tourism.** Reuters. 17th July 2013. Available at: https://www.reuters.com/article/cyprus-spill/oil-spill-in-northern-cyprus-threatens-wildlife-tourism-idUSL6N0FN1Z320130717. Access on 19th November 2017.

YASIN, G. et al. Quality and chemistry of crude oils. **Journal of Petroleum Technology and Alternative Fuels,** v. 4(3), p. 53-63, 2013.

ZIEGLER, P.A. **Evolution of the Arctic-North Atlantic and the Western Tethys – A Visual Presentation of a Series of Paleogeographic – Paleotectonic Maps.** 1999. Available at: <http://www.searchanddiscovery.com/documents/97020/memoir43.htm%20Evolution%20of%20the%20Arctic-North%20Atlantic%20And%20The%20Western%20Tethys>. Access on 8th July 2015.

ZODIATIS, G.; DRAKOPOULOS, P.; BRENNER, S. Variability of the Cyprus warm core Eddy during the CYCLOPS project. **Deep Sea Research Part II: Tropical Studies in Oceanography.** v. 52, issues 22-23. p.2897-2910, 2005.

ZODIATIS, G. et al. Operational Ocean forecasting in the Eastern Mediterranean: implementation and evaluation. **Ocean Science**, v. 4, issue 1, p.31-47, 2008.

______. **The mesoscale circulation in the SE Levantine Basin. Oceanography Center Cyprus**. 2012. Available at: <www.oceanography.ucy.ac.cy/wp-content/uploads/2012/09/1030_Mesoscale_Eratosthenes%20SM_120903.pdf>. Access on 4th July 2015.