

Oil Spill Simulation and Analysis of Its Behavior Under the Effect of Weathering and Chemical Dispersant: a Case Study of the Bacia de Campos—Brazil

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Abstract Offshore oil spills are a critical form of marine pollution, requiring researchers to mitigate their impacts. In this sense, this paper contributes to a better understanding of oil behavior after spillage and the improvement of contingency measures. Using Bacia de Campos as the study area, which accounts for approximately 32% of daily oil and gas production in Brazil, information regarding the properties of light, medium, and heavy oils, seawater, wind and wave weather conditions, and oil spill characteristics was used to perform simulations to identify the percentage of oil remaining after the offshore spill and the effectiveness of the chemical dispersant in dispersing this oil. The results show that after the weathering simulation, on average, 55% of the spilled oil remains at sea in dispersed and remaining form and that the use of chemical

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dispersant under the conditions defined in this study did not result in significant oil removal.

Keywords Marine pollution · Oil spill · Oil spill simulation · Chemical dispersant · Environmental impact

1 Introduction

Spills of crude oil and their derivatives are a major environmental problem and are considered a critical form of marine pollution (Alpers and Espedal 2004; Cheng et al. 2011; ITOPF 2020; Guo 2017). The resulting environmental disasters cause short- and long-term impacts on the environment, which may extend to socioeconomic activities (Baker et al. 1993; Verma et al. 2008; OPEC 2020). The actions to clean up marine waters affected by oil aim to reduce the scope and environmental and socio-economic impacts. However, the results are usually slower and less effective than desired, mainly because in the marine environment, the natural weathering processes cause the original characteristics of oil to be modified, mainly due to its physicalchemical characteristics and meteoceanographic conditions of the spill area.

Approximately 47% of the oil present in the ocean (about 600,000 metric tons) flows slowly into the ocean annually through cracks in the seabed (Hughes et al. 1995; Wells et al. 1995; NRC 2003), and this phenomenon is not considered pollution. The rest of the oil enters the ocean from anthropogenic sources in concentrated areas with a high flow rate, mainly through spills,

causing significant damage to the marine environment. The toxicity levels of these spills tend to persist over time and have been linked to highly visible local and regional disasters (Ocean Health Index 2020). For example, after 21 years of the Exxon Valdez oil spill, pollution in some areas of Alaska is almost as toxic as initial levels (Exxon Valdez Trustee Council 2016).

Although oil spills into the sea seem superficial, they have effects throughout a process chain on countless layers of water and can reach many coastal areas and still have instantaneous undetermined long-term effects (CETESB 2019). The most critical factors, however, are related to the amount and type of oil released and the environmental conditions of the scene, which determine the performance limits of all equipment or cleaning techniques (Lehr 1974). Although there are several causes and origins for oil spills, most occur due to shipping accidents. Restricting only tankers, from 1970 to 2019, an average of approximately 27.54 spills (7–700 t) and 9.32 spills (>700 t) have occurred, resulting in the spillage of 5.86 million tonnes of oil in the oceans (ITOPF 2020).

Oil spill models are used worldwide to simulate the evolution of an oil slick. Also, the use of mathematical models facilitates the organization of contingency plans developed in various countries through regulations and laws, better guiding decision-making regarding the individual emergency plan, aiming at optimizing management for spill containment and mitigation processes of oil spill (Otero et al. 2014; Ihaksi et al. 2011; Seager et al. 2007). Currently, some models are used for oil spill simulation, such as Oil Spill Contingency and Response Model (OSCAR), Spill Impact Model Application Package (SIMAP), and Oil Modeling Application Package (OILMAP) (GNOME/ADIOS). All of these models work by synthesizing information from various sources, including information about the ocean (tides, currents, climate, temperatures, and sea state), along with the development of spill scenarios (leakage, release time, oil type, etc.). Outputs include visual illustrations of potential impact areas, oil weathering profiles, mass balance data, and oil dispersion curve.

The input data of these models are usually those related to wind, waves, and ocean currents, being provided by environmental models (hydrodynamic, wind, and waves). Hydrodynamic models can be twodimensional or three-dimensional, while wind and wave models are typically two-dimensional, focusing on surface transport processes. Destination processes are modeled by transferring oil mass between environmental compartments (sea surface, atmosphere, water column, seabed, and shoreline) or by changing oil composition or physical characteristics (e.g., density, viscosity, and interfacial tension).

The oil in spilling models (crude oil, fuel oil, etc.) is described in terms of several components, typically related to their distillation comprising oil. These models track the location of oil by distributing the oil mass (total or per component) in space (on the sea surface and in the water column, but not usually in the atmosphere) and time. Component distribution is required to perform impact assessments where oil composition is critical for dissolution and biodegradation and impact on marine life (Spaulding 2017; Cheng et al. 2011; Lehr et al. 2002; NOAA 2019; Reed et al. 1999).

Cleaning up crude oil spills is a global challenge (Ge et al. 2017). It demands containment measures based on a plan that must be quick and efficient to avoid processes in which oil incorporates the structure of the marine environment, and it is important to monitor for possible identification of adverse reactions in the environment (Siddiqui and Verma 2018). When a spill occurs, oil containment and removal procedures are vital to ensure the reduction of both environmental and socio-economic impacts (Burgherr 2007; CETESB 2019).

Several areas of knowledge have been working together to help quantify the fluid dynamic and physicochemical processes that occur when oil hits water bodies: physics, chemistry, fluid mechanics, and even mathematical simulation (Giacoletti et al. 2018; Philibert et al. 2019; Ji et al. 2018; Lehr et al. 2002). Concerning simulation, it allows the planning for remediation measures of various sensitive and vulnerable areas for environmental impacts, as well as the application of methods to contain impacted areas.

In Brazil, oil exploration, production, and transportation activities occur mainly offshore, and Bacia de Campos is one of the leading country oil basins (ANP 2020). Considering the large volume of oil explored in the Campos Basin, studies must be carried out to identify the behavior of this oil in the sea, since we have not found studies on the behavior of Brazilian oils in the marine environment in the researched literature. Also, we have found no studies on the use of Brazilian dispersants to reduce and control the effects of pollution caused by spills. It is important to note that Brazilian legislation only allows the use of Brazilian dispersants. This study addresses this gap by simulating the spillage of three Brazilian types of oil (light, medium, and heavy) to identify and quantify the behavior of these oils in the marine environment of Bacia de Campos, under predetermined meteorological and oceanographic conditions. We also evaluated the effectiveness of the Brazilian chemical dispersant in dispersing such oil.

Another important contribution is the availability of information from simulations and primary data related to the characteristics of oils, obtained through laboratory analyses that followed international standards for laboratory analysis, such as the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM), which may be used by other researchers.

2 Materials and Methods

2.1 General Approach

This study had two objectives: the first was to understand the oil behavior after spilled offshore to identify the percentage of oil remaining, evaporated, and dispersed, and the second was to analyze the effectiveness of the chemical dispersant in dispersing such oil. An approach was designed in four main steps: characterization of the study area, bibliographic research, simulation of oil behavior and chemical dispersant efficacy, and analysis of results.

2.2 The Study Area

Bacia de Campos is the main explored oil region in Brazil. Its area covers about 100,000 km² and extends from the state of Espirito Santo, near the city of Vitória, to Arraial do Cabo, on the north coast of the state of Rio de Janeiro. From the geological point of view, it is defined as a region of a continental margin between Alto de Vitória at 20.5° South and the high of Cabo Frio at 24° South, with the coast as the western border and the longitude of 38° West (REDEPETRO 2020).

In this basin, there is one of the largest maritime oil complexes in the world. Since the beginning of commercial oil production in 1977, the Bacia de Campos has played a valuable role in technological development in Brazil and the globalized scenario (Petrobras 2020), being responsible for approximately 32% of Brazilian oil, and also being the passage route to drain oil

production in the country by sea (Piquet et al. 2017; ANP 2020).

Bacia de Campos is in a tropical zone that is influenced by the subtropical South Atlantic Anticyclone that characterizes the wave and wind conditions in the region (Castro Filho et al. 2015). The masses that affect those basin weather conditions are mainly two: Tropical Maritime Air Mass and Polar Sea Mass. The first is situated over tropical ocean latitudes and is characterized by the action center called the Atlantic Subtropical anticyclone. The second mass is associated with the polar anticyclone, which lies behind the cold fronts (Pinho 2003).

The classification of the seas can be made according to the main meteorological systems that dominate the circulation in the region. For the classification of the seas of the Bacia de Campos region, the meteorological systems that dominate the circulation in the region and characterized the wave climates adopting the following classification that is based on the highest incidence on the region were identified (Pinho 2003; Parente 1999; Kampel and de Freitas 2017): good weather without swells, good weather with swells, bad weather with SW storms, and bad weather with SE storms.

2.2.1 Good Weather Without Swells

This is the most common sea and wind situation characterized by northern quadrant winds that can reach high intensities and not very severe seas. This combination can impair daily operations in the Bacia de Campos and cause fatigue in structures, especially surface structures such as monobuoys. This occurs when there is the dominance of South Atlantic Anticyclone (SAA) in the atmospheric circulation of the region.

Among the typical winds of the good weather situation, i.e., N, NE, and E, the most common wind is NE, with 35% of the total occurrence of these three directions. More than 55% of winds occur in directions between 15 and 45°. Regarding wind intensities, 40% is between 8 and 10 m/s. Of all wind data related to the good weather situation, the highest recorded wind intensity values had an approximate 20° direction.

In this sea situation, the analysis of individual waves indicates that the most frequent waves are between 0.5 and 1 m high and periods in the range of 4 to 5 s. Wavelengths of NE local seas are hardly more than 7.5 s, and if higher values than these are observed, they are associated with quasi-local seas of NE-E and E directions. The highest individual heights had values between 5 and 6 m, with corresponding periods between 6 and 9 s.

As for significant waves, which indicate the severity and energy of a sea, the most frequent significant periods are between 6 and 7 s and the most frequent significant heights between 1.5 and 2 m. The highest observed waves have a range between 3 and 4 m and with an associated spectral peak direction around 8 s. These waves are associated with the most severe weather conditions, characterized by seas and winds with typically northern directions. These situations tend to occur after a cold front pass. One hypothesis to explain this may be that there is a northward displacement of SAA caused by the influence of polar anticyclone coming to the region from the south.

2.2.2 Good Weather with Swells

This situation has the same wind and local sea characteristics as described for good weather without swells. So mainly we will discuss the differences with the previous situation due to swell.

Regarding the frequencies of individual heights, there was a small increase in the range from 0 to 1 m, with the highest occurrence being between 0.5 and 1 m. Waves larger than 5 m almost do not occur in this situation. Individual periods have a more homogeneous distribution than that observed in the no-shuffle condition, and there is a higher occurrence of more extended periods. The most frequent periods are between 4 and 6 s, and the most extended observed periods, which are associated with waves, are 18 to 20 s.

The frequency domain analysis is more accurate in characterizing the two types of sea present in this situation. The local sea is typically identified as having significant periods between 5 and 6 s and heights in the range of 1.5 to 2 m. Diving has more frequent periods between 11 and 12 s and significant heights, also between 1.5 and 2 m. The largest significant periods observed are between 16 and 18 s and the highest significant heights between 2.5 and 3.5 m. This is a situation that can be critical in some operations, as waves and wind can be severe and in opposite directions.

2.2.3 Bad Weather with SW Storms

They are the most challenging sea situations. They occur when extratropical cyclones pass over the region. The most frequently observed winds in this situation have directions between 200 and 220° , and the most frequent intensity range is between 5 and 7 m/s and higher values exceeding 20 m/s.

The highest individual height observed in the entire dataset was 11.7 m, and its direction was 211°. About 40% of the waves had heights between 1 and 2 m. The most frequent individual waves were about 6 s of the period and about 1 m in height. The largest individual period observed was 23.9 s. When taken together, the highest heights (greater than 8 m) are associated with periods between 10 and 15 s, and the longest periods (greater than the 20s) with heights between 1.5 and 3.5 m.

Significant waves have more frequent heights between 1.5 and 2 m, and most frequent peak periods in the 8- and 12-s range. The highest significant height and period values are approximately 6 m and 16 s, respectively, and are associated with the 210° spectral peak direction.

2.2.4 Bad Weather with SE Storms

The domain of wind circulation is dominated by a polar anticyclone moving behind a cold front. During this situation, there was a higher occurrence of winds with directions between 120 and 135° and intensities between 6 and 9 m/s. Most individual waves have heights between 0.5 and 1 m and period between 4 and 5 s. The largest waves (heights greater than 8 m) had a period between 10 and 15 s. The waves with the longest periods, ranging from 18 to 20 s, had a height ranging between 0.5 and 3.5 m. The most frequent significant waves had periods between 9 and 12 s and heights between 2 and 3 m. The largest significant periods observed are less than 14 s, and the highest peak periods were between 14 and 16 s. The highest significant heights have values between 4 and 4.5 m.

2.3 Oil Behavior Simulation and Chemical Dispersant Effectiveness

Considering that Bacia de Campos serves as a gateway for the transportation of oil from other regions of Brazil, three characteristic oils have been defined according to the definition established by the National Petroleum, Natural Gas and Biofuels Agency (ANP 2020), which classifies petroleum characteristic of any area of the country in light, medium, and heavy, according to

Table 1 Oil classification according to ANP criteria

Oil Classification	°API
Light oil Medium oil	> 31 22 up until 31
Heavy oil	< 22

Table 1. The oil properties of the samples used are shown in Table 2.

Regarding wind and wave information, Table 3 presents the pre-established climatic conditions of Bacia de Campos. We used the following parameters regarding seawater property information: (a) salinity of 32 g/kg and (b) water and sediments of 5 mg/l. We used the following parameters regarding information about oil leaking: (a) continuous leakage, (b) leakage duration of 5 days (maximum set by the software), (c) quantity of leaked oil of 527 barrels, which was the average of the last large-scale accident in Brazil in 2011, and (d) constant winds.

For each type of oil, the following percentages were calculated: (a) Evaporated percentage, which considers the oil slick on the surface, the aromatic compounds of hydrocarbons (the most toxic one) pass into the atmosphere under direct interference from weather conditions; (b) Dispersed percentage, which considers the oil stain fragmented into droplets as a result of the agitation of the sea, wind, and waves (natural dispersion), which starts in the first hour, occurring more intensely in the early hours; (c) Remaining percentage that considers that the heaviest components of oil that do not dissolve in water adhere to small inorganic particles and floating solid materials (debris, twigs, and waste) and tend to sink to the bottom, which occurs most intensively from 24 h to a month after the leak and can last several years. These percentages were calculated for each type of oil, considering the following conditions:

- T1—wind: 5 m/s; direction: 35; and wave: 1.5 m
- T2-wind: 5 m/s; direction: 223; and wave: 3.0 m

Table 2 Oil properties of the samples used

Properties	Light oil	Medium oil	Heavy oil	Test method	
°API	46.4	26.7	15.1	ISO 12185	
Density (a 20/4 °C)	0.7915	0.8907	0.9618	ISO 12185	
Pour Point (°C)	-21	-12	0	ASTM D 5853	
Viscosity at 20C (68F) (cSt) (mm2/s)	3.374	48.56		ASTM D 7042	
Viscosity at 30C (86F) (cSt) (mm2/s)	2.534	31.17		ASTM D 7042	
Viscosity at 40C (104F) (cSt) (mm2/s)		20.88	2606	ASTM D 7042	
Viscosity at 50C (122F) (cSt) (mm2/s)		14.77	1138	ASTM D 7042	
VBALIC5 (iso-pentane (v/v))-accrued	4.71%	2.39%	1.14%	ASTM D2892	
VBALNC5 (N-pentane (v/v))-accrued	7.90%	3.78%	1.35%	ASTM D2892	
VBAL050 (volume yield (v/v))-accrued	8.55%	4.13%	1.41%	ASTM D2892	
VBAL075 (volume yield (v/v))-accrued	14.00%	6.22%	2.17%	ASTM D2892	
VBAL095 (volume yield (v/v))-accrued	18.30%	7.79%	2.77%	ASTM D2892	
VBAL125 (volume yield (v/v))-accrued	26.24%	10.39%	3.72%	ASTM D2892	
VBAL149 (volume yield (v/v))-accrued	34.06%	13.23%	5.07%	ASTM D2892	
VBAL200 (volume yield (v/v))-accrued	45.05%	18.91%	8.40%	ASTM D2892	
VBAL250 (volume yield (v/v))-accrued	53.26%	25.39%	12.40%	ASTM D2892	
VBAL300 (volume yield (v/v))-accrued	60.45%	32.62%	17.34%	ASTM D2892	
VBAL350 (volume yield (v/v))-accrued	67.06%	40.46%	23.70%	ASTM D2892	
VBAL400 (volume yield (v/v))-accrued	73.27%	48.84%	31.77%	ASTM D2892	
VBAL450 (volume yield (v/v))-accrued	79.06%	57.91%	40.78%	ASTM D5236	
VBAL500 (volume yield (v/v))-accrued	84.26%	67.24%	49.94%	ASTM D5236	
VBAL550 (volume yield (v/v))-accrued	88.70%	75.88%	59.06%	ASTM D5236	

Condições Good weather		Good weather with swells	Bad weather with SW direction	Bad weather with SE direction	
Wind (m/s)	5	5	25	10	
Wave (m)	1.5	3.0	3.0	2.5	
Direction	35	223	223	120	

Table 3 Climatic conditions of Bacia de Campos

- T3—wind: 25 m/s; direction: 223; and wave: 3.0 m
- T4—wind: 10 m/s; direction: 120; and wave: 2.5 m

We used the software ADIOS® (Automated Data Inquiry for Oil Spills) by NOAA (National Oceanic and Atmospheric Administration—USA) to simulate these conditions. This software is an oil spill response tool that models how different types of oil suffer weathering in the marine environment due to climate action.

3 Results

Table 4 presents the results of each climate condition for light oil (46.4 $^{\circ}$ API), and Fig. 1 shows the behavior of oil.

In condition T1 (good weather), the oil obtained an evaporation percentage of 60%, meaning that such percentage will go to the atmosphere, and 40% will remain at sea either in dispersed or sedimented form.

In condition T2 (good weather with swells), there was an increase in wave size and change of wind direction. Compared with condition T1, it can be observed that the evaporation rate has decreased, as well as the remaining oil, increasing the value of oil dispersion. Therefore, the increase in wave size has contributed directly to the increase of the dispersion phenomenon.

In condition T3 (bad weather with SW direction), there was a considerable increase of wind, being the most extreme in terms of weather conditions addressed by this paper. In this condition, it can be observed as a

Table 4 Results for each climate condition for light oil

Conditions	T1	T2	Т3	T4	
Evaporation rate	60%	56%	94%	59%	
Dispersion	16%	28%	5%	17%	
Remaining oil	24%	16%	1%	24%	

result of a very high evaporation rate, reaching approximately 94%. It can be seen that in extreme conditions, only 6% of the oil would be in the sea, the rest would go to the atmosphere.

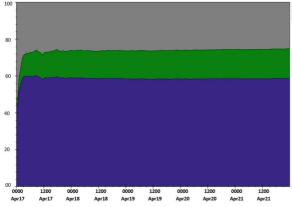
In condition T4 (bad weather with SE direction), there was an increase of wind and wave and can be considered as a medium condition. Under these parameters, an evaporation rate result of 59% is observed, being very close to the T1 condition. Thus, for light oil, small variations in wind and wave conditions bring little variation in evaporation rate.

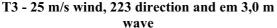
The results suggest that for light oil (46.4° API), the most favorable condition for oil to be evaporated in a higher percentage to the atmosphere is the most extreme condition. However, it is also possible to consider that small variations in wind and sea conditions, close to good weather conditions, do not add much to increase the evaporation rate. And that greater agitation through waves contributes to a smaller extent to evaporation, and more to dispersion formation. Also, the action of the extreme wind is the one that most influences the increase in oil evaporation at sea. Table 5 presents the results of each climate condition for medium oil (26.7° API), and Fig. 2 shows the behavior of oil.

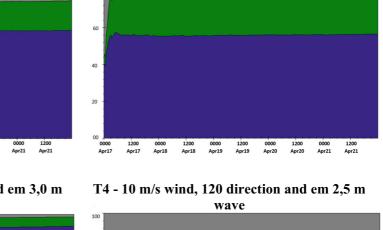
In condition T1 (good weather), there is a favorable and calm climate condition. In such condition, an evaporation rate result of 32%, lower than light oil, can be observed as it contains a larger quantity and hydrocarbon families. In condition T2 (good weather with swells), an evaporation rate result of 31% can be observed, being close to the level of condition T1. However, the dispersion condition increased as it did in light oil, as agitation has increased by increasing the wave.

In condition T3 (bad weather with SW direction), there is a considerable increase in wind. And under these parameters, a higher evaporation rate result is reached, getting to 66%. Thus, in the most extreme climatic condition, 34% of the oil that would be left at sea is obtained, and the remainder would go to the atmosphere.

T1 - 5 m/s wind, 35 direction and em 1,5 m wave T2 - 5 m/s wind, 223 direction and em 3,0 m wave







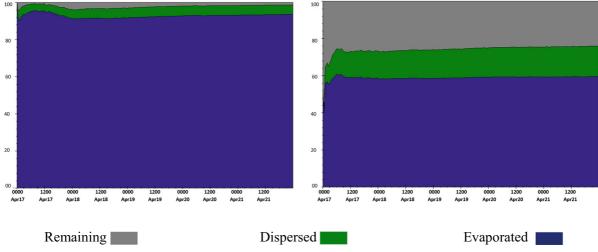


Fig. 1 Light oil behavior

In condition T4 (bad weather with SE direction), there is an average condition. And it can be observed as a result of the evaporation rate of 42%. Thus, for medium oil, small variations in wind and wave

 Table 5
 Results for each climate condition for medium oil

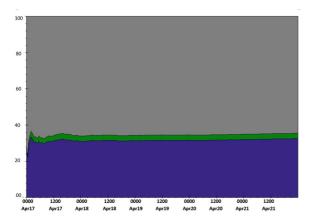
Conditions	T1	T2	Т3	T4	
Evaporation rate	32%	31%	66%	42%	
Dispersion	3%	6%	3%	5%	
Remaining oil	65%	63%	31%	53%	

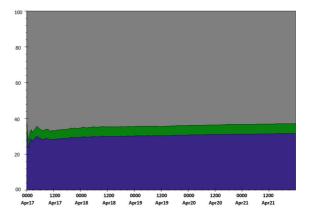
conditions bring variation in the evaporation rate, unlike light oil, when this factor was not so relevant.

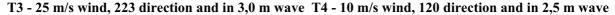
With these global results, it can be concluded that the most favorable condition for oil to be evaporated, in a higher percentage to the atmosphere, is the most extreme condition, as it is for light oil. However, due to the intrinsic characteristics of medium oil, it assumes lower evaporation rate values than light oil, so this type of oil is in higher concentrations in the sea, requiring more significant remediation measures. It was also observed that small wind variations interfere with evaporation and improve their percentages. Table 6 presents the results of each climate condition for heavy oil (15.1° API), and Fig. 3 shows the behavior of oil.

T1 - 5 m/s wind, 35 direction and in 1,5 m wave

T2 - 5 m/s wind, 223 direction and in 3,0 m wave







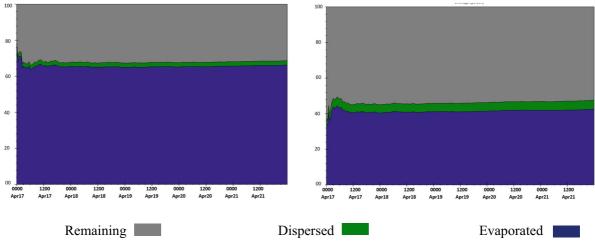


Fig. 2 Medium oil behavior

In condition T1 (good weather), there is a calm climate condition. And under these parameters, an evaporation rate result of 22% can be observed, being the smallest under these conditions compared with light and medium oils. This is explained precisely by being oil with typical quantities and families of hydrocarbons.

In condition T2 (good weather with swells), there was an evaporation rate result of 22%, close

Table 6 Results for each climate condition for heavy oil

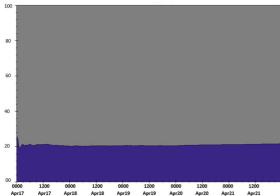
Conditions	T1	T2	T3	T4
Evaporation rate	22%	22%	52%	31%
Dispersion	0%	0%	0%	0%
Remaining oil	78%	78%	48%	69%

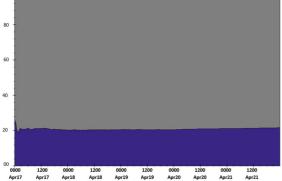
to the previous one, showing that for heavy oil, small wave variations do not make a difference in the evaporation rate.

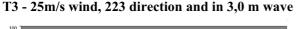
In condition T3 (bad weather with SW direction), there was an increase in wind and wave variables. In this condition, a higher evaporation rate result can be observed, reaching the level of 52%. Thus, in the worst climate conditions, the best evaporation rate values for heavy oil are reached.

In condition T4 (bad weather with SE direction), there was an intermediate condition. And a 31% evaporation rate result can be observed. Thus, for heavy oil, small variations in wind and wave conditions bring variation in evaporation rate as well, thus being relevant wave agitation and modification of mass balance via wind. With the global results of heavy oil, it can be

T1 - 5m/s wind, 35 direction and in 1,5m wave







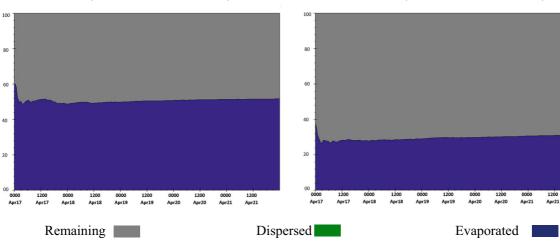


Fig. 3 Heavy oil behavior

concluded that the most favorable condition for oil to be evaporated, in greater percentage for the atmosphere, is the T3 condition, the same for light and medium oils. However, due to the intrinsic characteristics of heavy oil, the dispersion values are zero, which means that no oil is fragmented into surface droplets. It was also observed that small wind variations interfere in evaporation and improve their percentages.

For a better understanding of the subject and interpretation of the data, four more fictitious weather conditions were analyzed to interpret which variant (wind or wave) most impacts the evaporation rate, dispersion, and remaining oil. Such conditions were:

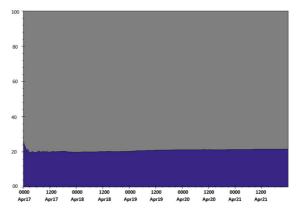
- T5-wind: 10 m/s; and wave: 0.0 m
- T6-wind: 1 m/s: and wave: 2.5 m
- T7-wind: 30 m/s; and wave: 0.0 m

T8—wind: 1 m/s; and wave: 10.0 m

A limiting point is that in the ADIOS software, it is not possible to set the wind parameter to zero, so the minimum condition of 1.0 m/s has been assigned to T6 and T8. Table 7 presents the results of each climate condition for light oil (46.4° API), and Fig. 4 shows the oil behavior. From the analysis of Fig. 4, it is possible to conclude that for light oil, the wind variable has a greater influence on oil, and thus condition T7 leaves the smallest amount of oil remaining in the sea. Therefore, increasing wind increases the evaporation rate of oil proportionally.

Table 8 presents the results of each climate condition for medium oil (26.7° API), and Fig. 5 shows the oil behavior. Figure 5 shows that it is possible to consider that wind is the variable that most influences the average

T2 - 5m/s wind, 223 direction and in 3,0m wave



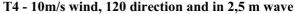


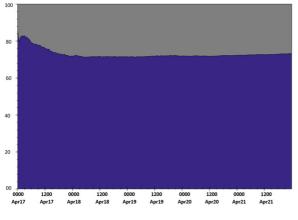
Table 7 Results for each climate condition for light oil

Conditions	T5	Т6	Τ7	Т8	
Evaporation rate	73%	45%	97%	28%	
Dispersion	0%	26%	0%	71%	
Remaining oil	27%	29%	3%	1%	

oil concerning the evaporation rate, reaching the lowest residual oil index in condition T7. It is also possible to notice that by increasing the wave size considerably— 10 m of wave height—the dispersion percentage reaches moderate levels of 16%. That is, the intrinsic characteristic of medium oil shows a limitation for dispersion.

Table 9 presents the results of each climate condition for heavy oil $(15.1^{\circ} \text{ API})$, and Fig. 6 shows the

T5 - 10.0 m/s wind and em 0.0 m wave



T7 - 30.0 m/s wind and em 0.0 m wave

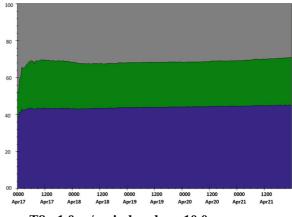
 Table 8 Results for each climate condition for medium oil

Conditions	T5	Т6	T7	Т8
Evaporation rate	44%	22%	72%	20%
Dispersion	0%	4%	0%	16%
Remaining oil	56%	74%	28%	64%

behavior of oil. Figure 6 shows that it is possible to realize that wind is the only variable that influences heavy oil, being the wave variable irrelevant and does not bring any modification to the system. Condition T7 also shows the lowest remaining oil level.

The overview of the general weather results for light, medium, and heavy oil can be seen in Table 10.

T6 - 1.0 m/s wind and em 2.5 m wave



T8 - 1.0 m/s wind and em 10.0 m wave

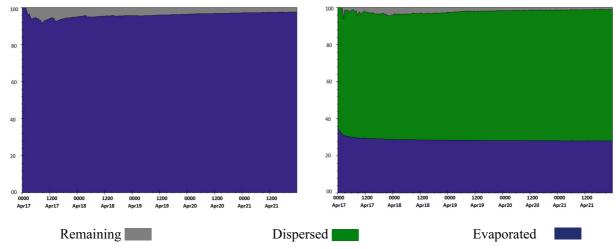
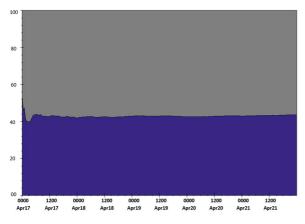


Fig. 4 Light oil behavior

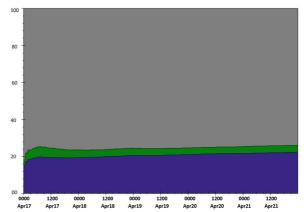
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T5 - 10.0 m/s wind and em 0.0 m wave





T6 - 1.0 m/s wind and em 2.5 m wave



T8 - 1.0 m/s wind and em 10.0 m wave

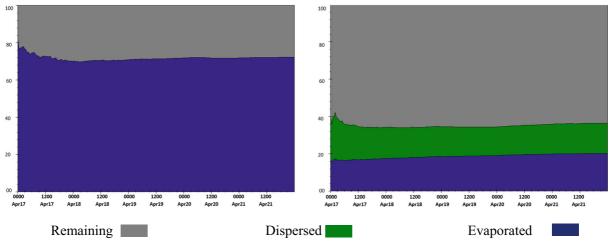


Fig. 5 Medium oil behavior

An important point to note is that as oil gets heavier, evaporation rates decrease, which shows an inversely proportional relationship between oil type and evaporation rate. It is also possible to verify that wind is the climatic condition that contributes to reducing the amount of oil remaining in the sea. Conditions T5, T6, T7, and T8 are fictitious extreme conditions as it is not possible to have no wind or wave in the environment.

Table 9 Results for each climate condition for heavy oil

Conditions	T5	Т6	Τ7	Т8	
Evaporation rate	30%	14%	56%	13%	
Dispersion	0%	0%	0%	0%	
Remaining oil	70%	86%	44%	87%	

Therefore, T3 (bad weather) condition is the one that most contributes to lower residual oil levels.

When comparing the distillation data in Table 2 with the modeling results in condition T3 in Table 10, we can see that in Table 2, the evaporation percentages for light, medium, and heavy oils are 88.7%, 75.88%, and 59, 06%, respectively, distilled at 550 °C, which was the last level used in the distillation. For medium and heavy oils, the results of the simulation in T3 condition (66% and 52%) are below these levels. For light oil, the results of the simulation in the T3 condition are 94% while the value of the last level of the distillation is 88.7%. We believe that some factors may have influenced this result.

The first is that the boiling of a liquid is governed by its vapor pressure and is influenced by two factors: the temperature (the higher the temperature, the higher the

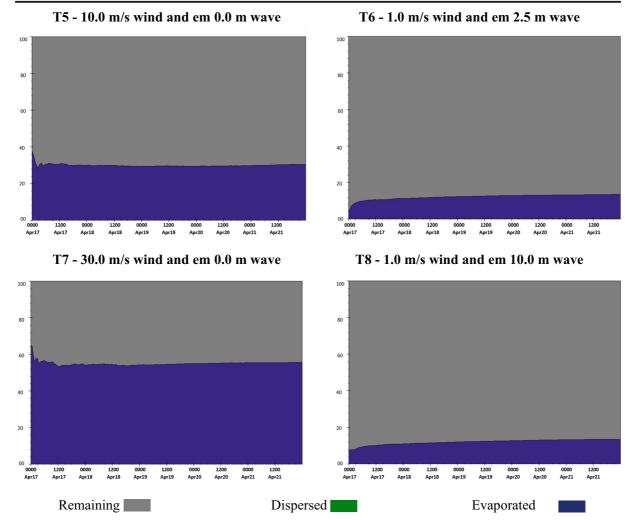


Fig. 6 Heavy oil behavior

vapor pressure, as the rise in temperature, favors the evaporation of the liquid) and the nature of the liquid (the stronger the intermolecular interactions, the more difficult it will be for the molecule to detach and go to the vapor state).

The second is that in the simulation of the evaporation rate based on pseudo-components, the oil is described in terms of its corresponding fractions, and each corresponding fraction is described according to its boiling temperature (boiling point). The proportional volume of each of these fractions is obtained using the true flashpoint (True Boiling Point), which is obtained through a standard method of the American Society for Testing and Materials (Table 2). In the environmental condition, the evaporation speed for each fraction is proportional to the partial vapor pressure of each component weighted by temperature and wind speed.

The third is that the ADIOS 2 software compensates analytical method deficiencies by using a hybrid algorithm that incorporates parts of the pseudo-component method in the Mackay method (Lehr et al. 2002). In the software approach, the relative molar volume for each pseudo-component is estimated from an empirical correlation between the molar volume and the respective flashpoint of the alkanes, and the vapor pressure is obtained from Antoine's equations. This premise starts from the approach that oil can be treated as being formed by alkanes, being, of course, an approximation.

Through Fig. 7, Fig. 8, and Fig. 9, it is possible to realize that the wind condition is the one that most influences the percentage of evaporated oil. It is possible

Table 10 General conditions of the oils used

Oil behavior	Clim	Climate conditions							Average	Min	Max
	T1	T2	Т3	T4	T5	T6	Τ7	Т8			
Light oil											
Evaporation without dispersant (%)	60	56	94	59	73	45	97	28	64	28	97
Dispersion without dispersant (%)	16	28	5	17	0	26	0	71	20	0	71
Remaining oil without dispersant (%)	24	16	1	24	27	29	3	1	16	1	29
Medium Oil											
Evaporation rate without dispersant	32	31	66	42	44	22	72	20	41	20	72
Dispersion without dispersant	3	6	3	5	0	4	0	16	5	0	16
Remaining oil without dispersant	65	63	31	53	56	74	28	64	54	28	74
Heavy oil											
Evaporation rate without dispersant	22	22	52	31	30	14	56	13	30	13	56
Dispersion without dispersant	0	0	0	0	0	0	0	0	0	0	0
Remaining oil without dispersant	78	78	48	69	70	86	44	87	70	44	87

to interpret that concerning the data referring to the dispersed and remaining oil phases (Table 10), on average, light oil leaves 36% of oil at sea, the medium 59%, and the heavy 70%.

Therefore, considering these three results, on average, 55% of the spilled oil remains at sea. Thus, containment and removal measures for this oil should be put in place in order to avoid damage to the local and coastal environment if it gets there (Etkin 2000; Michel and Fingas 2016) and more significant financial loss such as, for example, related to fines. The most common techniques for removing these oils at sea are oil containment, chemical dispersion, mechanical dispersion, oil burning, and recovery (Owens 2017; NOAA 2020; Fingas 2003). The use of dispersants is a common technique to use, especially when there is a risk of fire or safety from oil spills. Therefore, protecting public health and welfare remains a priority in any spill (Walker et al. 2018).

We used the chemical dispersion technique, along with the use of the ADIOS software, to analyze the

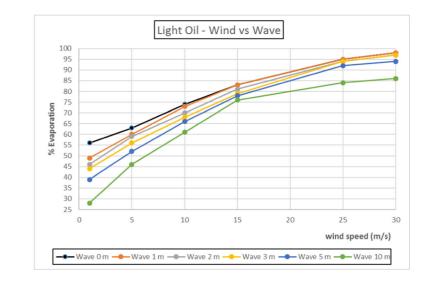
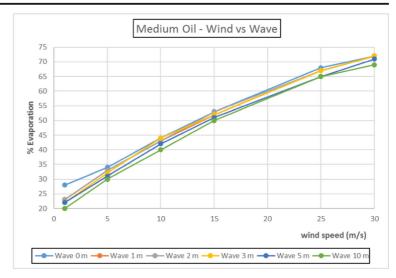


Fig. 7 Light oil comparison (wind versus wave)

Fig. 8 Medium oil comparison (wind versus wave)



removal level for the three oils (light, medium, and heavy) in the previously treated climatic conditions.

Dispersants and their effectiveness, according to Fingas (2011) and Moreira (2016), may range from 0 to 28%, based on West Texas Intermediate (WTI) oil, which is traded on the New York Stock Exchange and is quoted on the US and worldwide markets. The area to be covered by the dispersant application must be 80%, the minimum percentage established by CONAMA Resolution No. 472/2015. This resolution also establishes the application of the dispersant must be carried out as soon as possible, preferably within the first 24 h.

We simulate for the eight climatic conditions the oil's behavior after dispersant application in

three concentration variations: 14%, 28%, and 42%. The results are presented in Table 11 and Figs. 10, 11, and 12.

According to the used dispersant and the stipulated concentrations (14%, 28%, 42%) for the three types of oils (light, medium, and heavy), the results show that in the application conditions of the dispersant, the absolute number variation was from 1 to 5%, not showing a considerable improvement justifying its application. Exception made for light oil in T4 condition (10 m/s wind, direction 120 and 2.5 m wave), in the three dispersant percentages used, where the evaporation, dispersion percentage, and the amount of remaining oil suffered a relevant variation. That is, the use of dispersant in this

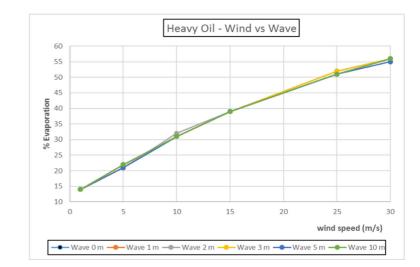


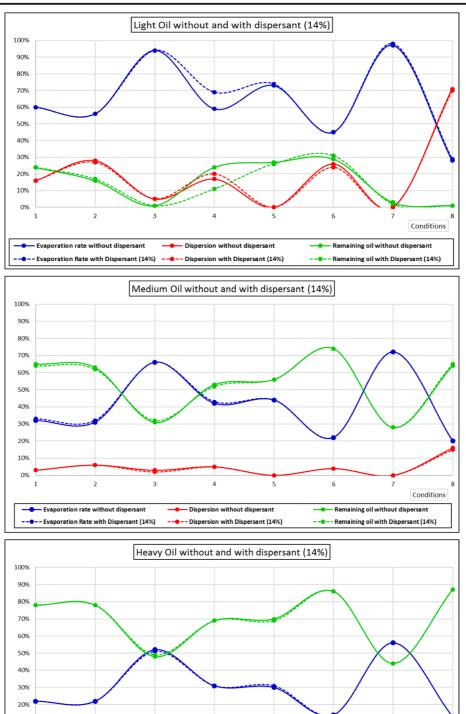
Fig. 9 Heavy oil comparison (wind versus wave)

Table 11 General conditions of oils after dispersant use

Oil behavior	Climate conditions (%)							
	T1	T2	T3	T4	T5	T6	Τ7	Т8
Light oil—with dispersant (14%)								
Evaporation with Dispersant (14%)	60	56	94	69	74	45	98	29
Dispersion with Dispersant (14%)	16	27	5	20	0	24	0	70
Remaining oil with Dispersant (14%)	24	17	1	11	26	31	2	1
Light oil-with dispersant (28%)								
Evaporation with Dispersant (28%)	60	57	94	70	74	46	98	30
Dispersion with Dispersant (28%)	15	25	4	19	0	23	0	69
Remaining oil with Dispersant (28%)	25	18	2	11	26	31	2	1
Light oil-with dispersant (42%)								
Evaporation with Dispersant (42%)	60	57	94	70	74	46	98	31
Dispersion with Dispersant (42%)	14	25	4	19	0	21	0	68
Remaining oil with Dispersant (42%)	26	18	2	11	26	33	2	1
Medium oil-with dispersant (14%)								
Evaporation with Dispersant (14%)	33	32	66	43	44	22	72	20
Dispersion with Dispersant (14%)	3	6	2	5	0	4	0	15
Remaining oil with Dispersant (14%)	64	62	32	52	56	74	28	65
Medium oil-with dispersant (28%)								
Evaporation Rate with Dispersant (28%)	32	31	66	43	44	22	73	20
Dispersion with Dispersant (28%)	3	5	2	5	0	4	0	14
Remaining oil with Dispersant (28%)	65	64	32	52	56	74	27	65
Medium oil-with dispersant (42%)								
Evaporation Rate with Dispersant (42%)	33	31	65	43	43	22	72	21
Dispersion with Dispersant (42%)	3	5	2	4	0	3	0	13
Remaining oil with Dispersant (42%)	64	64	33	53	57	75	28	66
Heavy oil-with dispersant (14%)								
Evaporation with Dispersant (14%)	22	22	51	31	31	14	56	13
Dispersion with Dispersant (14%)	0	0	0	0	0	0	0	0
Remaining oil with Dispersant (14%)	78	78	49	69	69	86	44	87
Heavy oil-with dispersant (28%)								
Evaporation with Dispersant (14%)	22	22	51	31	31	14	57	14
Dispersion with Dispersant (14%)	0	0	0	0	0	0	0	0
Remaining oil with Dispersant (14%)	78	78	48	69	68	86	43	86
Heavy oil-with dispersant (42%)								
Evaporation with Dispersant (14%)	21	22	51	31	31	14	57	14
Dispersion with Dispersant (14%)	0	0	0	0	0	0	0	0
Remaining oil with Dispersant (14%)	79	78	49	69	69	86	43	86

condition improved the indicators, showing to be interesting its use for oil remediation conditions at sea.

The concentration value of 14% is the minimum level of dispersant that has the maximum effect in the T4 condition, and only for light oil. Concentrations below this value generate an even smaller improvement for the T4 condition, and concentrations above 14% produce the same improvement. It is possible to conclude that changes in dispersant concentrations do not significantly change the dispersion improvement in all other



5

6

7

Remaining oil without dispersant

--- Remaining oil with Dispersant (14%)

Conditions

4

Fig. 10 General conditions of oils before and after dispersant (14%) use

2

3

10% 0%

1

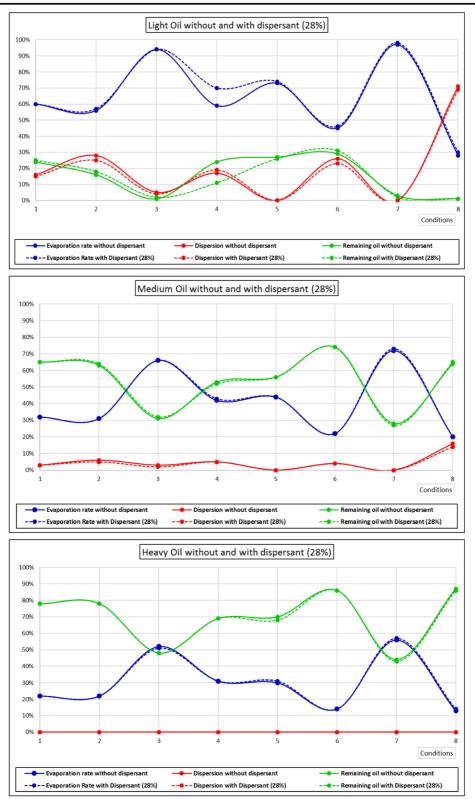
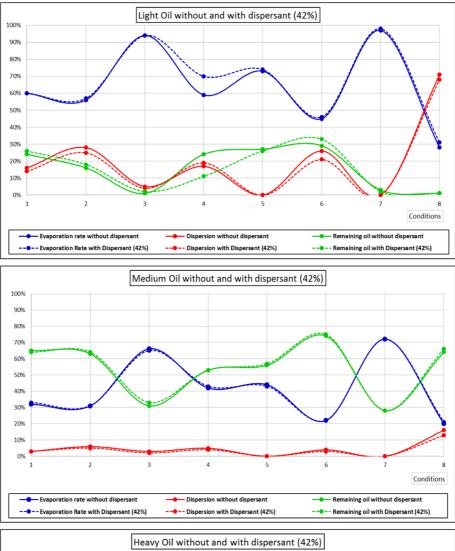


Fig. 11 General conditions of oils before and after dispersant (28%) use



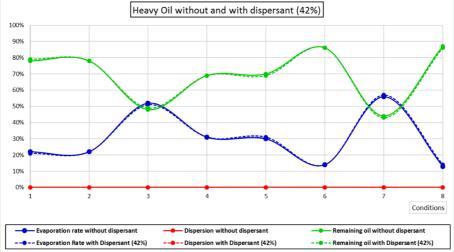


Fig. 12 General conditions of oils before and after dispersant (42%) use

conditions (T1, T2, T3, T5, T6, T7, and T8). Only in the T4 condition does the variation in the dispersant concentration have any effect only for light oil. However, in this condition, the dispersant facilitated the reduction of the amount of light oil remaining from 24 to 11% and improved the evaporation rate from 59 to 69%. The dispersion rate, the main objective for applying the use of the dispersant, improved only from 17 to 20%.

The natural dispersion process removes part of the oil from the surface by distributing it through the water column. The most usual is to consider this process in terms of variables that express turbulent energy, such as wind and waves. Thus, the entry of fractions of oil in the sub-surface layers of the sea is forced by the action of waves and winds, which mechanically inserts the droplets into the water column. Part of these inserted droplets do not return to the surface, but will gradually disperse permanently in the water column. When the marine environment has sufficient energy provided by the wind speed and wave size, the natural degradation process will be able to carry out the dispersion without the need for dispersants.

This context may have influenced the results obtained, since the addition of dispersant in the climatic conditions used in the simulation did not produce significant influence, suggesting that the dispersion level is at a higher level of an asymptotic characteristic curve influenced by the wave and/or wind interference, which end up promoting natural mechanical dispersion.

4 Conclusions

Spills of crude oil and its derivatives have increasingly aroused the interest of the scientific community. The main focus has been studies focused on the prevention, control, and remediation of spills to reduce the resulting environmental and socio-economic impacts and also impacts on human health.

Despite significant progress in actions to reduce oil spills, which are mainly operationalized through technological measures, regulation, and best practice developments, spills continue to occur in Brazil and worldwide and have significant impacts.

This paper is inserted in the context of "Emergency Plan" adopted in many countries, contributing to a better understanding of the behavior of oil after a spill on the high seas, identifying the percentage of remaining, evaporated, and dispersed oil in pre-established situations, and analyzing the effectiveness of chemical dispersant to disperse such oil, which contributes to the improvement of the operational techniques used to remove oil at sea. It also contributes to the existing literature on the subject.

Through mathematical simulation it was possible to verify that, for the three types of oil analyzed, the climatic conditions (wind and wave) and their levels of variation have direct interference on the amount of evaporated, dispersed, and remaining oil, being the wind and its speed the conditioner that most affects the rate of oil remaining at sea. It was also possible to verify that for the three types of oil, light oil leaves an average of 36% of oil at sea, the medium 59%, and the heavy 70%, taking into account the sum of the dispersed and remaining oil phases. Therefore, considering these three results, on average, 55% of the oil spilled remains at sea.

Through the analysis of chemical remediation using dispersant, under the conditions defined in this study, it was found little contribution to improve the evaporation and dispersion process, therefore little influence on the weathering of oil in the sea, which will require future studies aiming at determining the conditions for its usage.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

Code Availability Not applicable

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