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MAIN SPILLS OF DIESEL OIL AND FUEL OILS IN MANGROVE ECOSYSTEMS IN BRAZIL, FROM 1975 TO 2022

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Abstract: Oil spills in coastal and marine environments have been frequent from the second half of the 20th century to the first decades of the 21st century, resulting in varied socio-environmental impacts on mangrove ecosystems, estuaries and beaches. Port areas, marinas, and areas where the supply and maintenance of automotive, road, rail and boat vehicles are carried out, in addition to fuel distribution stations, are also prone to leaks, causing percolation of oil residue and long-term bioaccumulation. term, even in small quantities.On the other hand, large spills result in more persistent damage to affected ecosystems. In some regions, mangroves share space with port areas, refineries and pipelines, being exposed to leaks and accidents, affecting their inestimable environmental, economic and ecological importance.We sought to identify the main spills that occurred with diesel oil and fuel oils, which reached estuaries and mangroves on the Brazilian coast between the years 1975 to 2022 and to discuss the ecotoxicological and ecophysiological evidence of the presence of diesel oil in these ecosystems. Some accidents and spills with crude oil were also included only in the temporal analysis, given their significant relevance both in terms of volume spilled and in terms of extension of the affected coastal zone.Data, metadata and document analysis were used, including scientific articles, technical reports from public or private companies in the environment, sanitation, academic reports and from government public managers, academic dissertations, legal processes, among others. The results showed that diesel oil accidents are among the most frequent in chemical and petrochemical waterway terminals and caused severe damage to mangroves, other coastal ecosystems and the human population.

Keywords: hydrocarbons, oil spill, mangrove, coastal zone, environmental impact.

INTRODUCTION

The mangrove is a coastal ecosystem of transition between land and sea, characteristic of tropical and subtropical zones, being, among the existing ecosystems, one of the most productive on the planet, having a close connectivity with other environments beyond the coast (YOKOYA, 1995). ; MOCHEL, 2011; ICMBIO, 2018). It has its ecological, economic and social importance highlighted by several authors such as Mochel (2002, 2011 and 2016), Mochel and Fonseca (2019), Corrêa et al. (2021), Paula (2012) and Soares (1997), among others. According to these authors, there are numerous benefits that mangroves provide, however, despite their importance, they are among the most threatened coastal ecosystems and have suffered great loss through degradation, which can be either of natural or anthropic origin.

Oil pollution is characterized as a tensor that produces negative effects on the environment, especially those that are more sensitive, such as the mangrove ecosystem, which is assigned level 10 in the Coastal Sensitivity Index (ISL) described in the Letters of Environmental Sensitivity to Oil Spills (SAO Letters) by the Ministry of the Environment (MMA, 2016), the highest and most sensitive level characterized in the letters. Several authors (SOARES et al., 2003; 2006; PINHEIRO and SILVA, 2020) point to the conjunction of adverse natural conditions allied to human activities in environmental persistence and slowness of the recovery processes of coastal ecosystems, especially mangroves, being the oil exposure, largely through accidents, one of the most damaging tensioners.

In mangrove forests, in cases where the restoration of previously existing environmental conditions is delayed, due to damage caused by prolonged contact with the oil, there may be repercussions for other negative impacts in addition to those that occur on plants, such as environmental degradation. by erosion, invasion of opportunistic species, changes in hydrological flows, among others (SILVA, 2006; MOCHEL E FONSECA, 2019).

Petroleum-derived fuels, such as diesel oil, gasoline and Liquefied Petroleum Gas (LPG), are characterized as the most important source of energy used in the world. From the 1950s onwards, its exploitation gradually and considerably increased and became indispensable in modernity for the functionality of several segments ranging from fuels for automotive vehicles, aviation, maritime transport, engines, thermoelectric plants, as well as used as raw material in the manufacture of plastics, lubricants, rubbers, asphalt products, kerosenes, paints, cosmetics, among others (THOMAS, 2001; MARSICO, 2008). Despite the growing consumption over the years, the sector suffered a decrease in demand due to the challenges imposed by the COVID-19 Pandemic situation in 2020, even so, the oil market is recovering and the demand for its derivatives, in subsequent years, promises to increase, according to the International Energy Agency (2021). This agency, as well as the Energy Research Company (EPE, 2019), point to the world demand for oil by product, demonstrating that diesel oil is one of the main fuels traded worldwide.

There are several routes through which petroleum derivatives pass, from their refining to their final distribution (road, pipeline, rail and waterway), and, in the course of this transport logistics, there are various risks of accidents both in small and large proportions that can reach the environment resulting in harmful effects in the short and/or long term (acute and/or chronic effects). According to Matos, Cunha and Cutrim (2019), in Brazil, there is a greater number of environmental accidents involving road and water transport, and that aquatic ecosystems are one of the most affected natural environments, mainly by oil.

It must be noted that an accident involving a large oil spill can cause several negative impacts to both flora and fauna and to people as well, due to the toxicity that involves its components. IBAMA (2009;2014) emphasizes the importance of knowing the type and quantity of the product that reaches the environment so that there is a better assessment of the impact that has occurred. Results of studies such as this one tend to contribute to the formation and management of public and environmental policies, also helping to promote mitigating measures in areas where accidents occur.

MATERIAL AND METHODS

Mangroves are distributed along the Brazilian coast from 4° in Cabo Orange, in the state of Amapá, to 28° 30' S, in the municipality of Laguna, in Santa Catarina. The most extensive areas are located on the Amazon coast, comprising the states of Maranhão, Pará and Amapá. (Figure1).

Figure 1 -Distribution of mangroves in Brazil, from the State of Amapá (in Cabo Orange, latitude 4o N) to the State of Santa Catarina (in Laguna, latitude 28o30' S). Source: Adapted from ICMBIO, 2018

The research was based on data, metadata and document analysis, including scientific articles in indexed media, technical reports from public or private companies in the environment, sanitation, academic reports and governmental public managers, legal proceedings (Public Prosecutor's Office, legal expert reports environmental issues, among others), and also reports and textual information published by Non-Governmental Organizations. The data collection period covered the second half of the 1970s until January 2022. From the data collected, data were tabulated and analyzed using Excell Office 2016 (OLIVEIRA, 2016).

RESULTS AND DISCUSSION

Table 1 shows the main spills of diesel and fuel oils in mangroves in Brazil over 47 years, from March 1975 to January 2022. CONAMA Resolution 398 of June 2008 classifies oil spills as small (up to 8m3), medium (up to 200 m3) and large (over 200 m3).

In March 1975 a freighter chartered by Petrobras (Iraqi ship Tarik Ibn Ziyad) broke the hull and leaked 6 million liters of oil into the waters of the bay. Among the spills that have already occurred in Baía de Guanabara, this was the largest in terms of the amount of oil leaked into the environment (NITAHARA, 2016). After this event, other accidents with oil spills occurred in Baía de Guanabara (Table 1), however on a smaller scale in terms of the amount of oil spilled, but which also caused several damages to the local flora and fauna, as well as to the fishing population. of the area.Still in Baía de Guanabara, the second largest oil spill event occurred in January 2000, characterized as one of the largest oil spills in Brazil, in a mangrove area. The accident occurred after the pipeline between the Duque de Caxias Refinery and the Ilha d'Água Terminal broke and caused a leak of 1 million and 300 thousand liters of marine fuel oil (a mixture of diesel oil and heavy fuel oil). The disaster occurred during high syzygy tide causing a greater impact on mangrove areas, both in acute and chronic effects (SOARES et al., 2006; CETESB, 2013). The results of this environmental impact had repercussions on the affected mangroves, causing several effects such as a high mortality rate of seedlings, young and trees, reduction in the recruitment of propagules,

Poffo et al. (2007) drew attention to the various damages caused by oil spills to mangroves and fishing communities on the coast of São Paulo that occurred between 1976 and 2004. mangroves in the region of Santos, São Paulo, on the occasion of the partial sinking of Barcaça Giela, in Santos, at the terminal in Alemoa (POFFO, 2010). An analysis carried out on accidents that occurred at chemical and petrochemical terminals in Santos revealed that among the oily substances spilled into estuaries and adjacent ecosystems, diesel oil (land and sea) and marine fuel oil (marine fuel oil) were the predominant ones (POFFO, 2008).

In São Marcos Bay, Maranhão, in 1990, the ship Orade Nassau, loaded with 33 thousand tons of diesel oil, collided with the Korean ship Hyunday New World, already stranded since 1987 on the Cavalos sandbar, releasing the of the load in the estuary, being considered one of the most serious accidents in the region (PORTOSMA, 2018).

The explosion of the Chilean tanker Vicuña, on November 15, 2004, in the Port of Paranaguá, leaked 425 m^3 of IFO180 marine fuel oil, 1,130 m^3 t of diesel and lubricating hydraulic oils and about 5,000 tons of ethanol (FIGUEIRA, 2019). ; CUNHA, 2012; CARNERO, 2005). The Center for Scientific Support in Disasters – UFPR (2004) registered the largest oil spill in the Bay of Paranaguá in 20 years, both due to the prolonged exposure of the area to toxic substances, as

Date	Location	Leaked volume *	Characteristics of spills in mangroves in Brazil
03/1975	Baía de Guanabara (RJ)	6 thousand tons	A freighter chartered by Petrobras leaked oil in Baía de Guanabara.
10/1983	Bertioga (SP)	3 million liters	Petrobrás pipeline rupture affected extensive mangrove area and 32 km of beaches
02/1984	Cubatão (SP)	700 thousand liters	Gasoline leak after the explosion of a Petrobras pipeline in the Vila Socó favela, reached an extensive area of mangrove.
06/1984	Santos (SP)	20 thousand liters	Diesel oil leaked from the Alemoa terminal pipeline rupture
09/1984	Santos (SP)	500 thousand liters	Leakage of diesel oil from the wreck of the Barge Gisela at the Alemoa terminal.
02/1986	Santos (SP)	140,000 liters	Marine fuel oil spill caused by the collision of the barge Gisela with the wreckage of the wrecked ship Ais Georgius, reached the estuary, mangroves, beaches and caused damage to artisanal fishing and loss of quality of leisure.
nineteen ninety	Sao Luis (MA)	33 thousand liters	Diesel oil spill in São Marcos Bay, after the collision of the Orade Nassau ship with the Hyundai New World ship, stranded since 1987, on the cavalos sandbar
04/1992	Mãe de Deus (BA)	48 thousand liters	Crude oil spill hit more than 30 km of mangroves
03/1994	Santos (SP)	700 liters	Marine diesel oil spill by transshipment from the Norma Tank Ship, at the Alemoa terminal. The oil slicks entered the estuary with the rising tide, hitting the fishermen.
05/1994	Several municipalities (SP)	2 million and 700 thousand liters	On 18 beaches on the north coast of São Paulo, reaching mangroves.
03/1997	Baía de Guanabara (RJ)	2 million and 800 thousand liters	Leakage of fuel oil in mangroves, after rupture of the pipeline connecting the Duque de Caxias Refinery (RJ) and the DSTE-Ilha D'Água terminal
08/1997	Ilha do governador (RJ)	2 thousand liters	Petrobras fuel oil leak on five beaches and mangroves.
01/2000	Duque of Caxias (RJ)	1 million and 300 thousand liters	Fuel oil leak reached mangroves, after rupture of the pipeline connecting the Duque de Caxias Refinery and the Ilha d'Água terminal.
03/2000	São Sebastião (SP)	7 thousand and 250 liters	Oil spill in the São Sebastião channel, from the FNP ship Mafra.
05/2000	Sao Luis (MA)	25 thousand liters	Leakage of diesel oil in mangroves during supply of locomotives of the then CVRD
06/2000	Baía de Guanabara (RJ)	380 liters	A kilometer-long oil slick appeared near water island.
07/2000	Ponta Grossa (PR)	60 thousand liters	Leakage of diesel oil from the train derailment of Companhia América Latina Logística (ALL)
07/2000	Ponta Grossa (PR)	20 thousand liters	Leakage of diesel oil and gasoline (one week later) by ALL train derailment, reaching a permanent preservation area.
09/2000	Morretes (PR)	4 thousand liters	Fuel leak by ALL train derailment, in Caninana stream.
11/2000	Ilhabela and São Sebastião (SP)	86 thousand liters	Accident with a Petrobras cargo ship polluted beaches and mangroves.
02/2001seba	Morretes (PR)	4 million liters	Leakage of diesel oil due to rupture of a Petrobras pipeline, in the Caninana stream, a tributary of the Nhundiaquara River, affecting an extensive area of mangroves.

Date	Location	Leaked volume *	Characteristics of spills in mangroves in Brazil
04/2001	Curitiba (PR)	30 thousand liters	Leak resulting from an accident with a Petrobras truck on BR-277, reached Rios do Padre and Pintos and mangroves.
/2001	Santos/SP	43,000 liters	Diesel oil spill from the collision between two fishing vessels
10/2001	Baia Paranaguá (PR)	392 thousand liters	The oil tanker Norma collided with a rock in the bay, spilling 392,000 liters of the product in an area of 3,000 square meters.
02/2002	Baía de Guanabara (RJ)	50 thousand liters	Fuel oil leak from the English ocean liner Caronia, moored at Praça Mauá Pier,
05/2002	Ilha de Grande Bay (RJ)	16 thousand liters	Light oil spill from Transpetro's Brotas vessel (Nigerian type) in the Angra dos Reis region.
08/2002	São Sebastião (SP)	3 thousand liters	Oil leak during Greek flag ship loading.
15/2004	Port of Paranaguá (PR)	425 m^3 of IFO180 marine fuel oil; 1,130 m^3 t of lubricating diesel and hydraulic oils; 5 thousand tons of ethanol	The explosion of the cargo ship Vicuña spilled marine fuel, diesel and hydraulic oils, in addition to part of the ethanol transported that was not burned, reaching mangroves, sandbanks and leading to the ban on fishing.
05/2007	Port of Santos (SP)	862 liters of lubricating oil and 5,862 liters of marine diesel oil	Spillage of marine diesel oil and lubricating oil after the collision of the Pegasus tugboat with the wreckage of a sunken ship near the Port.
04/2013	São Sebastião (SP)	3 thousand and 500 liters	Oil leak from the pier of the Almirante Barroso Waterway Terminal (Tebar), in São Sebastião, reached the north coast of São Paulo.
03/2015	Ilha Grande and Sepetiba Bays (RJ)	25 thousand liters	Oil leak at sea, during a ship to ship double banking operation, of oil transfer carried out between the ships "Navion Gotemburg" and "Nave Buena Sorte", at the docking pier of the terminal
06/2015	Itaguaí and Mangaratiba (RJ)	600 liters	Oil leak in a Petrobras pipeline reaching mangroves in Coroa Grande and Itacuruçá.
06/2018	Baia de todos os santos (BA)	-	Oil leakage caused by rupture of a Petrobras pipeline contaminates the Todos-os-Santos Bay (BA), affecting the lives of quilombola communities that depend on fishing and mangroves.
12/2018	Baía de Guanabara (RJ)	60 thousand liters	Extensive area of mangroves affected by oil leakage from the Transpetro pipeline, in the region of the Guapimirim APA.
08/2019	Northeast and Southeast coast	Estimated between 5 and 12.5 million liters	Biggest oil spill in Brazil, affecting mangroves, beaches and coastal ecosystems, in 11 states of the Northeast and Southeast coast, in an area greater than 4 thousand kilometers.
01/2022	Coast of Ceará	4 thousand liters	Crude oil slicks on several beaches; unidentified causes.

*When there was controversy regarding the volume of oil leaked, the lowest value reported in the sources surveyed was maintained.

Table 1 - Main spills of diesel oil and fuel oils in mangroves in Brazil, from March 1975 to January 2022. Although, in the table, the emphasis is on diesel oil and fuel oil spills, some of the large spills of crude oil, gasoline and LPG.

Source: the authors, 2022.

well as the impacts and damage generated to the ecosystem and society. The oil polluted and contaminated about 30 km including the Bay of Paranaguá, Ilha do Mel and part of the open sea. The accident resulted in the contamination of sediments, in the mortality of the three species of mangrove trees, fishing was prohibited, in addition to fatalities.One year after the spill, it was still possible to witness the mortality of several species in the impacted area (UMEZU, 2019).

In terms of the number of occurrences, from the data analyzed, most of the spills and accidents that affected mangrove areas occurred in the Southeast region (Figure 2). It is in this region where large refineries, petrochemical terminals, an intricate network of oil and gas pipelines are concentrated, numerous port areas that include the movement of mass tourism vessels (maritime cruises), favoring potential risks and effective accidents of oil spills. There is also prospecting for oil and gas on the platforms of the Campos Basins (RJ), Santos Basin (SP), and others, where spillage risks are foreseen in their EIA/RIMA, since tidal oceanographic conditions, winds, currents, can cause a spill to reach the coast and enter mangroves, estuaries and other coastal ecosystems.

The southern and northeastern coastal regions also have diesel and fuel oil spills and leaks in mangrove areas to a lesser extent (Figure 2). These regions, in relation to the SE, have less installed infrastructure, however, accidents with vessels and in petrochemical terminals are causes of leaks that degrade the development and healthy growth of mangrove forests and affect the quality of life of traditional communities.

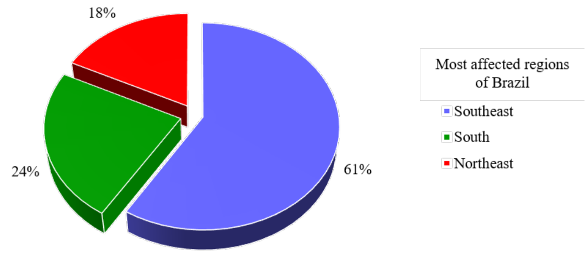

Figure 2 -Brazilian regions most affected by major oil and fuel oil spills in mangroves from the second half of the 1975s to January 1, 2022.

Source: The authors.

IBAMA reports in 2009 and 2014 showed that in 2008, 2009, 2013 and 2014, diesel oil was the product with the highest accident rate and also the highest volume leaked, with oil spills being the most occurrence.

According to the EPE (2019) and the International Energy Agency (2021), diesel oil is currently the main fuel consumed in the world (Figure 3). This statistic also increases the potential for ecosystem degradation caused by accidents with this product and, according to Thompson and Thompson (2020), one of the main forms of coastal and marine pollution occurs through accidents with oil used as fuel or transported. on ships and vessels. These authors emphasize that because they are widely affected, coastal and marine environments suffer several impacts that weaken them over time. This way, it is important to observe the negative impacts that several accidents, which have already occurred with diesel oil, have caused to coastal environments.

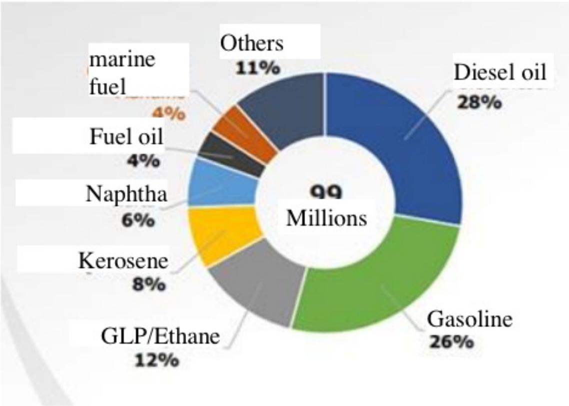

Figure 3 -World oil demand by product. Diesel oil is the most consumed fuel.

Source: IEA/EPE, 2019

There are currently several types of diesel oil on the market.(Figure 4). ANP Resolution No. 65/2011 classifies the types of diesel oil sold in Brazil as Diesel Oil A (Without the addition of biodiesel) and Diesel Oil B (With the addition of biodiesel), it also establishes the sulfur content they contain, as follows: S- 10 (10mg/kg or 10ppm[1]), S-50[2](50mg/kg or 50ppm), S-500 (500mg/kg or 500ppm) and S-1800[3](1800mg/kg or 1800ppm), the first three being for road use and the S1800 used in rail transport, power generation in thermoelectric plants and mining.

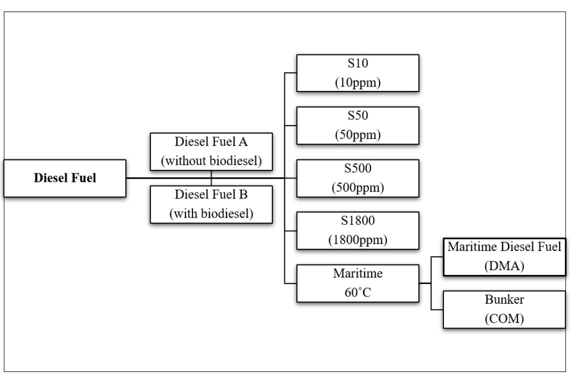

Figure 4- The types of diesel oil in Brazil.

Source:the authors, based on ANP Resolution 65/2012 and EPE (2019)

The two most commonly used types of diesel are automotive diesel and marine diesel. Automotive diesel oil is normally characterized by its sulfur content, the most common being S-10 (10ppm), while marine diesel oil is usually characterized by its flash point (60ºC), containing 0.5% sulfur (5000ppm) – (FINOTTI et al., 2001; CETESB, 2012; COMPANY OF ENERGY RESEARCH, 2019; PETROBRAS, 2021). The S-10 automotive diesel oil, with or without the addition of biodiesel, is the most common, used in vehicles built after 2012, due to its low sulfur content (10ppm) and the increase in the cetane number, which increased to 48, both considered a relevant improvement compared to other types of diesel oil. (FINOTTI,*et al.*,2001; SILVEIRA, 2014; PETROBRAS, 2021).

S-10 diesel has numerous chemical compounds that are more complex than gasoline. In this chemical composition there is a complex mixture of hydrocarbons containing from 10 to 22 carbon atoms where each group of hydrocarbons varies according to the origin of the petroleum; it also has additives such as: aromatics (25 to 35%), low concentrations of sulfur, nitrogen, oxygen andBTEX – benzene, toluene, ethylbenzene and xylene – (FINOTTI,*et al.*,2001; CETESB, 2012; SZKLO and ULLER, 2012). Due to its higher molecular weight, it is less volatile, less dense and less soluble in water and has less mobility in the environment than gasoline. With a strong odor, its color varies, according to the type of diesel, from transparent to yellow, red, orange or brown. Due to their nature, they tend to cause damage when in direct contact with the environment (PETROBRAS, 2021). Among the most common risks are explosion, emission of vapors denser than air,

1. Amount of sulfur parts/particles per million.
2. S-50 diesel oil is no longer commercialized since 2013, replaced by S-10 (ANP Resolution No. 50/2013).
3. The S1800 diesel oil is no longer marketed since 2014, replaced by the S-500.

which makes breathing difficult and causes irritation to exposed skin. It is a substance that has carcinogenic potential, being fatal if ingested (PETROBRAS, 2007).

Baker (1970) considers that the harmful effects of oil on plants depend on the composition and amount of oil disposed in the environment, as well as on environmental conditions and the species affected. The mangrove can suffer several imbalances in contact with diesel oil, resulting in very harmful and delicate degradation (SOARES et al., 2006; CETESB, 2012). Several authors (in: UMEZU, 2019) have reported harmful effects of the presence of oily compounds on the mangrove ecosystem, such as degradation and loss of leaves, reduction of primary production, contamination and mortality of fauna by chemical toxicity. By forming a film on the surface of the water, diesel oil lowers the levels of dissolved oxygen and coats the mangrove trees, promoting the obstruction of the lenticels in the rhizophores, causing the compromise of respiratory rates and the asphyxia of the trees. Diesel oil also has a high bioaccumulative potential in aquatic organisms and its low evaporation rate makes it remain in the environment for several days, leaving some residue that does not evaporate at room temperature. Due to its higher molecular weight, in case of spillage into the environment, diesel oil adsorbs more to soil particles and percolates less quickly than gasoline. (HAYES et al, 1992; DUKE et al, 1998; FINOTTI et al, 2001; PETROBRAS, 2021). Due to its higher molecular weight, in case of spillage into the environment, diesel oil adsorbs more to soil particles and percolates less quickly than gasoline. (HAYES et al, 1992; DUKE et al, 1998; FINOTTI et al, 2001; PETROBRAS, 2021). Due to its higher molecular weight, in case of spillage into the environment, diesel oil adsorbs more to soil particles and percolates less quickly than gasoline. (HAYES et al, 1992; DUKE et al, 1998; FINOTTI et al, 2001; PETROBRAS, 2021).

The oil spill (crude oil) that reached the most extensive area of mangroves in Brazil, until the period of this research, was identified in August 2019, and reached 11 states in the Northeast and Southeast regions, along 4,334 km of the coastal zone. In addition to mangroves, estuaries, beaches, lagoons and coral reefs were affected, causing the loss of ecosystem goods and services that are essential for environmental balance and the survival, economy and health of municipalities and traditional communities. This accident highlighted both the vulnerability of social groups that live off artisanal fishing, as well as the need for sanitary and health policies for these communities (PENA et al 2020).In 2020, the Ministry of Agriculture, Livestock and Supply reported that the health of 360,000 artisanal fishermen in Northeast Brazil was threatened by the oil spill (MAPA apud PENA et al 2020).

Martins and Mochel (2021) emphasize the importance of well-implemented and implemented coastal management to mitigate the socio-environmental impacts in the Coastal Zone, as it enables several sustainable actions. However, not all Brazilian coastal states have their State Coastal Management Plan (PEGC) or Municipal Plan (PMGC) as listed in the instruments of the National Plan (PNGC,). This fact makes it difficult to implement plans and programs, further aggravating environmental impacts, especially when there are disasters, such as oil spills in areas previously impacted by deforestation, erosion, disorderly occupation, among others. PROCOSTA (2018), established by Ordinance No. 76/08.

CONCLUSION

In the coastal zone, the system of loading, unloading, refining and transporting oil and derivatives shares with mangroves the establishment in sheltered estuarine areas, with low hydrodynamic energy, making them the most vulnerable ecosystem to the risks of oil spills in Brazil. Although crude oil spills cause severe damage to mangroves, other coastal ecosystems and the human population, they are much less frequent than diesel and fuel oil spills. Diesel oil, due to its ecotoxicity and being the main oil used daily, is underestimated both in the media (small unreported spots) and in studies of a socio-environmental nature. Due to its frequent presence in estuarine and mangrove areas, we point out, in this work, the importance of diesel oil as a compound of interest for conducting research on its effects on the various structural and functional compartments of the mangrove ecosystem. These studies may contribute to the knowledge of the ecophysiology and ecotoxicology of mangroves, to promote actions for their ecological recovery, as well as improvements in public policy procedures and management of the Brazilian coastal zone.

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