STACIOL APDIA

Chemical Science

OIL SPILLS: THREAT TO MARINE LIFE

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ABSTRACT Millions of people as well as flora and fauna are getting affected by the above calamities all over the world. In the recent times there seems to be a quantitative increase in the frequency of natural diasters. In this context need of the hour is to foster proper disaster mangement strategies. Disaster management (or emergency management) is the creation of plans through which communities reduce vulnerability to hazards and cope with disasters. Disaster management does not avert or eliminate the threats; instead, it focuses on creating plans to decrease the effect of disasters. Among the various natural disasters, the one man made disaster which is posing the utmost threat to aquatic marine life is oil spills. The consequences of spills adversely affect harbours, beaches, wild life, fisheries, tourism and society. An oil spill is the release of liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity and is a form of pollution. This term is usually applied for marine oil spills, where oil is dispersed into the oceans or coastal water accidently. Dispersants are the chemicals that break up the oil. They act like soap, breaking the oil up into tiny droplets. These droplets are then eaten up by the bacteria present in the sea. So, chemical dispersants can be used to break down the oil and speed up its natural biodegradation. However, many dispersants are toxic chemicals themselves, and are used sparingly. Dispersants should not be used as it can affect marine organisms.

KEYWORDS : Disaster management, oil spill, environmental impacts, Dispersants, toxicity.

1.INTRODUCTION:

World is undergoing through severe environmental crisis. The population is on ever increasing trend exerting tremendous pressure on our natural resources .Today the incidents of landslides, soil erosion, oil spills are getting more frequent than what it used to be earlier. Millions of people as well as flora and fauna are getting affected by the above calamities all over the world. In the recent times, there seems to be a quantitative increase in the frequency of natural diasters. In this context need of the hour is to foster proper disaster mangement strategies. Disaster management (or emergency management) is the creation of plans through which communities reduce vulnerability to hazards and cope with disasters. Disaster management does not avert or eliminate the threats; instead, it focuses on creating plans to decrease the effect of disasters.

The natural disaster mitigation or management in order to be effective, has primarily two major dimensions. First, most importantly, what kind of relief measures are put in place to assist those who have been seroisly affected and secondly what measures do we take as could be expected to reduce the rigours of disaster. Among the various natural disasters, the one man made disaster which is posing the utmost threat to aquatic marine life is oil spills.

Spilled oil poses serious threats to environment. Its after effects can seriously create problem that can damage the mere existence of all the living beings. Impact of this spill can be so severe that if prventive measures are not implemented at the right time, damage can be irreparable. Any oil spills, onshore or offshore needs to be analyzed seriously.Spill in any form; be it from Oil or hazardous substances is one of the major threats for the marine environment.

The consequences of spills adversely affect harbours, beaches, wild life, fisheries, tourism and society. Oil spill control is still neophyte topic among various disaster management programs worldwide. When you fully understand the situation, it is worse than you think. If you drill, there's going to be a spill. Thus we need to create Oil Spill awareness and persistence efforts in preventing, minimizing, and effective recovery and clean-up operations through various mediums. In this chapter, we would try to focus on the variuos aspects of oil spills ranging from the chemical compstion to deep envrionmental impacts and clean up methods keeping in mind the toxicity of commercial cleaning agents.

LARGEST OIL SPILLS

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The most notorious oil spill in history was the Exxon Valdez catasrophe in 1989. This disastrous oil spill released 11 million gallons(more than 41 millio liters) of crude oil into the Prince William Sound in Alaska, and largely served as a wake- up call to the detrimental effects of oil spills on the ecosystem. Crude oil and refined fuel spills from tanker ships accidents have damaged vulnerable ecosystems in Alaska, the gulf of mexico, the galapagos Islands,

France, the Sunarbans, Ogoniland and many other places. The quantity of oil spilled during accidents has ranged from a few hundred tons to several hundred thousand tons (e.g. Deepwater HorizonOil Spill, Atlantic Empress, Amoco Cadiz) but volume is a limited barometer of damage or impact. Smaller spills have already proven to have a great impact on ecosystems such as the Exxon Valdezoil spill because of the remoteness of the site or the difficulty of an emergency environmental response.

One of the biggest oil spills seen in history happened during Gulf war when approximate 240 to 336 gallons of crude oil flowed into the Persian Gulf. It was considered one of the worst disasters, beating the Ixtoc 1 oil spill in Mexico.

Amy Merten, an environmental scientist at the U.S. National Oceanic and Atmospheric Administration (NOAA), said the study gives information on a worst-case scenario that should be considered in trade-off decisions. This includes choosing whether to disperse oil into the water and risk harming coral versus getting the oil slick off the surface of the water "so birds, mangroves, and nesting turtles aren't as affected," she said.

Oil spills at sea are generally much more damaging than those on land, since they can spread for hundreds of nautical miles in a thin oil slick which can cover beaches with a thin coating of oil. These can kill seabirds, mammals, shellfish and other organisms they coat. Oil spills on land are more readily containable if a makeshift earth dam can be rapidly bulldozed around the spill site before most of the oil escapes, and land animals can avoid the oil more easily.

An oil spill represents an immediate fire hazard. The Kuwaiti oil fires produced air pollution that caused respiratory distress. The Deepwater Horizonexplosion killed eleven oil rig workers. The fire resulting from the Lac-Megan tic derailment killed 47 and destroyed half of the town's centre.

Spilled oil can also contaminate drinking water supplies. For example, in 2013 two different oil spills contaminated water supplies for 300,000 in Miry, Malaysia; 80,000 people in Coca, Ecuador,. In 2000, springs were contaminated by an oil spill in Clark County, Kentucky.

Contamination can have an economic impact on tourism and marine resource extraction industries. For example, the *Deepwater Horizon* oil spill impacted beach tourism and fishing along the Gulf Coast, and the responsible parties were required to compensate economic victims. An oil spill represents an immediate fire hazard. The Kuwaiti oil fires produced air pollution that caused respiratory distress. The Deepwater Horizonexplosion killed eleven oil rig workers. The fire resulting from the Lac-Mégantic derailment killed 47 and destroyed half of the town's centre.

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INDIAN PERSPECTIVE

Mumbai oil spill

Two cargo ships collided off the Mumbai coast on August 7 2010 causing an oil spill that spread quickly through Maharashtra's coastline. MSC Chitra ruptured its tank when it hit incoming MV Khalijia and ran aground at Colaba, near Prongs Reef Lighthouse. The vessel contained about 1,200 tonnes of fuel oil in its tanks of which 800 tonnes spilled into the Arabian Sea before the leaks could be plugged two days later. In scale, the spill was much smaller than the one in the Gulf of Mexico in April. But it proved a major threat to the marine ecology of the area and the coast.

Chennai oil spill

On 28 January 2017, two cargo ships collided off the Ennor coast in Chennai causing oil to spill into the sea. The spill has been polluting Chennai's beaches too. Due to wave action and the southern current, the spill spread some 34 km till Vettuvankeni in the south, making patterns in the sand. At least a thousand volunteers have been removing the sludge. In its report on the health impact of oil spill, the fact-finding team said that it found a number of workers and residents complaining of various health issues, including skin, eye and throat irritation, tightness in the chest, cough, headaches, nausea and vomiting. The most commonly occurring chemicals in the oil include Benzene, Toluene and Xylene (BTX). BTX are carcinogenic in humans, toluene can cause kidney and liver damage, and exposure to Xylene can lead to visual blurring, tremors, heart beat irregularities, paralysis.



*Source : https://scroll.in

2. Chemical composition of oil spills

An oil spill is the release of liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity and is a form of pollution. This term is usually applied for marine oil spills, where oil is dispersed into the oceans or coastal water accidently. Oil and water being immiscible, and oil is lighter than water as a result, lighter oil particles rises to the surface and spread over it. On determination of the source of the spill, the optimal methods for cleanup and safety issues are recommended by the chemists. This is based on the unique properties of oil released because crude oil is majorly a mixture of hydrocarbons. Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, nonvolatile compounds. The hydrocarbon structures found in oil include saturates, aromatics, and polar compounds that include resins and asphaltenes. The resins and asphaltenes are largely recalcitrant in the environment. They evaporate, dissolve, and degrade poorly and thus may accumulate as residues after a spill. The percentage of the saturates and aromatics-herein called the light components, in comparison to the heavy, residue-forming resins and asphaltenes-varies with oil type

3. Crude Oil Properties

(a) Composition

Petroleum hydrocarbons are composed of either aromatic compounds or alkanes. Aromatics are based on a six carbon ring and tend to be the molecular compounds in oil that are most toxic to marine life. For example, Polycyclic aromatic hydrocarbon (PAH's) having multiple carbon rings which are quite persistent in the environment. On the other hand, alkanes are comparatively less toxic and are more readily biodegradable. Most of them can be ingested as food by few microorganisms. In this context, the oil spill from 2010 Deepwater Horizon can be cited which was relatively high in alkanes and low in PAH's. Though, like all crude oils, it contained very toxic and carcinogenic benzene toluene and xylene.

It is to be noted that crude oil does not have a clear chemical formula due to the complexity of its makeup, though most oils are composed of hydrocarbons i.e. hydrogen and carbon and the quantity of these two are determined on the basis of make up of that particular oil.

(b) The flash point

The flash point of oil is the temperature at which the liquid produces vapors sufficient for ignition by an open flame. A liquid is considered to be flammable if its flash point is less than 60°C. There is a broad range of flash points for oils and petroleum products, many of which are considered flammable, especially when freshly spilled. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils and diluted bitumen have an abundance of volatile components and may be flammable for a day or longer after being spilled, depending on the rate at which highly volatile components are lost by evaporation. On the other hand, undiluted bitumen and heavy crude oils typically are not flammable.

(c)Adhesion

The adhesion or "stickiness" of some crude oils has been noted as a problem at several spills. The adhesion of a crude oil to the surfaces of rocks, built surfaces, and vegetation can greatly impede cleanup. Although important in the context of oil spill response, adhesion is a property that is not measured during industry-standard analyses of crude oils. However, a quantitative measure of adhesion has been developed. The test measures the mass of oil, or of weathered oil, that will adhere to a steel needle that has been immersed in the sample for 30 min and then allowed to drain for a while.

Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, nonvolatile compounds. The hydrocarbon structures found in oil include saturates, aromatics, and polar compounds that include resins and asphaltenes. The resins and asphaltenes are largely recalcitrant in the environment. They evaporate, dissolve, and degrade poorly and thus may accumulate as residues after a spill. The percentage of the saturates and aromatics—herein called the light components, in comparison to the heavy, residue-forming resins and asphaltenes—varies with oil type.

4.Effects of oil spills

In general, spilled oil can affect animals and plants in two ways:

(a)Direct from the oil (b) from the cleanup process. There is no clear relationship between the amount of oil in the aquatic environment and the likely impact on biodiversity. Sometimes, a smaller spill at wrong reason or time may prove hazardous than a large spill in same environment.

1. Environmental Impacts:

One of the most major effects of oil spill is on the aquatic flora and fauna. The animal life living in or on the shore is adversely affected by spill. Oil can kill corals by directly enveloping and suffocating them. Oil simply chokes the animal to death. The oil penetrates in the fur and plumage of animals reducing its insulating ability and making them more vulnerable and exposed to temperature fluctuations and less buoyancy. So birds and mammals find it difficult to float in water and regulate their body temperature.

Due to blockage of detection of body's scent, parents find it difficult to trace their babies leading to their starving death. When a bird tries to preen themselves to get rid of oil, they accidently swallow the oil and dies due to toxic effects, irritating the digestive tract, altering liver function and causing kidney damage. Dolphins, fishes, sea offers, countless species of birds and many oceanic animals face these consequences. Some birds exposed to petroleum also experiences hormonal imbalances like changes in luteinizing protein. Oil can also blind an animal leaving it defenceless. Animals can be poisoned and may die from oil entering the lungs or liver.

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*Source: https://energyinfrapost.com

A dead turtle washes up on the shore in Chennai. The oil slick floating along

2. Effect on Economy:

The second important effect of an oil spill is seen on economy. Due to loss of considerable amount of precious crude oil or refined petroleum, the amount of petroleum and gas available for use is seriously affected leading to import of more barrels of oil. Then, cleaning of oil spill requires lot of finances, although the company responsible for spill to clean it up, but still there is a lot of government help required of this stage both financially and loyally.

Workers employed in cleaning may face serious health hazards. Their medical and treatment becomes responsibility of government. Putting all recovery methods into place and monitoring them involves all resources from other work and thus hits the economy in subtle yet powerful ways.

3. Effect on tourism industry:

Due to toxic effects of an oil spill, the local tourism industry faces a huge setback as most of the tourists stay away from such places. Dead birds, sticky oil, foul smell, huge tarball creates a scene of dislike. It results in discontinuation of activities like sailing, swimming, rafting, fishing, parachute gliding. Industries that rely on sea water like marine resource extraction industries have to halt their operations till oil clean up.

Long term impacts of oil spills and their effects is yet to be fully observed and understood, so that a solid plan for such disaster management can be chalked out in case of emergency. In addition to threat to marine life, other serious threats like increased pollution, contamination of industrial chemicals and exploitation of resources are also to be taken into deep concerns.



*Source: https://www.smithsonianmag.com

5. Cleaning up of an oil spill

There are three main ways in which the cleanup is done:

(I) Burning:

If the oil is thick and concentrated, it can be burned off in low wind but this cause serious atmosphere pollution releasing carbon dioxide; soot particles and unburnt oil into the air. Therefore, this method of cleaning up discouraged

(ii) Skimming

In this method, long buoyant booms, which are large solid or inflatable, plastic tyre tubes are put in the see to surround the spill. The booms rise about 3 feet/1 meter above water level.

This arrests the spread of oil due to water currents and is attacked to a skirt which is hanged under water. They are brought closer and closer to concentrate the oil. From the surface, skimmers suck or scoop the oil into containment tanks or collecting ships. However, this method also does not work if the oil is very light and spread over a large area like the Gulf spill. Also under the condition of high winds or on high seas it

becomes difficult to use booms and skimmers because skimming requires calm waters at all times during the process.

(iii) Dispersion methods

One of the most important techniques for cleaning an oil spill is to use chemical dispersants to break down the oil.

Dispersants are the chemicals that break up the oil. They act like soap, breaking the oil up into tiny droplets. These droplets are then eaten up by the bacteria present in the sea. So, chemical dispersants can be used to break down the oil and speed up its natural biodegradation. However, many dispersants are toxic chemicals themselves, and are used sparingly. Dispersants should not be used as it can affect marine organisms because marine life serving as sea food can absorb toxic chemicals and broken down oil which can then enter into the food chain. Some of the commercial dispersants available are Slickgone, Petrotech, Inipol, Biorierco, Emulgal and Dispolen. There are now regulations the world that requires using environmental friendly dispersants.

Dispersants break the slick into oil droplets so that it becomes easier for oil and water to mix, as a result, the slick gets absorbed into aquatic system.

(iv) Add biological agents to the spill

Biodegradation can be achieved by bacteria and other micro bio organisms which breaks down the oil into harmless substances like fatty acids and carbon dioxide. By adding fertilizing nutrients like nitrogen and phosphorous, growth of micro organisms can be encouraged which can fasten the process of bio degradation. But this natural process of biodegradation can take months. On the other hand, chemical dispersants work immediately that's why people use them but its not a solution as the oil won't be visible but it will remain in the water.

(v) Let the oil break down naturally

If there is no possibility that the oil will pollute coastal regions or marine life, the oil could be left to disperse naturally. The sun, wind, currents or waves can disperse and evaporate most oils, though light oils can disperse quicker than heavy oils.

(vi) Dredging

This process is used for oils dispersed with detergents and other denser than water such as bacteria Alcaniovorax, Methylocelle Silvestris.

(vii) Vacuum and centrifuge

Oil can be sucked up along with water and then using a centrifuge, oil and water can be separated. Usually, the water is returned to sea making the process more efficient but allowing small amount of oil to go back as well. This issue has hampered the use of centrifuges due to United states regulation limiting the amount of oil in water returned to the sea.

(viii) Beach Raking

This process involves picking up of coagulated oil that is left on beach using machinery like shovels and other road equipments.

6. How Oil spill cleaning agents work?

There are four different types of oil spill cleaning agents namely dispersants, surface washing agents, bioremediation agents and solidifiers. All of these help in oil spill cleaning in different ways:

(a) Dispersants

Dispersants are most helpful in fastening the process of degrading the oil in to naturally occurring substances. They can be applied directly to spitted oil, and helps to remove oil from the water surface. It works by first breaking the surface oil. Dispersants are molecules contain lipophilic polar heads and hydrophilic hydrocarbon tail, therefore the molecules gets attacked to the oil, thus reducing interfacial tension between the oil- water interface which breaks the oil slicks. After breaking the slick, it disperses oil as fine droplets into the water column through natural mixing actions like wave action or turbulence which dilutes the sub surface oil concentration. This disperse oil from water surface to natural process of bio degradation.

(b) Surface Washing agents

It involves the process of emulsification. These agents are mostly

applicable for use in all types of oil. They work on the basis of two principles.

(i)Lift and Disperse method: where oil is dispersed, emulsified and encapsulated.

(ii)Life and float method: where oil floats readily on water and is recoverable. After application of surface washing agents, the wash water from the products should be flushed into contained water bodies, recovered and properly treated. They also help in separating oil from large volume of water.

(c) Bio remediation agents

uses micro organisms to convert hydrocarbons of oil into lighter compounds like water and carbon dioxide by process called mineralization in which all organic carbons are transformed into mineral carbons. These agents include fertilizers which promotes action of naturally occurring micro flora (probiotics) to aid in breaking down the oil and bacterial consortiums which inoculates the environment to be treated breaking down oil spill into harmless substances.

(d) Solidifiers

They help in cleaning up oil spills by bringing change in physical state of spilled oil from liquid to semi-solid. Solidifiers are composed of tiny floating dry ice pellets and hydrophobic polymers which can both adsorb and absorb. When sprayed on the shore or sea surface, solidifiers form a physical bond with the oil increasing its viscosity, solidifying the oil into rubber like solid which accelerates easy removal of oil. Solidifiers are basically polymers which gets attracted to oil due to Vander Wall forces. Solidifiers are insoluble in water therefore removal of solidifier are soluble in excess solvent, continues application of solidifiers will increase the viscosity of the oil.

In today's scenario, petrochemicals are of utmost importance in all spheres of manufacturing units ranging from lubricants, adhesives, agro chemicals to food additives, packaging and pharmaceutical products. In order to synthesise different petro chemicals; crude oil is subjected to recombination and alteration. Refining of crude oil to produce fuel oils like gasoline or diesel does not alter the molecular composition of oil. Components of petroleum are separated by fractional distillation method. It includes both naturally occurring unprocessed crude oil and petroleum products made from refined crude oil.

Bioremediation Accelerator:

Oleophilic, hydrophobic chemical, containing no bacteria, which chemically and physically bonds to both soluble and insoluble hydrocarbons. The bioremediation accelerator acts as a herding agent in water and on the surface, floating molecules to the surface of the water, including soluble such as phenols and BTEX, forming gel-like agglomerations. Undetectable levels of hydrocarbons can be obtained in produced water and manageable water columns. By over spraying sheen with bioremediation accelerator, sheen is eliminated within minutes. Whether applied on land or on water, the nutrient-rich emulsion creates a bloom of local, indigenous, pre-existing, hydrocarbon-consuming bacteria. Those specific bacteria break down the hydrocarbons into water and carbon dioxide, with EPA tests showing 98% of alkanes biodegraded in 28 days; and aromatics being biodegraded 200 times faster than in nature they also sometimes use the hydro fire boom to clean the oil up by taking it away from most of the oil and burning it.

7. Environmental Sensitivity Index

Environmental Sensitivity Index (ESI) maps are used to identify sensitive shoreline resources prior to an oil spill event in order to set priorities for protection and plan cleanup strategies. By planning spill response ahead of time, the impact on the environment can be minimized or prevented. Environmental sensitivity index maps are basically made up of information within the following three categories: shoreline type, and biological and human-use resources.

Shoreline type

Shoreline type is classified by rank depending on how easy the target site would be to clean up, how long the oil would persist, and how sensitive the shoreline is. The floating oil slicks put the shoreline at particular risk when they eventually come ashore, covering the substrate with oil. The differing substrates between shoreline types vary in their response to oiling, and influence the type of cleanup that will be required to effectively decontaminate the shoreline. In 1995, the US National Oceanic and Atmospheric Administration extended ESI maps to lakes, rivers, and estuary shoreline types. The exposure the shoreline has to wave energy and tides, substrate type, and slope of the shoreline are also taken into account—in addition to biological productivity and sensitivity. The productivity of the shoreline habitat is also taken into account when determining ESI ranking. Mangroves and marshes tend to have higher ESI rankings due to the potentially long-lasting and damaging effects of both the oil contamination and cleanup actions. Impermeable and exposed surfaces with high wave action are ranked lower due to the reflecting waves keeping oil from coming onshore, and the speed at which natural processes will remove the oil.

Biological resources

Habitats of plants and animals that may be at risk from oil spills are referred to as "elements" and are divided by functional group. Further classification divides each element into species groups with similar life histories and behaviors relative to their vulnerability to oil spills. There are eight element groups: Birds, Reptiles, Amphibians, Fish, Invertebrates, Habitats and Plants, Wetlands, and Marine Mammals and Terrestrial Mammals. Element groups are further divided into sub-groups, for example, the 'marine mammals' element group is divided into dolphins,manatees, pinnipeds (seals,sealions&walruses), polarbears, seaotters and whales Problems taken into consideration when ranking biological resources include the observance of a large number of individuals in a small area, whether special life stages occur ashore (nesting or molting), and whether there are species present that are threatened, endangered or rare.

Human-use resources

Human use resources are divided into four major classifications; archaeological importance or cultural resource site, high-use recreational areas or shoreline access points, important protected management areas, or resource origins. Some examples include airports, diving sites, popular beach sites, marinas, natural reserves or marine sanctuaries.

8. Estimating the volume of a spill

By observing the thickness of the film of oil and its appearance on the surface of the water, it is possible to estimate the quantity of oil spilled. If the surface area of the spill is also known, the total volume of the oil can be calculated.

Oil spill model systems are used by industry and government to assist in planning and emergency decision making. Of critical importance for the skill of the oil spill model prediction is the adequate description of the wind and current fields. There is a worldwide oil spill modelling (WOSM) program. Tracking the scope of an oil spill may also involve verifying that hydrocarbons collected during an ongoing spill are derived from the active spill or some other source. This can involve sophisticated analytical chemistry focused on finger printing an oil source based on the complex mixture of substances present. Largely, these will be various hydrocarbons, among the most useful being poly aromatic hydrocarbons. In addition, both oxygen and nitrogen heterocyclic hydrocarbons, such as parent and alkyl homologues of carbazole, quinoline, and pyridine, are present in many crude oils. As a result, these compounds have great potential to supplement the existing suite of hydrocarbons targets to fine-tune source tracking of petroleum spills. Such analysis can also be used to follow weathering and degradation of crude spills.

9. Prevention:

- Secondary containment- methods to prevent releases of oil or hydrocarbons into environment.
- Oil Spill Prevention Containment and Countermeasures (SPCC) program by the United States Environmental Protection Agency.
- Double-hulling build double hulls into vessels, which reduces the risk and severity of a spill in case of a collision or grounding. Existing single-hull vessels can also be rebuilt to have a double hull.
- · Thick-hulled railroad transport tanks.
- Spill response procedures should include elements such as;
- A listing of appropriate protective clothing, safety equipment, and cleanup materials required for spill cleanup (gloves, respirators, etc.) and an explanation of their proper use;
- Appropriate evacuation zones and procedures;

- Availability of fire suppression equipment;
- Disposal containers for spill cleanup materials; and
- . The first aid procedures that might be required.

10. CONCLUSION:

Marine oil spills have a severe effect on marine life as well as the economic coastal activities and the communities that exploit the resources at sea.. Generally the effects of toxicity of oil depends on number of factors like composition and characteristics(physical and chemical).Oil spills can have disastrous consequences for society; economically, environmentally, and socially. As a result, oil spill accidents have initiated intense media attention and political uproar, bringing many together in a political struggle concerning government response to oil spills and what actions can best prevent them from happening. One must understand that oil spill is not the only threat that marine life faces. Increasing pollution, contamination of industrial chemicals, exploitation of the resources they provide are also some of the serious threats.

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