Chapter

Possible Oil Spills Disposal for Environmental Water-Body Protection

Veronika Veľková, Helena Hybská and Tatiana Bubeníková

Abstract

The possibilities of the oil spill cleanup from the water environment are presented. Mechanical methods of oil recovery are described—the oil containment booms, oil skimmers, and use of sorbents. The sorption capacity of various sorbents is compared based on laboratory tests according to the ASTM F726 methodology. The results of the determination of residual oil pollution of water after the cleaning process are presented. The properties of the absorption sock during the sorption of crude oil and the oil/water mixture were also presented.

Keywords: oil spill, oil contamination, sorbents, absorbent sock, sorption capacity

1. Introduction

Water and soil represent important components of the environment, which are strongly affected by contamination with foreign substances. Oil and oil products are important contaminants. Oil substances get into water and soil in various ways, either during the normal use and processing of oil or during accidental spill. Oil contamination is known mainly "thanks" to large-scale oil spills in oil tanker accidents (Exxon Valdez Accident in 1987) or oil platforms (Deepwater Horizon Blowout in 2010), where after the release of several million tons of oil, large and long-term damage to the environment occurred at sea and on the coast, such as also to damage the economy in the given areas [1–3]. There are some of the greatest oil spills in the history in the **Table 1**. The greatest accidental oil spill occurred in the 2010 after blow out at the BP's oil rig Deepwater Horizon. More than 200 million gallons of oil spilled into the Gulf of Mexico, which meant enormous damage to the aquatic ecosystems, the coastal ecosystems, the life of aquatic and terrestrial organisms, and the life of the entire society in Louisiana. The fishing in the Gulf was damaged, the food industry collapsed, and also the tourism industry completely fell. The economic and social life of Louisiana was so destroyed, and the solution to the accident required such interventions that a special web page was set up to inform people [6, 7].

Despite the fact that the number of such large oil spills is decreasing as a result of the increase in safety during the transportation of oil and oil products, the improvement of technological processes, emergency situations, and gradual releases of oil

Incident	Location	Date	Oil amount
Iraq-Kuwait war	Persian Gulf	January 1991	380–520 mil. Gallons
BP Deepwater Horizon accident	Gulf of Mexico	April 22, 2010	206 mil. Gallons
Ixtoc I accident	Bay of Campeche off Ciudad del Carmen	June 3, 1979	140 mil. Gallons
Atlantic Empress accident	The seaside of Trinidad and Tobago	July 19, 1979	90 mil gallons
Castillo de Bellver accident	Saldanha Bay South Africa	August 6, 1983	79 mil. Gallons
ABT Summer accident	Off the coast of Angola	May 28, 1991	79 mil. Gallons
Amoco Cadiz accident	Portsall, France	March 16, 1978	69 mil. Gallons

Table 1.
The greatest oil spills in the history [4, 5].

substances into the environment occur continuously, so there is always room for the development of methods and techniques for removal of oil contamination [1]. Depending on the amount of leaked substances (the size of the oil spill), the environmental conditions (type of water source—calm or flowing water), and technical possibilities, the main cleaning procedures include oil booms, separators, and separators (skimmers), various types of sorbents, in-situ burning, chemical cleaning (dispersion of petroleum substances), and bioremediation [2].

2. Effects of oil spills to the water environment

Oil and petroleum substances represent the basic raw material for the needs of industry, and their impact on all components of the environment is not negligible [8]. The consequences of environmental pollution with oil substances can appear immediately or after a longer period of time.

An oil spill usually affects the entire affected region, destroys the aquatic environment and life in it, and if it reaches the coast, great damage appears there as well (**Figure 1**).

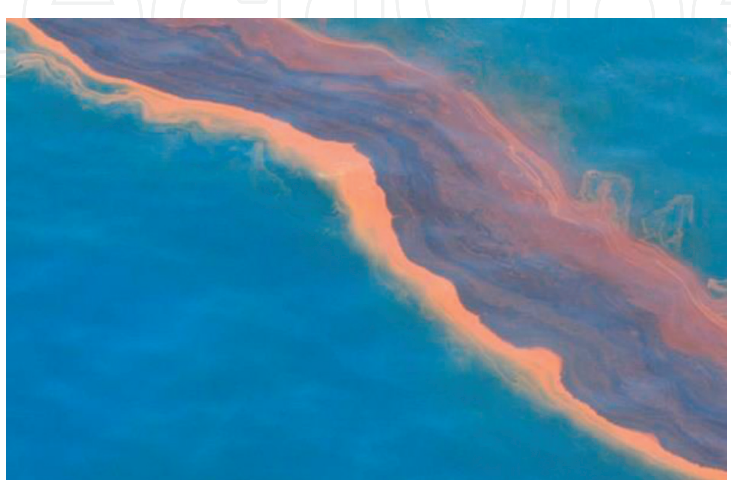

Figure 1.
Deepwater Horizon oil spill on May 12, 2010 [9].

Figure 2.
Oiled bird (© Guardian Unlimited) and oiled seal (© Tom Loughlin, NOAA) [10].

Oil spills directly or indirectly kill fish and aquatic organisms, birds, plants, affect the oxygen regime, disrupt the natural cycle of ecosystems, and change the physical and chemical properties of the aquatic environment (**Figure 2**).

2.1 Mechanism of oil spill pollution in water bodies

When oil leaks into an open water body, it forms a thin layer on the water surface. In the case of strong winds and strong currents, the oil layer can quickly cover a relatively large area. For example, 1 ton of oil can cover an area of up to 12 km^2 with a 1 mm thick layer [11]. The created layer is affected by various factors such as wind, waves, water currents, UV light, the presence of various types of microorganisms, and the oil weathering process occurs [11–13]. Weathering is a process in which leaked oil is gradually lost from the formatted spill depending on the current environmental conditions. The weathering process can be understood as a combination of various physical and chemical changes such as evaporation, dispersion, emulsification, sedimentation, oil entrainment to the water column, biodegradation [11–13]. The study in the year 1992 in the Exxon Valdez accident area shows that 20% of oil evaporated, 50% biodegraded, 14% was cleaned up, 13% remained in subtidal sediments, 2% remained on shorelines, and less than 1% remained in the water. [1, 14].

The speed of the weathering process significantly depends on the strength and cohesion of the oil film on the surface. Yan et al. [12] studied the forces affecting the entrainment ability of petroleum substances into the water column. According to them, the difference between the surface tension of water and oil and the viscosity of oil are decisive. Waves on the water surface act on the oil layer, which "break" it. A single strong wave can work, but weaker repeated waves are also effective. A "sandwiching" of water and oil occurs, the oil film becomes thinner until it disintegrates [12, 13].

Oil pollution of seawater also affects the formation and properties of marine snow [15]. After the Deepwater Horizon accident (2010), a high formation of marine snow was observed in the Gulf of Mexico. Passow et al. [15] assume three possible ways of formation of marine snow: increased production of mucous webs by oil-degrading bacteria combined with floating oil particles on the surface; coagulation of oil particles produced by the interaction of oil with sedimenting particles; coagulation of phytoplankton with oil droplets into larger aggregates. They also pointed out that oil significantly affects the sinking and breaking up of marine snow, while environmental conditions also interact. Snow in the natural environment of the Gulf of Mexico, composed mostly of oil particles and low-density mucus, disappeared in about a month after its appearance, while under laboratory storage conditions in the dark and at about 4°C, it remained on the surface for up to 2 years [15].

2.2 Oil substances in the water environment

The change in physical and chemical properties is significantly influenced by free oil substances that create an oil film on the surface, which reduces the transfer of oxygen to the water. Another process in which oxygen is pumped out of the water is the ongoing microbial oxidation of oil pollution. The result of both processes is a change in the concentration of dissolved oxygen, which causes a change in the course of chemical reactions in the process of photosynthesis, which is very unfavorable for the life of aquatic organisms, algae and other plankton are strongly affected [16].

Chemical composition of oil is very variable, present are straight and branched alkanes, alkenes, aromatic compounds, oxygen, and sulfur compounds and in small amount also nitrogen compounds and some metals. Polycyclic aromatic hydrocarbons have a significant presence, which have toxic, carcinogenic, and mutagenic effects. The easier ones remain in the oil film on the surface or are dispersed in the water column, the more difficult to settle in the sediments, and represent long-term hidden dangers. It is important to know the localization and persistence of these substances in nature [16, 17]. When analyzing the composition, it is possible to focus on some specific substances or to monitor the entire group according to normative methods, for example, PAHs or nonpolar extractable substances (NES) [16].

The acceptable concentration limit of these compounds can be determined using bioassays on appropriately selected sensitive organisms. Ecotoxicological studies have shown the impact of harmful effects of chemical substances on living organisms [18] and are one of the main tools suitable for assessing the effects of specific chemical compounds on environmental components. For acute and chronic toxicity tests, test organisms such as fish, daphnia, rats, birds, and seeds are suitable choices [19]. Due to their low price and good sensitivity (germination), the seeds of suitable plants are important toxicological tests for assessing the effects of toxic substances or organic inhibitors [20]. Tamada [21] monitored biodegradability by respirometric tests and compared different levels of toxicity of lubricating oils using toxicological tests. Tests were performed using earthworms (*Eisenia andrei*), arugula seed (*Eruca sativa*), and lettuce seed (*Lactuca sativa*) in mineral, synthetic, and used lubricating oil for different periods of their biodegradation in soil. Toxicity tests were used to indirectly measure the biodegradation of pollutants. The used lubricating oil proved to be the most toxic. Mineral and synthetic oils were efficiently metabolized in the soil, although they were still toxic after 180 days [21]. In their work, Cecutti and Agius [22] present the results of a study in which they successfully applied test organisms such as algae, pearl oysters, and fish to assess the ecotoxicological properties of various oils, including bio-oils new—before use and used—after 1000 hours of use in the aquatic environment. Bordulina [23] report the results of laboratory experiments, where they studied the effect of different concentrations of oil in the water environment on the algae *Chlorella vulgaris* Beijer and the abalone *Daphnia magna* Straus in model samples. They found that as the concentration of the oil increased, the survival of the test organisms decreased. Martinez [24] found acute toxic damage to daphnia after a 48-hour test. Authors, Bordulina [23] and Hybská et al. [25], confirmed that as the concentration of oil in the water increases, the survival rate of abalone decreases. They found that at a concentration of 0.2 mg of oil/1 l of water, regardless of its origin (mineral and bio oil—sunflower oil), there was no difference in the number of immobilized individuals [24, 26].

3. Oil spills cleanup techniques

A series of procedures and methods can be used to stop oil spills and their subsequent removal from the environment. These are mechanical methods for stopping the spread and collection of contaminating substances, chemical methods for the purpose of dispersion and emulsification of oily substances, burning in-situ, and bioremediation using microorganisms. Mechanical containment with the subsequent recovery of oily substances is one of the most used procedures with relatively high efficiency both in the USA and in European countries [14, 27].

3.1 Oil containment booms

The main function of the oil spill containment boom is "to close" the oil spill and to prevent from further spreading and floating oil to larger surface. It helps protect coasts or precious ecosystems from contamination. An oil containment boom represents a physical barrier that will ensure the containment and concentration of floating oil contaminants to enable their collection. It is usually the first resource to be deployed and the last to be removed when solving an accident [1, 14].

Oil containment booms come in many shapes, sizes, and lengths from smaller and lighter designed for manual use to deal with smaller leaks to robust, huge ones designed for use on the open sea using ships and ship cranes (**Figures 3** and **4**). In general, they all consist of the following basic parts [14].

- freeboard floating above the water surface contains the oil and prevents from slash-over

Figure 3.
Use of the oil containment boom [28].

Figure 4.
The oil containment boom in a ship lock [14].

Figure 5.
Weir oil skimmer [30].

- subsurface skirt below the surface
- rope or chain to stabilize the boom

The effectiveness of containment booms is significantly determined by the movement of water on the stream and the surrounding conditions (currents, waves, wind). The boom should be flexible enough to resist water movement and retain so much oil as possible [3, 14].

3.2 Oil skimmers

The next step in cleanup process after containing of oil spill is recovery of oil substances as much as possible from the water environment. Oil skimmers are intended for collecting oil from the water surface. Oil skimmers are devices floating on the surface and collecting oil substances [14, 29]. They consist of two parts—the device that keeps the oil skimmer on the surface and the collecting part itself. Depending on the conditions, especially the roughness of the surrounding water, self-propelled

Figure 6.
Drum oil skimmer [31].

skimmers can be used, skimmers controlled from the shore or from the vessel. Based on the construction, we are talking about [29]:

- weir skimmers (**Figure 5**)—they remove oil from the water surface via a weir. The disadvantage is that they collect a relatively large amount of water at the same time, and they also collect water even when the oil is no longer present.
- drum or disc skimmers (**Figure 6**)—they collect oil from the surface on the principle of adhesion to metal or plastic disks or oleophilic belts or ropes.

The collected oil is usually stored in a containment tank or an additional temporary storage device is required. In some cases, it is necessary to heat the tanks in order to preserve the good ability of the collected oil to flow. The effectiveness of the oil recovery via a skimmer is determined by how quickly the skimmer can collect the oil and how well it minimizes the water–oil ratio [14]. The operation of skimmers can significantly limit the occurrence of floating foreign material on the surface, e.g., branches, leaves, algae, grass, waste.

3.3 Sorbents

Another method of oil and oil products recovery is represented by sorbents. Sorbents are used to clean smaller oil spills, for final removing of oil substances or in places where skimmers cannot be used. Sorbents are solid, in water-insoluble material, which can absorb gaseous or liquid substances due to their physical and chemical composition. They work through the adsorption or absorption mechanism. Adsorbents become coated with oil substances on the surface, in pores and capillaries, binding can be both physical and chemical in nature. In order to be effective in oil spills disposal, sorption materials must be partly oleophilic and at the same time water-repellent. Absorbents pick up and retain liquids distributed throughout its molecular structure, typically is the volume increasing [2, 14, 32].

Sorbent material can be divided in three basic groups: natural organic material, natural inorganic, and synthetic.

Natural organic sorbents are mostly carbon-based products, such as straw, sawdust, coconut fibers, peat moss, etc., which can be in granular or fibrous form. These materials can adsorb more three times their weight of oil. Some of organic sorbents tend to break down to smaller particles, and it could be complicated to collect it. Other organic materials could sink to the bottom due to water absorption [14, 32].

Natural inorganic sorbents are used as granular materials such as perlite, clay, sand, ash. They can adsorb more than four times their weight in oil. As with organic sorbents, these materials also can have collection problems due to the breakdown into smaller particles.

Synthetic sorbents are composed of man-made materials, especially plastics such as polyurethane, polypropylene, polyethylene modified to adsorb liquids like a sponge. Other synthetic sorbents include cross-linked polymers and rubber materials, which absorb liquids into its solid structure, causing the sorbent material to swell [14]. Synthetic sorbents can absorb up 40–50 times their own weight in oil [14, 33].

3.3.1 Oil sorbent sorption capability tests

The most significant property of all sorbents is their ability to bind several times the amount of contaminant relative to their own weight, the sorption capability. The sorption capacity of the sorbent mainly depends on the size of the surface area to which the dangerous substance, oil product can adhere as well as surface type (surface structure). The size of the surface of the sorbents and the increase in their sorption capacity are influenced by various cracks such as pores and capillaries. The average surface area of the sorbent is expressed in units of area (m^2) per unit mass (g, kg). Sorbents have a surface area most often about 1,000,000 $m^2\ kg^{-1}$ [33, 34]. The sorption capacity expresses how many times the sorbent binds more liquid to its weight or how many grams of contaminant bind 1 g of sorbent.

The American Society of Testing and Materials unified the methods of testing the sorption capacity of sorbents—ASTM F 726: Standard Test Method for Sorbent Performance of Adsorbents [35]. This test method describes laboratory tests that describe the “Short-term Oil-Absorption Test” and other non-emulsion floating, non-emulsion liquids from the water level. The comparison of sorption capability different sorbent material is given in **Table 2**.

3.3.2 Water contamination after cleanup process

No cleaning process can be 100%. Various studies document that after mechanical cleaning, 10–15% of oil substances remain in the water [14, 32]. We made an experiment, where the samples of surface water (1 liter) were contaminated with diesel fuel and engine oil in amount of 1 g, 5 g, and 10 g. The layer of petroleum substance was built on the bottom of water. The oil film was stronger after application of engine oil. On the oil substances was applicated sorbent (expanded perlite) in the way to cover entire bottom of water level, which treated on oil substance. Contaminated sorbent was removed after 3 (diesel fuel) or 10 min (engine oil), and the amount of NES was determined in the water samples. The results are in **Table 3**.

Comparing the determined amounts of NES in “cleaned” water samples with legislative limits, we can say that all samples are still contaminated. The highest amount of NES was determined in the sample contaminated with diesel fuel (contamination with 10 $g.L^{-1}$). Amount of NES was in all samples higher than 0.1 $mg.L^{-1}$, what according to research of Hybská et al. could lead to toxicological treat of aquatic organisms in the first step and cumulation of oil substances in other environment components [25].

Sorbent/sorbent form	*Oil kind*	*Oil sorption*	*Reference*
Expanded perlite/granulate	motor oil	Up to 3 x	[26]
Expanded perlite/granulate	diesel fuel	Up to 4.5 x	[26]
Expanded perlite/granulate	gasoline	To 3 x	[34]
Expanded perlite/granulate	diesel fuel	Up to 3 x	[34]
Cellulosic waste/fiber material	gasoline	1.2 to 1.3 x	[34]
Cellulosic waste/fiber material	diesel fuel	1.7 to 1.9 x	[34]
calcium carbonate and clay/granulate	motor oil	1.4 x	[33]
Diatomaceous earth (moler) granulated, calcined	motor oil	1.1 x	[33]
Polypropylene/fiber	motor oil	14 x	[33]
Leaves residues	motor oil	7.4 x	[33]
Peat moss	motor oil	Up to 6 x	[33]
Needles	motor oil	4.4 x	[33]
Saw dust	motor oil	Up to 3.3 x	[33]
Urethane-isocyanate-alcohol polymer/granulate	motor oil	34.4 x	[32]
Polypropylene/fiber web	crude oil	10 x	[32]
Exfoliated graphite	crude oil	80 x	[32]
Cellulose	crude oil	Up 20 x	[32]
CF3-functionalized silica aerogel	crude oil	Up to 237 x	[32]
Acetylated rice straw	motor oil	Up 20 x	[32]

Table 2.
Comparison of different sorbent materials.

Contaminant	*Sorbent*	*Added amount of contaminant ($g.L^{-1}$)*	*Amount of NES after contamination ($mg.L^{-1}$)*	*Amount of NES after clean up ($mg.L^{-1}$)*
Engine oil	Expanded perlite	1	795	0.474
		5	3.980	3.569
		10	9.152	19.77
Diesel fuel		1	680	17.55
		5	4.370	24.13
		10	8.525	25.84

Table 3.
Determined NES amount in the water samples before and after sorbent treatment [26].

3.3.3 Absorbent sock (absorbent snake)

The sorption sock, called also sorption snake (**Figure 7**), is a combination of the containment function (the oil) booms and function of the oil contamination collecting function (sorbents).

Figure 7.
The absorption sock (absorption snake) [36].

Figure 8.
The use of the absorption socks on solid surface (left) and on the water surface (right) [37].

The sorption snakes are intended for solving minor of oil spills—rivers and streams, lakes, ponds, etc., and also for use on solid surfaces (**Figure 8**). These are means intended for manual operations. Their primary function is to contain the oil spill so that the contamination does not spread to a larger area or to the shores similar to oil containment booms.

We can meet sorption socks in various designs—longer with a small diameter or on the contrary, a shorter larger diameter. The sorption snakes consist of two types of adsorbents. Adsorbent I forms the textile cover of the sorption sock, and adsorbent II represents the filling. Any loose sorbent can be used as a filler.

In our experiment, we tested the sorption capacity of the sorption sock according to the ASTM F 726 methodology. The cover was tested separately as adsorbent I and the filling as adsorbent II. Subsequently, the entire absorption snake was also tested. All materials were tested for the absorption of oil and water/oil mixtures. The results are shown in **Table 4**.

From the results, it seems at first sight that the sorption capacity of the absorbent sock as a whole is low on average. However, it is necessary to realize the primary role that the sorption sock fulfills—the containment of the oil spill. Oil recovery is an associated task.

It is also necessary to remember that neither the cover nor the filler is in contact with the contaminant in its entire volume. As can be seen in **Figure 9**, about half of the

Sorbent	*Sorption capacity g of oil/g of sorbent crude oil*	*Sorption capacity g of oil/g of sorbent oil + water mixture*
Textile (cover)	7.15 ± 0.47	6.50 ± 0.17
Granulate (filler)	4.6 ± 0.42	5.83 ± 0.30
Absorption sock	1.67 ± 0.13	1.06 ± 0.09

Table 4.
Results of sorption capacity test of absorption sock.

Figure 9.
The absorption sock after absorption of crude oil (left) and oil from the water/oil mixture(right).

sorption sock was soaked with oil. This can be considered as excellent results, which show that the use of an absorption sock for small oil spill disposal is a very suitable choice.

The combination of mechanical methods (oil containment booms, oil skimmer, or sorbents) of cleaning oil spills is one of the most used and also the most effective [2, 14]. Complications for the effective operation of booms, skimmers, and sorbents are adverse weather (strong wind and rain), strong waves and currents. These significantly affect oil spill behavior and also make difficult operations with the equipment. Commonly used booms operate at a maximum wave speed of 7 knots. At higher speeds, it is necessary to deploy special types of booms as well as special equipment [14]. Otherwise splash-over or sinking of the boom may occur. It is very important to choose the right type of containment boom for using, because the boom is the first deployed device on the site and the last one, which will be remoted. Depending on the current wind-, waves-, and currents conditions and the size of the oil spill, the type of sorbent to be used is also chosen. Particles that are too light can be blown into the open sea by strong winds, and on the contrary, particles that are too heavy could settle to the bottom together with bounded oil particles. Adverse conditions such as wind and waves, in addition to complicating the operations with the equipment, significantly increase the economic costs of oil spill cleaning. Despite these disadvantages, mechanical methods of oil spill cleanup are among the most widely used. Advantages include the possibility of recovery of captured oil, not introducing additional chemicals into the environment, the possibility of combination with biotechnological methods [2, 3, 14, 27, 38].

Alternatives to mechanical methods are in-situ burning, chemical dispersion, biological methods. In-situ burning is suitable for rapid burning of oil on the water surface in case of large spills. The disadvantage is the production of a huge amount of smoke containing toxic substances. These can spread over large areas in windy weather and affect light conditions and air quality in them. During chemical dispersion, surfactant substances are sprayed onto the oil layer, disrupting it, reducing the surface tension of water, which leads to emulsification and dispersion of oily substances throughout the water column. A major disadvantage of both mentioned methods is the secondary pollution in the vicinity of the accident, which contributes to the damage of natural aquatic and terrestrial ecosystems [14, 27, 38].

Against the background of these facts, mechanical methods of removing oil spills are considered highly effective and also advantageous from an environmental point of view [2, 14, 38]. Since it is not entirely possible to prevent oil spill accidents, the research and development of these methods is one of the challenges of many scientists. Improvement occurs mainly in the development of new or modified sorbents in order to increase their sorption capacity, the ability to recover oil, ease of handling. Cost reduction and environmental suitability are also important factors. Organic and synthetic materials are investigated (multi-layered graphene, chitosan, kenaf fiber, ZnO), waste material is used, surface treatment of the sorbent, creation of composite sorbents with the addition of nanoparticles, additive substances inducing the magnetic properties of the sorbent, etc. [2, 3, 14, 27, 39–43].

4. Conclusions

Oil is an important industrial commodity worldwide. Although there is a lot of talk about replacing it in the context of climate change, its use is unlikely to stop in the next few years. Its extraction, transport, and use are associated with leaks into the environment during accidents or during normal operation. Petroleum substances have a very harmful effect on the environment, affect the oxygen regime in water and soil, are toxic to aquatic organisms and animals as well as to humans.

The chapter deals with mechanical methods for oil spill removal. The first part briefly describes the interactions of oily substances in the water environment, the distribution of oil particles in water bodies, their harmful effects and ecotoxicity. The main part deals with the possibilities of cleaning oil spills using physical (mechanical) methods. The use of oil containment booms, oil skimmers, and sorbents in accidental oil spills solutions is explained and described.

Based on research, experiments, and studies, the effectiveness of several types of sorbents is compared. The determination of nonpolar hydrocarbons in water after cleanup process proved that these cleaning procedures must be combined with other methods, because the water does not meet the limit requirements for surface water. Although the removal of oil pollution was very effective, not a single water sample met the criteria for discharge into the recipient. The chapter also describes testing the sorption capacity of absorption sock, which can be used for smaller oil spills removal, because it is advantageous to combine two functions—containment of oil and recovery of oil compounds.

The advantages and disadvantages of individual cleanup methods are summarized too. Although development and progress in the use of new procedures, innovative technical equipment and devices, progressive materials, and cleanup process methods are still progressing, the best way for humanity and the environment is to prevent and avoid oil spills and at the same time be as well prepared as possible to deal with accidents.

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