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# **Removal Techniques of Oil from Marine and Soil Environments**

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## **Abstract**

Hydrocarbon components may cause soil and marine pollution. Oil pollution is a growing problem. It is estimated that a cubic meter of oil can pollute a million cubic meters of water.

This paper introduces factors affecting the removal of oil, spilled in marine and soil environments. The ecotoxicological examination of petroleum products is also presented. The effect of these products on the environment is described by four components: organisms, soil, water, and type of oil. Moreover, the formulation and the effect of emulsion on the removal of oil spills are presented.

In order to prevent or minimize environmental damage due to pollution by oil spill or soil pollution, special treatment techniques must be applied. The criteria of selection of treatment techniques depend on: sensitivity, practicability, time consumption and availability of the technique. In this paper a laboratory investigation of the application of different chemical solvents for the recovery of hydrocarbon components from the polluted soil is presented. The objective of this study is to optimize and to determine the suitable solvents for soil remediation. The results have identified a large variation in the efficiency of the applied solvents, depending on the solvents and the type of oil.

**Keywords:** Hydrocarbon, Oil Spills, Oil Removal, Contaminated Site, Soil Pollution, Oil Extraction, Environmental Protection.

## **Introduction**

Crude oil deposits have been formed probably from plant and animal remains deposited in marine sediments over long periods of geological time. Processes of bacterial decomposition followed by chemical change at high temperatures, and in the absence of oxygen, produced extremely complex mixtures that are found today. Crude oil contains a huge number of different chemical compounds. Precise description of the chemical composition of crude oil is not easily attainable because of the complexity of the crude oil, and the fact that oils from different regions and even from within a particular formation, differ greatly in composition. Thus, differences are sufficiently large to permit the identification of crude oil spillages from tankers at sea by gas-liquid chromatography.

However, useful generalizations can be made that hydrocarbons are the most abundant compounds in crude oils accounting for 50-95% of the total composition (Clark and Brown, 1977). The quality of crude oils can be classified either according to hydrocarbon type, product fractions, or sulfur content. Many operations in petroleum exploration, production and transportation have the potential to affect the environment in different degrees. In petroleum transportation, tankers and/or pipelines usually transport the crude oils to the refinery site and are stored in tanks before being processed. The pipelines are mainly installed underground, which require a good insulation, corrosion protection and continuous monitoring for leaks to minimize soil contamination of the oil. However, oil leakages from pipelines, oil wells, drill cuttings and fuel transporters are major contributors to oil contamination of the soil. In marine environments most oil spills result from tankers and from sub-sea pipelines. Figure 1 shows the quantity of oil spilt during the last thirty years. It shows that oil spills has decreased significantly during this period. The average amount of oil spilt per year during the 1990s was about a third of that recorded during the 1970s. The majority of tanker spills were from collisions, groundings and loading/discharging operations (ITOP, 2001).

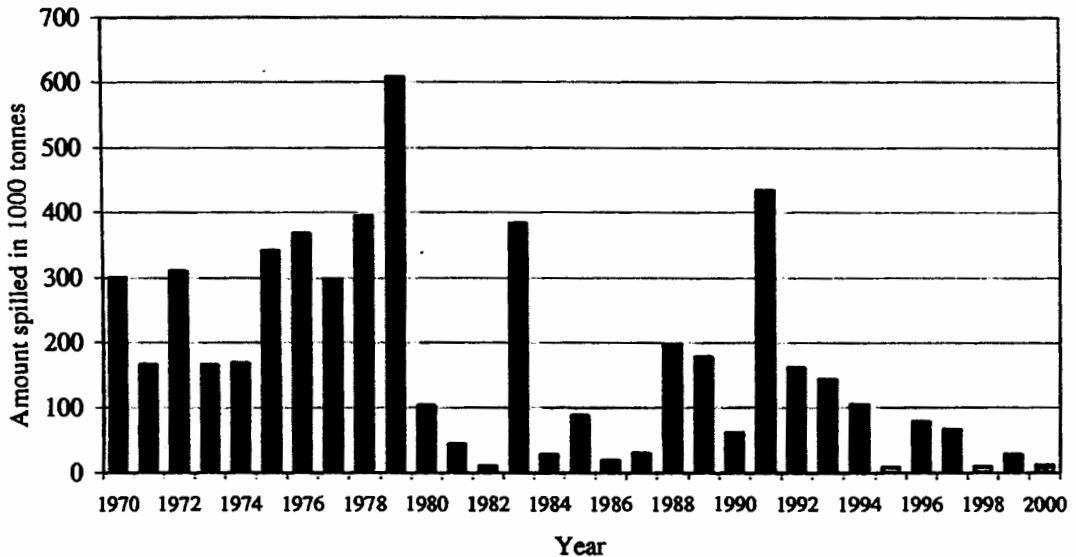


Figure 1: Quantity of oil spilt for the years 1970-2000.

The study of the reasons and causes of tanker incidents could lead to minimizing the oil spills in the marine environment. Besides the tanker spills, offshore drilling operations contribute a large share of pollution.

The last estimate of oil spills indicates that one ton of oil is spilled for every million tons of oil transported. Tanker spills and oil spills from offshore drilling operations are important subjects in the petroleum industry with the aim to minimize or prevent harmful effects of oil spills on the marine environment and on the commercial and public amenities, because once oil has spilled, it is virtually impossible to completely remove or contain it (Terry, 1996). In order to meet these challenges, oil companies are developing and implementing an environmental management system and contingency planning with high standards of environmental quality to prevent marine oil spill accidents and to respond

rapidly and effectively to such accidents (Kenawy and Mohamed, 1998; Jaggernauth and Seeram, 2001)

This paper emphasizes the importance of the removal of oil components from the marine environment as well as from soil to reduce ecotoxicological effects. It presents also different methods applied to remove spilled oil from marine as well as from soil environments. A laboratory investigation of chemical extraction using different solvents is also presented.

### **Toxicity of Oil Components**

The investigation of the toxicity effects of petroleum products in the marine as well as in the soil is important. Types of oil components and their concentration levels, which are potentially harmful for the environment, need to be detected. These components can be identified by laboratory investigations and screening tests. However, any applied identification method should follow the criteria of sensitivity, reliability, practicability, reproducibility, time consumption and possibility of standardization (National Research Council (USA), 1989; Neumann-Hensel et. al., 1999). Measuring toxicity of the oil components in the marine environment is mostly sufficient by analyzing water samples, while in soil the effect of oil components should be performed on water, organisms and soil.

Water samples containing dissolved oil components can cause severe toxicity. Therefore, a collection of water samples for chemical analysis and toxicological testing, in case of oil spills, is enough to identify the source of the toxicity (Neumann-Hensel et. al.; 1999 Hokstad et. al., 2000)

However, toxicological evaluation of oil components in a contaminated site is to be performed on water, soil, and organisms. Due to adsorption and wettability effects of oil components on soil, it is important to characterize the toxicological effect of these components on the contaminated soil. The toxicity potential of the oil components can be also determined by the investigation of the available indigenous organisms. Also, water samples can be collected and analyzed.

The chemical analysis of water samples includes the quantification of the volatile organic compounds ( $C_5$ - $C_9$ ), including the mono-aromatics (benzene, toluene, xylene) and quantification of semivolatiles ( $> C_{10}$ ) including poly-aromatics (PAH) and polar organic compounds. A number of hydrocarbon components, such as volatile compounds and aromatics, are somewhat water soluble in varying concentrations.

The toxicity of the oil components can be revealed by the counts of the viable cells of the microorganisms in the water and soil.

The severity of the toxicity depends on the following factors: oil type, oil loading rate, weathering and biological factors (Ghazaly and Sayed, 2000; Hokstad et. al., 2000). In order to minimize or prevent the impacts of oil components on the soil and marine environments, the oil spills from the water surface and from soil should be removed.

## Oil Removal Techniques

Many techniques are nowadays available to remove oil spills from the water surface and from soil. The implementation of these techniques depends on the amount and properties of discharged oil, sensitivity of the location, spectrum of contaminants, potential environmental consequences, weathering properties and effectiveness of the selected method. There are many requirements to be set on any method applied to combat oil spills, such as: removal of all hydrocarbons including emulsions, absorption of oil without absorbing water, maximizing response effectiveness, saving time and disposal costs.

### *Oil Removal from Sea Surface*

When oil is spilt at sea, it will spread over the water surface area. After a short time (one hour) the thickness of the oil film on the water surface will amount to less than 1 mm. The velocity of propagation of the oil on the water surface depends on the type of oil, water temperature, and weathering processes such as; atmospheric temperature, wind and tide.

Immediately after oil is spilt evaporation will take place. Evaporation of the light components occurs and up to around 40 % of a crude oil may evaporate during a short period of time (Hokstad et. al., 2000). This process will lead to an increase in the viscosity of the spilled oil. Another part of the oil will be loaded into the water, since some volatile hydrocarbon components, such as benzene, toluene, and the xylenes have some water solubility and are toxic. However, oil toxicity decreases with the weathering processes due to vaporization of the volatile components.

Also there are processes like adsorption, dispersion and solubility that lead to oil/water or water/oil mixture and these processes lead also to a reduction of the toxicity. Figure 2 shows schematically the factors affecting the oil spilled at the water surface

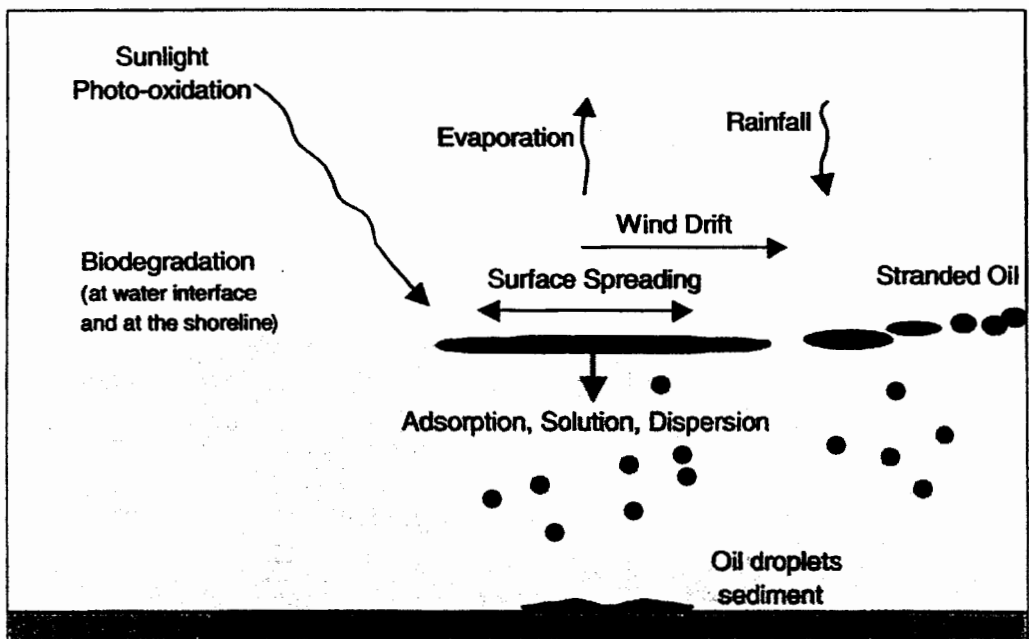


Figure 2: Schematic overview of factors affecting oil spills in the marine environment.

There is also the phenomenon of water/oil emulsion, which can be promoted by wave activity and turbulence at the water surface. These particles will be of varying sizes (0.5 – 1 cm) and some will remain at the surface. The advantage of formation of water/oil emulsion is that the particles come together to form separated stripes instead of an oil slick, which can promote the penetration of oxygen into water. The disadvantage of the emulsion is its high viscosity and high specific density. Some of these particles will remain in suspension in the water column or deposited while some may be stranded. Moreover, the degradation process of the emulsion is time consuming and it may take several years.

The removal techniques of oil spills depend mainly on the weathering process and include the following options: natural dispersion, mechanical recovery system and the use of chemical dispersants. The natural dispersion deals with the removal of the oil spills without any response. Oil can be removed by different natural factors (figure 2).

Chemical dispersants (surfactants) are used to accelerate the process of natural dispersion and to reduce the interfacial tension between the oil and the water and thereby reduce the risk that oil will threaten the environmental resources at the surface and in the coastal areas. Mechanical recovery methods include set-up of barriers, skimmers, and special nets to collect the oil. Water jets or air jets can be used as mechanical recovery to divert the spilled oil. The use of the chemical dispersants compared to mechanical recovery depends on the wind speed. Chemical dispersants become more favorable compared to mechanical recovery as the wind speed increases. *Singsaas et. al.* studied the three major options for responding to oil spills. The results indicated that the use of chemical dispersants gives generally a faster removal than that of mechanical recovery. However, the use and the efficiency of any of the removal methods are limited by weather conditions, mainly wind speed (*Singsaas et. al., 2000*)

### ***Oil Removal from Contaminated Sites***

Pipeline leaks caused by corrosion or human error are a major source for soil contamination on land. If hydrocarbon contamination occurs in soil, the affected portion of soil must be remediated to prevent subsequent pollution of groundwater. Contamination of groundwater resources can result from migration of hydrocarbon components into the ground. There are two options available for responding to remediate contaminated sites, namely in-situ and/or off-site remediation (*Jaggernauth and Seeram, 2001*)

The application of the in-situ processes requires that the contamination in the subsoil must not be excavated or scraped. Treatment is carried out in the subsoil (in-situ) either by biological means such as oil degradation by microorganisms, or chemical-physical processes such as incineration, air sparging, and soil air suction extraction or through combinations of the two processes, depending on the spectrum of contaminants. Bioremediation can be also applied with the help of spreading units in case the contamination occurs at the surface. However, the degradation of oil in the in-situ process requires availability of a sufficient amount of oxygen. Therefore, the selection of any method using this technique depends also on the penetration depth of the hydrocarbon into the soil and on the nature of the soil if it is groundwater saturated or unsaturated.

With the ex-situ processes the contaminated soil must be removed to an off site remediation facility. This method can be applied if the amount of contaminated soil is small or if the oil contamination occurred at the surface in residential areas or industrial

estates, in which an in-situ treatment is not possible. Ex-situ treatment of contaminated sites leads in many cases to a greater degree of remediation as compared to in-situ treatment due to controllability of many factors (moisture, temperature, salinity, pH).

The soil can be combusted in incinerating plants or chemical extraction can be undertaken to remove the hydrocarbon components.

In the following section different solvents have been tested in the laboratory to investigate their ability to remove hydrocarbon components from the soil.

## Experimental Work

### *Raw Materials and Testing Methods*

Sand samples and two different crude oils were used for the preparation of the contaminated soil. The size of the sand particles ranged between 600  $\mu\text{m}$  and 80  $\mu\text{m}$ . The sand samples were cleaned with distilled water and placed in an oven for 24 hours.

The chemical composition of the crude oils was determined using Thin-layer Chromatography with Flame Ionization Detection (TLC/FID). Table 1 shows the percentage of the organic compounds found in the tested oil samples.

Table 1. Organic compounds of used oil samples

Oil sample	Saturated compounds [% wt.]	Aromatic compounds [% wt.]	Polar compounds [% wt.]
Oil SA	74.8	16.5	8.7
Oil AR	9.5	49.3	41.2

The oil sample SA is light oil and paraffin rich while the oil sample AR is heavy oil and rich in aromatic and polar compounds.

The polluted soil was prepared by adding oil to the sand. Both components were very gently mixed. The artificially polluted soil was left for 24 hours. The grade of contamination was gravimetrically adjusted at 2% of crude oil.

To remove the hydrocarbon from the polluted sand, chemical extraction was performed using the following chemical solvents; liquid carbon dioxide ( $\text{CO}_2$ ), toluene ( $\text{C}_7\text{H}_8$ ), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), and 1,1,2 trichlorotrifluoroethane (CFE) ( $\text{C}_2\text{Cl}_3\text{F}_3$ ), separately. Table 2 lists the properties of the used solvents relevant for this study (Handbook of chemistry and physics, 1991).

Table 2. Properties of the used solvents

Parameter	Toluene	Acetone	1,1,2 trichlorotrifluoroethane	Carbon dioxide
Molecular weight, g/mol	92.14	58.08	187.38	44.01
Boiling point at 1.0 atm., $^{\circ}\text{C}$	110.6	56.2	47.7	-78.5
Density, $\text{g}/\text{cm}^3$	0.8669	0.7899	1.5635	1.101 (at $-37^{\circ}\text{C}$ )

The extraction with the liquid CO<sub>2</sub> was carried out in high-pressure autoclave soxhlet-extractor, which was equipped with a heating plate, glass soxhlet, inlet and outlet valves, condenser and pressure gauge. The CO<sub>2</sub> was loaded into the autoclave, in which the extraction thimble was filled with 20 g of the polluted sand. The CO<sub>2</sub> pressure was gradually increased up to 60 psi. The temperature of the heating plate inside the autoclave was adjusted at 45 °C and the temperature of the cooling medium was set at 1.5 °C. The extraction time varied between 30 and 600 minutes. At the end of each experiment, the autoclave was dismantled and the sand was weighed to determine the hydrocarbon recovery.

The extraction with C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub> (CFE) and C<sub>7</sub>H<sub>8</sub> (toluene) was performed in a soxhlet extractor (Figure 3). In the case of CFE extraction, 30 g of polluted sand was placed in an extraction thimble and 200 ml of CFE as an organic solvent was used in the flask. The heating temperature was set slightly above the boiling point of the CFE. The extraction with the toluene followed by placing 15 g of the polluted soil in the extraction thimble and 100 ml of toluene was added into the flask. The extraction time was four hours.

In addition to the soxhlet extraction, CFE was used for the extraction without heating (cold extraction) by mixing 15 g of polluted soil with 20 ml of CFE in a flask, which was placed on a shaker for 30 minutes. The extract-enriched solvent was separated from the polluted soil by filtration.

The same procedure (cold extraction) was applied for the acetone extraction, in which 20 g of polluted soil was used with 50 ml acetone and the mixture was shaken for 15 minutes. After the separation of the extract-enriched solvent, the procedure was repeated by adding 50 ml of fresh acetone. The determination of the hydrocarbon recovery was followed gravimetrically and the efficiency of the solvents in removing the hydrocarbon was compared.

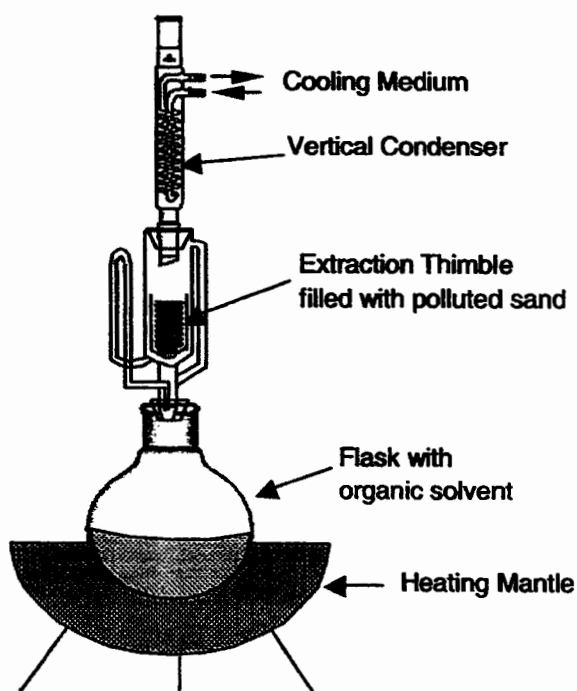


Figure 3: Schematic diagram of the soxhlet extraction system.



## Results and Discussion

Chemical extraction is one of the important methods applied in ex-situ remediation of oil-contaminated sites. In the first part of this study, liquid CO<sub>2</sub> was used to extract the oil from the artificially polluted soil. Figure 4 shows the extracted hydrocarbon over the extraction time. It shows that the extractable oil increases with the extraction time for both oil samples and reaches almost constant value after 10 hrs.

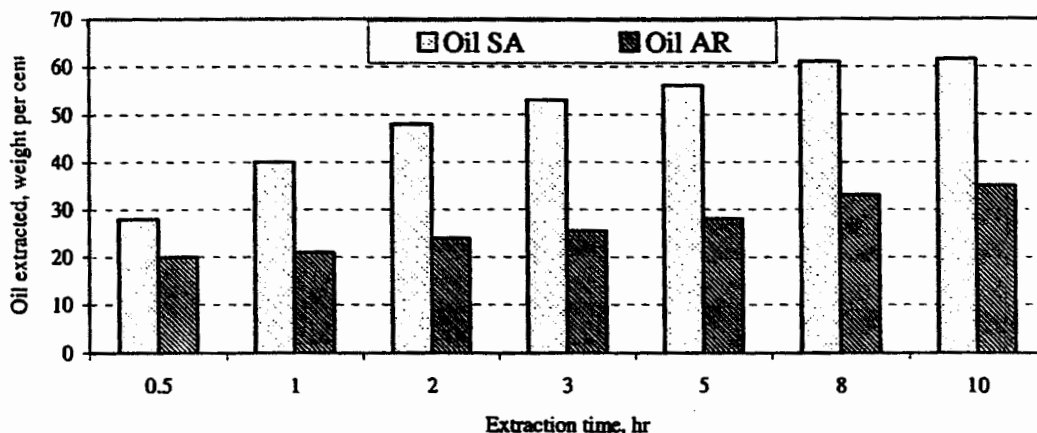


Figure 4: Extraction recovery using liquid CO<sub>2</sub>

The extracted hydrocarbons using liquid CO<sub>2</sub> were analyzed by TLC/FID-chromatography. Figure 5 represents the recovered values of the compounds of oil AR, while figure 6 shows same compounds for oil SA. The results indicate that the extracted aromatics increased slightly, while the saturated compounds decreased with increasing extraction time. This trend is clearer in case of oil AR (figure 5) than for oil SA (figure 6) due to high percentage of aromatics and polar compounds contained in oil AR. The increase in the aromatics is about 5.7% and 3.5% in the polar compounds in case of oil AR after an extraction time of 10 hours. In case of oil SA, the part of extracted aromatics increased about 1.8% and the part of the polar compounds showed an increase of 0.5%.

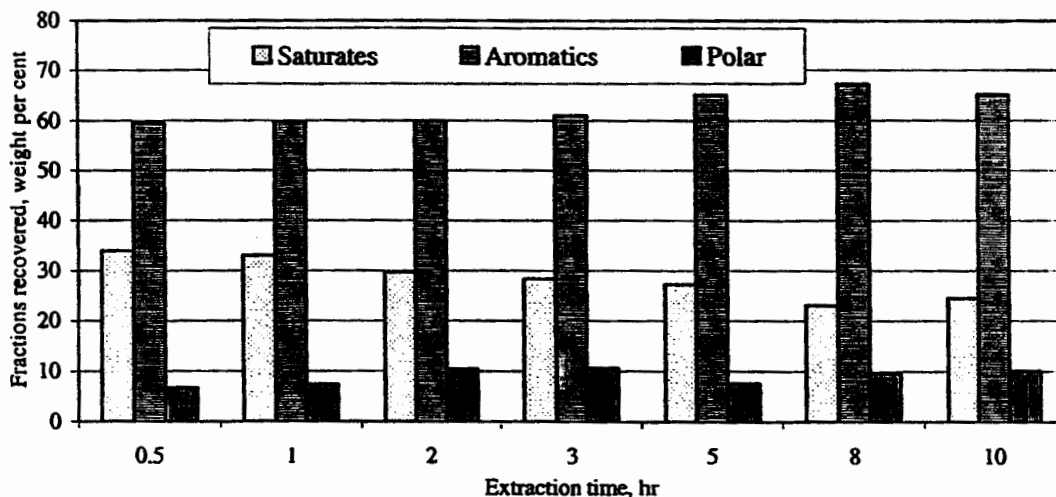


Figure 5: Oil compounds recovered by CO<sub>2</sub> extraction of the oil sample AR.

The extracted oil using the other chemical solvents are given in table 3. It shows that soxhlet extraction results in more oil recovery from the polluted soil than that of the cold extraction. In soxhlet extraction toluene showed better results than CFE and in the cold extraction acetone recovered more oil than CFE (cold). However, using toluene as the chemical solvent has proven to be most suitable for both types of oil.

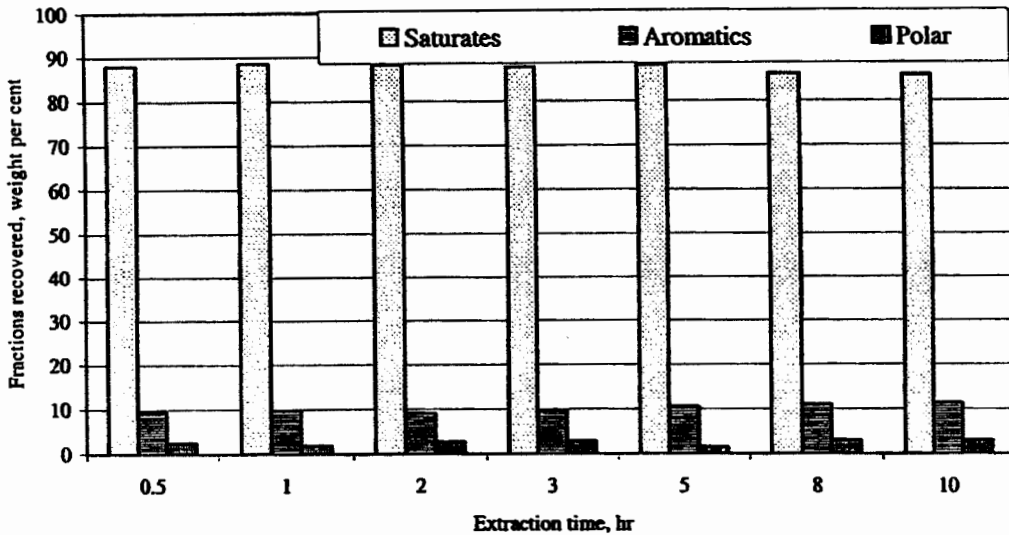


Figure 6: Oil compounds recovered by CO<sub>2</sub> extraction of the oil sample SA.

Table 3. Extracted oil using different chemical solvents

Oil Sample	CFE (cold)	CFE (soxhlet)	Acetone (cold)	Toluene (soxhlet)
Oil SA, % wt	76.9	95.8	82.0	97.2
Oil AR, % wt	66.1	94.7	74.1	96.2

The extracted hydrocarbons using chemical solvents were analyzed by TLC/FID-chromatography and are given in table 4. The TLC/FID analysis revealed that acetone is the best solvent for saturated and for polar compounds, which are water-soluble and are potent toxicants. In the soxhlet-extraction, a high extraction of the polar compounds can be achieved using both solvents namely toluene or CFE. A high percentage of aromatic compounds can be extracted using toluene.

Table 4. Analysis of oil compounds using TLC/FID-chromatography

Solvents	Oil Sample	Saturates, % wt	Aromatics, % wt	Polar, % wt
CFE (cold)	Oil SA	79.9	15.8	4.3
	Oil AR	11.5	48.8	39.7
CFE (soxhlet)	Oil SA	80.1	15.9	4.0
	Oil AR	10.5	49.3	40.2
Acetone (cold)	Oil SA	80.3	13.5	6.2
	Oil AR	12.3	44.1	43.6
Toluene (soxhlet)	Oil SA	79.3	15.6	5.1
	Oil AR	9.3	50.8	39.8

## Conclusions

There are many practices to handle oil spills and oil contaminated sites. Although, these are able to reduce hydrocarbons from the polluted environment, many factors have to be considered in the selection of any oil removal method and special attention has to be paid to ensure a proper procedure to remove the hydrocarbons especially the toxic components. However, the removal of the oil from the water surface or from contaminated sites depends mainly on oil type, weather conditions, penetration depth of the hydrocarbons and soil type. It is also important to respond immediately to any oil accident whether onshore or offshore to minimize the potential environmental consequences.

Oil contamination occurring on land can be handled using two different procedures, namely in-situ or ex-situ remediation. The selection of one of these procedures to remediate the contaminated sites depends mainly on the sensitivity of the location, on the toxicity of the chemical composition and on the penetration depth. Chemical extraction is one of the approaches used in handling contaminated sites ex-situ. The results of this study have identified the ability of different chemical solvents to extract oil components from the soil. The effect of these solvents in removing hydrocarbons depends on the type of oil. For instance liquid CO<sub>2</sub> can remove high amounts of saturated and aromatic compounds in contrast to the polar compounds, which are water-soluble and can contaminate the ground water. The use of CFE for extraction is generally suitable for liquid/liquid extraction. It can be used to remove hydrocarbon components from water, sludge or sewage. CFE also has the ability to remove a high percentage of polar components from contaminated sites (liquid/solid extraction) and the extraction can be performed without a soxhlet-system (cold-extraction). The extraction with acetone recovered high amounts of saturated and polar compounds. However, the highest recovery of polar compounds as well as aromatic compounds was achieved using toluene extraction.

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