İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

DESIGNATION OF THE COMPENSATION OF THE ENVIRONMENTAL DAMAGE CAUSED BY OIL SPILLS WITH TOXICITY

M.Sc. Thesis by
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Department : Environmental Engineering

Programme : Environmental Sciences and Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PETROL DÖKÜLMELERİ SONUCU OLUŞAN ÇEVRESEL HASARIN TAZMİNATININ ZEHİRLİLİĞE BAĞLI OLARAK BELİRLENMESİ

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December, 2006 Ceren TOSUN

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SUMMARY

The risks related to hazardous materials and especially toxic properties of a material are difficult to evaluate in terms of environmental impact and damage. In this regard, the toxicity effect of the oil and petroleum derivatives in sea, deep sea and shoreline on living beings and environment caused by accidents is difficult to quantify. Determination of the toxicity, which is one of the material's hazard criteria, constitutes an important stage on establishing the hazard level of the environmental components and their protection. The toxic pollutants can disturb the sustainability of natural ecosystem by variety of effects on species, populations, communities, and ecosystem processes. The main materials threating sea and shorelines are wastes of the vessels and sea vehicles used for transportation and oil and petroleum derivatives spilled during accidents. The most important effects of the oil spill in marine environment are the acute and chronic toxicity effects and damages to sea surface, deep sea, and the contamination of shorelines, beaches, rocks and settlements due to the wave movements. In this research, the damage caused by 1578 tons of spilled heavy fuel oil from the vessel Volgoneft-248 broken during a storm on the year 1999 at the Marmara Coast in deep sea and on the full length of 2 km shoreline are established. Toxicity tests are performed on samples collected from sea water, deep sea sediment and beach in the accident area. Moreover, acute effects were compared with synthetic samples representing the accident moment. BioTox^{TM} test using *Vibrio fischeri* was used as a method. Extraction of the samples in the form of sludge and solid were obtained by Zero Head Space Extractor (ZHE) based on Toxicity Characterization of Leaching Procedure (TCLP) and the EC_{50} values of the extracts are evaluated. Based upon the experimental results toxicity parameters are developed for determination of compensation costs. This study puts forth a new method to determine the environmental damage and to calculate the compensation with the evaluation of the toxicity at the moment of accident, cleanup operations after the accident and the long-term effects.

PETROL DÖKÜLMELERİ SONUCU OLUŞAN ÇEVRESEL HASARIN TAZMİNATININ ZEHİRLİLİĞE BAĞLI OLARAK BELİRLENMESİ

ÖZET

Tehlikeli maddeler ile ilgili olarak ortaya çıkan riskler ve özellikle maddenin toksik özelliği sonucu çevresel etki ve hasar tespitinde zorluklar vardır. Petrol ve petrol türevlerinin kaza sonucu deniz, deniz dibi ve kıyı alanlarındaki canlılar üzerinde yarattığı zehirlilik tehlikesini belirlemek bu zorluklardan biridir. Maddenin tehlike kriterlerinden birisi olan toksisitenin belirlenmesi çevresel elemanların tehlike boyutunu belirlemede ve korunmasında önemli bir adımı teşkil eder. Toksik kirleticiler türlerin, popülasyonların, toplulukların ve ekosistem proseslerinin üzerindeki çeşitli etkileri ile ekosistemin sürdürülebilirliğini tehdit eder. Deniz ve kıyı alanlarını tehdit eden en önemli madde, taşımacılık faaliyetleri için kullanılan gemi ve deniz araçlarının atıkları ile kaza sonucu çevreye yayılan petrol ve petrol türevleridir. Deniz ortamına petrol dökülmesinin çevreye olan en önemli etkisi, dökülen petrolün ortam şartlarında, deniz yüzeyinde, deniz dibinde, ve dalga hareketlerine bağlı olarak kumsal, kaya ve yerleşim alanları gibi kıyı alanlarına kontaminasyonu ile ortaya çıkan akut ve kronik zehirlilik etkisi ve hasarıdır. Bu çalışmada, 1999 yılında Marmara kıyı alanında fırtına sonucu ikiye bölünmüş olan Volgoneft–248 adlı gemiden dökülmüş olan 1578 ton ağır fuel oilin 2 km.lik bir kıyı alanı ve deniz dibinde yaratmış olduğu hasar tespiti yapılmıştır. Bu kazaya ait belirlenen alandan alınan deniz suyu, deniz dibi çamuru ve kumsal alanı örneklerinde zehirlilik testleri yapılmıştır. Ayrıca kaza anını temsil eden benzer sentetik örnekler hazırlanarak akut etki ile karşılaştırılması da yapılmıştır. Yöntem olarak *Vibrio fisheri* bakterilerini kullanan BioTox^{TM} testi kullanılmıştır. Katı ve çamur formundaki örneklerin ekstraksyonu Toxicity Characterization of Leaching Procedure (TCLP) metoduna bağlı kalınarak Zero Head Space Extractor (ZHE) ile elde edilmiş ve ekstraktların EC_{50} değerleri değerlendirilmiştir. Deney sonuçlarından yola çıkılarak tazminat miktarının belirlenmesi için toksisite parametreleri geliştirilmiştir. Bu yöntemle ortaya konulan çevresel hasar tespiti yapılmış ve tazminat hesaplamalarına yardımı olabilecek bir yöntem oluşturulmuştur. Bu çalışma çevresel hasarı belirlemede ve toksisitenin kaza anı, kaza sonrası temizleme çalışmaları ve uzun vadeli etkilerinin değerlendirilmesiyle tazminat hesaplamada kullanılacak bir yöntem ortaya koymaktadır.

1. INTRODUCTION

The transportation of the oil and oil products by seaway involves significant environmental risks such as tanker accidents near the shoreline. Although the chronic or acute effects of the oil pollution after an accident on the aquatic plants and animals can not be quantified since an inventory is not available before accident, the lethal and adverse effects of the pollution on biota is certain and quantity and properties of the hazardous material are also known (Talınlı et al., 2003). The toxicity of a hazardous material is one of the most important hazard criteria. Therefore, determination of the toxicity is an important stage on assessing the hazard level of the environmental components and their protection. The assessment of environmental damage can be made by monitoring the toxicity, which may change by natural attenuation and cleanup operations. Toxicity measurements by BioTox^{TM} assay gives EC_{50} values.

Only half a mile wide at its narrowest point, the Bosphorus is one of the world’s most difficult waterways for navigation. The potential for collisions and groundings in Bosphorus is thus ever present, as evidenced by several major accidents. The latest major accident is the grounding and consequently breaking of Russian river tanker “Volgoneft-248” in 1999 resulting in oil spill in an environmentally and historically sensitive area of Marmara Sea. Although the spilled oil amount was not as high as the previous major accidents, this accident caused heavy fuel contamination in the shoreline and posed an environmental disaster because of the weather conditions. Approximately 300 tonnes of total 1578 tonnes heavy fuel oil immediately leaked to the seabed (ITOPF, 2000; Talınlı, 2002).

In this study, a series of experiments was conducted by BioTox^{TM} toxicity test using *Vibrio fischeri* on the samples (the sea water (SW), sediment (S) and the beach sand (BS)) taken from contaminated shoreline of the Marmara Sea to assess the toxic effects for five years period from the Volgoneft-248 accident moment till today. Based upon these experimental results toxicity parameters are developed for determination of compensation costs.

In the marine environment, it is hard to set a monetary value on resources and their degradation because of human activities. However, by considering certain assumptions cash figures may be assigned to ecological damage estimated by natural attenuation processes and the environmental residual damage. This study develops a methodology to add costs of environmental damage to the actual cleanup operations costs by considering assumptions regarding toxicity units (TUs).

1.1 Aim and Scope

The aims and scope of this study may be stated as:

- Investigation of the suitability of BioTox^{TM} bioluminescence test for the determination of toxic effects;
- Evaluation of the toxic effect and detoxification performance of the case study oil spill for a period of five years from the accident moment till today;
- Correlation of toxicity to the cost of cleanup operations, natural attenuation and residual environmental damages;
- Development of an approach for determination of the compensation costs incorporating environmental damages based on sound assumptions.

2. OIL POLLUTION

2.1 Petroleum and Petroleum Products

The word *petroleum*, derived from the Latin *petra* and *oleum*, meaning literally “rock oil” issued to describe a myriad of hydrocarbon-rich fluids that have accumulated in subterranean reservoirs. Petroleum (also called *crude oil*) varies dramatically in color, odor, and flow properties that reflect the diversity of its origin (Speight, 2002).

Petroleum is a naturally occurring mixture of hydrocarbons and generally, in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements. The fuels derived from petroleum contribute approximately one-third to one-half of the total world energy supply and are used not only for transportation fuels (i.e., gasoline, diesel fuel, and aviation fuel, among others) but to heat buildings. Petroleum products have a wide variety of uses that vary from gaseous and liquid fuels to near-solid machinery lubricants. Petroleum is perhaps the most important substance consumed in modern society. It provides not only raw materials for plastics and other products but also fuel for energy, industry, heating, and transportation.

Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, non-volatile compounds. This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil (Fingas, 2000).

Historically, physical properties such as boiling point, density, odor, and viscosity have been used to describe oils. Petroleum may be called *light* or *heavy* in reference to the amount of low-boiling constituents and the relative density (specific gravity). Likewise, odor is used to distinguish between *sweet* (low sulfur) and *sour* (high sulfur) crude oil (Speight, 2002). Density is the property used by the petroleum industry to define light or heavy crude oils (Fingas, 2000).

2.1.1 The composition of oil

The composition of crude oils from different drilling regions, and even from within a particular formation, can vary tremendously. Crude oils contain thousands of different chemical compounds owing to processes during petroleum formation resulting in "molecular scrambling". These compounds may vary by the hydrocarbon types, the range of isomeric hydrocarbons and the various types and isomers of heteroatom constituents. Therefore, it is not practical to perform individual compound analyses but often helpful to define the compounds present under broad classifications, such as aromatics, paraffins, naphthenes, and olefins (Speight, 2002).

Hydrocarbon compounds are composed of hydrogen and carbon, which are the main elements in oils. Hydrocarbons are the most abundant compounds in crude oils, accounting for 50-98 % of the total composition although the majority of crude oils contain the higher relative amounts of hydrocarbons (NRC, 1985). Percentage (in weight) of these two elements in different crude oils varies between 83 to 87 % for carbon and between 11 and 14% for hydrogen (IMO/UNEP, 1995).

Classes of hydrocarbons are determined based on the capability to isolate them by separation techniques. The four fractional types into which petroleum is subdivided are paraffins, olefins, naphthenes, and aromatics. Paraffinic hydrocarbons include both normal and branched alkanes, whereas olefins refer to normal and branched alkenes that contain one or more double or triple carbon – carbon bonds. Naphthene is a term specific to the petroleum industry that refers to the saturated cyclic hydrocarbons (cycloalkanes). Finally, the term aromatics includes all hydrocarbons containing one or more rings of the benzenoid structure. The nonhydrocarbon constituents are usually concentrated in the higher-boiling portions of the crude oil. The carbon and hydrogen content is approximately constant from crude oil to crude oil even though the amounts of the various hydrocarbon types and of the individual isomers may vary widely (Speight, 2002).

Oils also contain varying amounts of sulphur, nitrogen, oxygen, and sometimes mineral salts, as well as trace metals such as nickel, vanadium, iron, copper and chromium present at the part per million (ppm) level (Fingas, 2000; Speight, 2002). It cannot be expected to have a detailed and precise knowledge of each component of a certain crude oil or refined product (IMO/UNEP, 1995).

Attempts have been made to define or classify petroleum based on various distillation properties when combined with another property such as density. It has been suggested that a crude should be called asphaltic if the distillation residue contained less than 2% wax and paraffinic if it contained more than 5%. A division according to the chemical composition of the 250–300°C (480–570°F) fraction has also been suggested in Table 2.1 (Speight, 2002).

Table 2.1: Classification by Chemical Composition (Speight, J.G., 2002)

Composition of 250 – 300 ^{0}C (480 – 570 ^{0}F) Fraction (%)					Crude Oil Classification
Paraffinic	Naphthenic	Aromatic	Wax	Asphalt	
46 – 61	22 – 32	12 – 25	<10	<6	Paraffinic
42 – 45	38 – 39	16 – 20	<6	<6	Paraffinic - Naphthenic
15 – 26	61 – 76	8 – 13	0	<6	Naphthenic
27 – 35	36 – 47	26 – 33	<1	<10	Paraffinic - Naphthenic - aromatic
<8	57 – 78	20 – 25	<0.5	<20	Aromatic

Difficulties arise in using such a classification are that in the fractions boiling above 200°C (390°F), the molecules can be placed no longer in one group because most of them are of a typically mixed nature. Purely naphthenic or aromatic molecules occur very seldom; cyclic compounds generally contain paraffinic side chains and often even aromatic and naphthenic rings side by side. Hence, because fuel oils are complex mixtures of hydrocarbons, they cannot be rigidly classified or defined precisely by chemical formulae or definite physical properties. The arbitrary division or classification of fuel oils is based more on their application than on their chemical or physical properties (Speight, 2002).

2.1.2 Properties of oil

Crude oils vary widely in their physical and chemical properties because of their varying composition and constituents. As their composition varies, each type of oil or petroleum product has certain unique characteristics or properties. These properties influence how the oil behaves when it is spilled at sea and determine the effects of the oil on the environment. They also influence the efficiency of cleanup operations (Fingas, 2000). The main physical properties, which affect the behaviour and the persistence of an oil, are briefly explained below.

2.1.2.1 Viscosity

The viscosity of a fluid is a measure of its resistance to flow and is expressed as Saybolt Universal seconds (SUS), Saybolt Furol seconds (SFS), or centistokes (cSt, kinematic viscosity) (Speight, 2002). The higher the viscosity of the oil, the greater the tendency for it to stay in one place. The viscosity of the oil is largely determined by the amount of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity (USEPA, 1999b; Fingas, 2000).

As with other physical properties, viscosity is affected by temperature, with a lower temperature giving a higher viscosity. For most oils, the viscosity varies as the logarithm of the temperature, which is a very significant variation (Fingas, 2000). Since sea temperatures are often lower than cargo or bunker temperatures on board a vessel, viscosity-dependent cleanup operations such as skimming and pumping generally become more difficult as the spilled oil cools (ITOPF, 2002).

Spill viscosities range from 0.7 to over 20,000 centistokes (cst). Residual oils, weathered emulsions and high pour point crudes can even reach a semisolid state. Viscosities for crudes weathered for up to a day and emulsified by moderate seas are between 300 and 1000 cst (Liu, 1999).

2.1.2.2 Specific gravity

Specific gravity is the density of a substance compared to the density of water. Since most oils have a specific gravity below 1 and are lighter than sea water which has a specific gravity of about 1.025, they float on top of it. Heavier oils, vegetable oils, and animal fats may sink and form tar balls or may interact with rocks or sediments on the bottom of the water body (USEPA, 1999b; ITOPF, 2002).

Oil spill specific gravities range from 0.75 to 1.03. The lower values represent highly refined products such as gasoline, kerosene, and diesel fuels. The upper values represent residual oils. Crude oils have specific gravities between 0.8 and 1.0; however, this increases rapidly when the light ends (fractions) evaporate (Liu, 1999).

The American Petroleum Institute gravity scale (°API) is commonly used to describe the specific gravity of crude oils and petroleum products, and is calculated as follows:

$$^{0}API = \frac{141.5}{specific\,gravity} - 131.5 \qquad \textbf{(2.1)}$$

In addition to determining whether the oil will float, the specific gravity can also give a general indication of other properties of the oil. For example, oils with a low specific gravity (high °API) tend to contain a high proportion of volatile components and to be of low viscosity (ITOPF, 2002).

2.1.2.3 Surface tension

The surface tension, sometimes called oil/water interfacial tension, is the force of attraction or repulsion between the surface molecules of oil and water. Together with viscosity, surface tension is an indication of how rapidly and to what extent an oil will spread on water. The lower the interfacial tension with water, the greater the extent of spreading (Fingas, 2000).

Because increased temperatures can reduce a liquid’s surface tension, oil is more likely to spread in warmer waters than in very cold waters (USEPA, 1999b).

2.1.2.4 Solubility

Solubility in water is the measure of how much of an oil will dissolve in the water column on a molecular basis. Solubility is important in that the soluble fractions of the oil are sometimes toxic to aquatic life, especially at higher concentrations. As the amount of oil lost to solubility is always small, this is not as great a loss mechanism as evaporation (Fingas, 2000). However, this small fraction of the fuel oil soluble in water could cause long-term effects. This water-soluble fraction (WSF) has been observed to consist mainly of a variety of polyaromatic hydrocarbons (PAHs) and some quantities of aliphatic hydrocarbons (Navas et al., 2006).

2.1.2.5 Pour point

Pour point is the temperature below which an oil will not flow. The pour point is a function of the wax and asphaltene content of the oil. As an oil cools, it will reach a temperature, the so-called ‘cloud point’, at which the wax components begin to form crystalline structures. This increasingly hinders flow of the oil until it eventually changes from liquid to semi-solid at the pour point (ITOPF, 2002).

The pour point is the lowest temperature at which the crude oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where a petroleum product, depending on its thermal history, might appear in the liquid as well as the solid state. The pour point should not be confused with the freezing point, which is an index of the lowest temperature at which the crude oil will flow under specified conditions (Speight, 2002).

As oils are made up of hundreds of compounds, some of which may still be liquid at the pour point, the pour point is not the temperature at which the oil will no longer pour. The pour point represents a consistent temperature at which an oil will pour very slowly and therefore has limited use as an indicator of the state of the oil (Fingas, 2000).

2.1.2.6 Distillation fractions

Distillation characteristics of oil describe its volatility. As the temperature of an oil is raised, different components reach their boiling point one after another and evaporate. The distillation characteristics are expressed as the proportions of the parent oil, which distil within given temperature ranges. Some oils contain bituminous, waxy or asphaltenic residues which do not readily distil, even at high temperatures. These are likely to persist for extended periods in the environment (ITOPF, 2002). This data also provides useful insights into the chemical composition of oils. For example, while 70% of gasoline will boil off at 100°C, only about 5% of a crude oil will boil off at that temperature and an even smaller amount of a typical Bunker C. The distillation fractions correlate strongly to the composition as well as to other physical properties of the oil (Fingas, 2000).

2.1.2.7 Vapor pressure

The vapor pressure of an oil is a measure of how the oil partitions between the liquid and gas phases, or how much vapor is in the space above a given amount of liquid oil at a fixed temperature. Because oils are a mixture of many compounds, the vapor pressure changes as the oil weathers. Vapor pressure is difficult to measure and is not frequently used to assess oil spills (Fingas, 2000). Vapor pressure controls evaporation rate and air concentrations of hydrocarbons and, therefore, the fire hazard in the vicinity of spills (NRC, 1985).

2.1.2.8 Flash point

The flash point of an oil is the temperature at which the liquid gives off sufficient vapors to ignite upon exposure to an open flame. The flash point is used primarily as an index of fire hazards (Speight, 2002). A liquid is considered 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 fresh. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils have an abundance of volatile components and may be flammable for as long as 1 day until the more volatile components have evaporated. On the other hand, Bunker C and heavy crude oils generally are not flammable when spilled (Fingas, 2000).

2.1.3 Natural attenuation

Natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in the receiving media. These processes include weathering processes like biodegradation; dispersion; dilution; sorption; volatilization; and chemical or biological stabilization, transformation, or destruction of contaminants (USEPA, 1999a). Weathering processes contributing to natural attenuation are described in detail in the next section.

Natural attenuation (no treatment – recovery without intervention) is a suitable spill response option where active cleanup techniques would cause more damage than leaving the environment to recover naturally, when response techniques would not accelerate natural recovery, or when safety considerations place response personnel at risk. Figure 2.1 shows the relevant processes contributing towards natural attenuation of petroleum hydrocarbons in receiving media (USEPA, 1999a).

Natural attenuation has become a preferred response option for use on shoreline sites of limited public use that are contaminated with low concentrations of nonpersistent oil (Lee et al., 2003). Natural weathering processes of evaporation, dissolution and biodegradation can account for up to 30% removal of spilled petroleum in the first 72 h after release (Page et al., 2002).

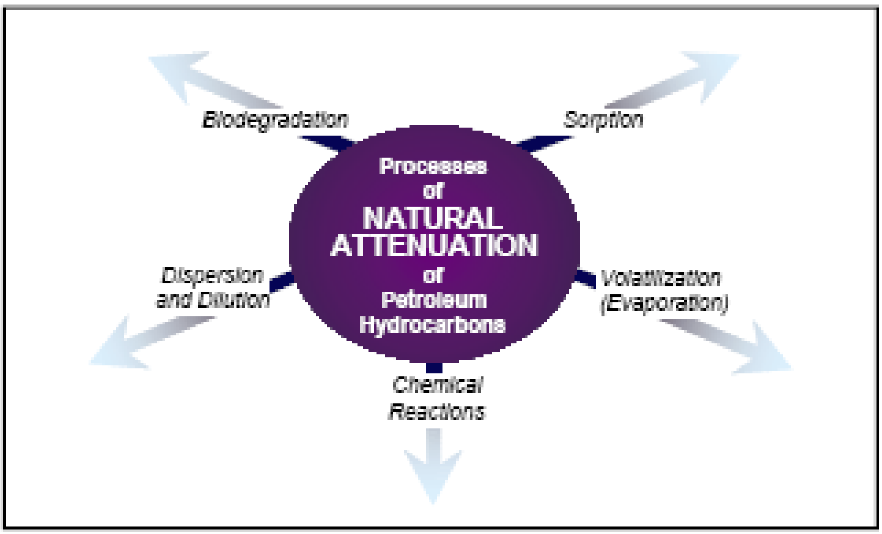


Figure 2.1: Processes of natural attenuation of petroleum hydrocarbons (USEPA, 1999a)

2.1.4 Weathering processes contributing to natural attenuation

Petroleum introduced to the marine environment goes through a variety of physical, chemical, and biological transformations during its transport by the advective and spreading processes. These physical, chemical, and biological processes leading to the dispersion and final removal of oil in the environment are collectively termed as weathering processes (McCay, 2004).

A detailed understanding of weathering processes is required to assess exposure, to estimate environmental damage, and to develop effective restoration strategies. Figure 2.2 shows the weathering processes acting on spilled oil. Figure 2.3 shows the occurrence of the processes with respect to time after spill where the width of each band indicates the importance of the process. Spreading, evaporation, dispersion, emulsification and dissolution are most important during the early stages of a spill whilst oxidation, sedimentation and biodegradation are longer-term processes, which determine the ultimate fate of oil. An understanding of the way in which weathering processes interact is important when attempting to forecast the changing characteristics of an oil during the lifetime of a slick at sea.

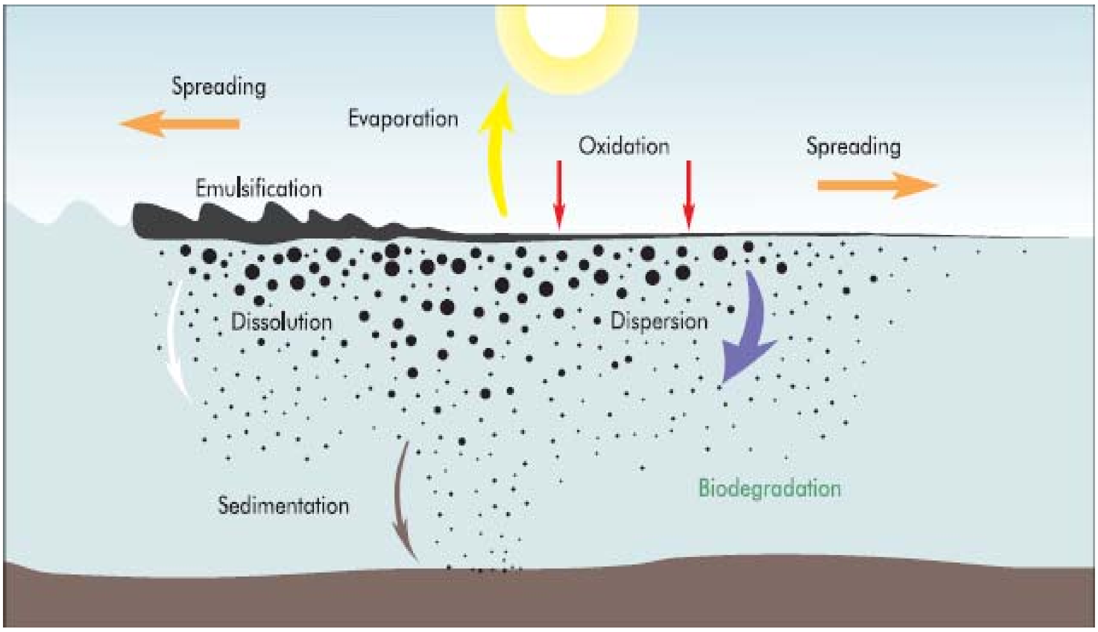


Figure 2.2: Processes acting on spilled oil (ITOPF, 2002)

Advection and spreading begin immediately after introduction of petroleum to the ocean and cause a rapid increase in the exposure area of the oil to subsequent "weathering" processes. Involved in all of these processes are chemical factors determined by the specific composition of the petroleum in question. Additionally, photochemical oxidation of some of the components of petroleum can be induced by sunlight. Dark or auto oxidation may also occur. The products of these processes include hydrocarbon fractions and reaction products introduced to the atmosphere, slicks and tar lumps on the surface of the ocean, dissolved and particulate hydrocarbon materials in the water column, and similar components in the sediments.

While physical and chemical processes are occurring, biological processes also act on the different fractions of the original petroleum in various ways. The biological processes considered include degradation of petroleum by microorganisms to carbon dioxide or organic components in intermediate oxidation stages, uptake by larger organisms and subsequent metabolism, storage, or discharge (NRC, 1985).

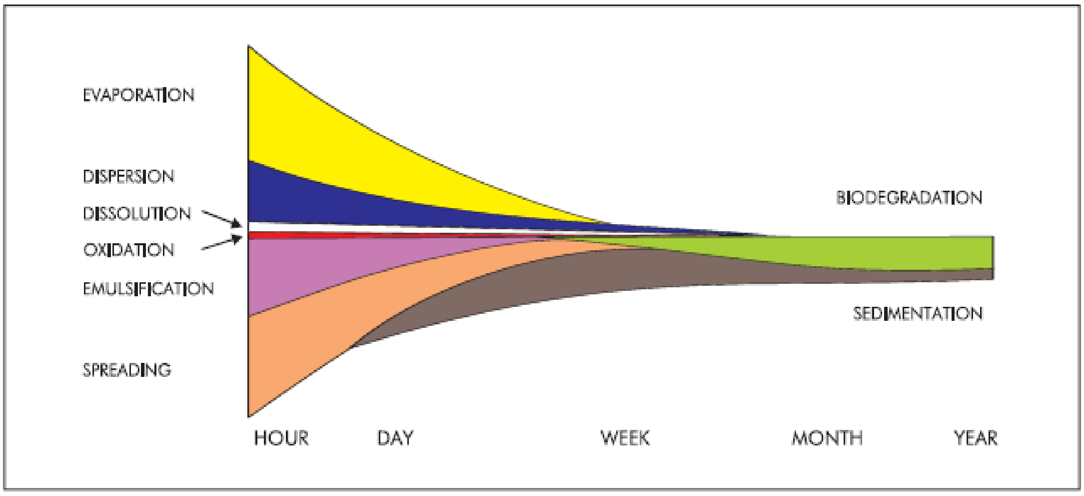


Figure 2.3: Fate of a crude oil spill showing changes in the relative importance of weathering processes with time (ITOPF, 2002)

Dissolution occurs immediately after the spill, and the rate of dissolution decreases rapidly after the spill as soluble substances are quickly depleted. Some of the soluble compounds also evaporate rapidly (Fingas, 2000). A few of the important weathering processes are summarized as under:

2.1.4.1 Evaporation

Evaporation is usually the most important weathering process. It has the greatest effect on the amount of oil remaining on water or land after a spill. Most oil spill behavior models include evaporation as a component of the process and output of the model (Fingas, 1995). Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of heavier Bunker C oil evaporates. The rate at which oil evaporates depends primarily on the oil's composition. The more volatile components an oil or fuel contains, the greater the extent and rate of its evaporation. Many components of heavier oils will not evaporate at all, even over long periods of time and at high temperatures (Fingas, 2000).

Oil and petroleum products evaporate in a slightly different manner from water and the process is much less dependent on wind speed and surface area. Oil evaporation can be considerably slowed down, however, by the formation of a "crust" or "skin" on top of the oil. This happens primarily on land where the oil layer does not mix with water. The skin or crust is formed when the smaller compounds in the oil are removed, leaving the larger compounds, such as waxes and resins, at the surface. These then seal off the remainder of the oil and prevent evaporation. Stranded oil from old spills has been re-examined over many years and it has been found that when this crust has formed, there is no significant evaporation in the oil underneath. When this crust has not formed, the same oil could be weathered to the hardness of wood (Fingas, 2000).

The major finding to date is that oil is not strictly boundary layer regulated. This has profound implications for most oils including (Fingas, 1995):

1. area of the spill is not important to evaporation prediction in most situations
2. wind speed is not important
3. temperature is the most important environmental consideration.

There are several fundamental differences between the evaporation of a pure liquid such as water and for a multiple-component system such as crude oil. First, the evaporation rate for a single liquid such as water is constant with respect to time. Evaporative loss, by total weight or volume, is logarithmic with time for crude oils and other multi-component fuel mixtures. This is due to the depletion of more volatile components. These are exponentially depleted with time. The second major difference is the effect of atmospheric conditions. Air can only hold a certain volume of water. The boundary layer above evaporating water mass governs the rate at which the evaporation occurs. Once this air layer is saturated with water (or any other evaporating component), evaporation ceases. Normal air does not contain a high level of benzene and similar oil components and furthermore, the saturation level of these in air is often well above concentrations that can be achieved from an evaporating slick.

The rate of evaporation is very rapid immediately after a spill and then slows considerably. In a few days, light crude oils can be reduced by up to 75% of their initial volume and medium crude up to 40% of their volume. Heavy or residual oils will only lose about 5% of their volume in the firs few days following a spill (Fingas, 1995).

2.1.3.2 Emulsification

Emulsification is the process by which one liquid is dispersed into another one in the form of small droplets. Water droplets can remain in an oil layer in a stable form and the resulting material is completely different.

The mechanism of emulsion formation is not yet fully understood, but it probably starts with sea energy forcing the entry of small water droplets, about 10 to 25μm (or 0.010 to 0.025 mm) in size, into the oil. Water-in-oil emulsions are unstable and difficult to form in highly refined oils. However, most crudes and all residual oils contain asphaltenes, resins, cresols, phenols, organic acids, metallic salts, and other surface-active agents that concentrate at the interface between entrained water droplets and the oil. If the oil is only slightly viscous, these small droplets will not leave the oil quickly. On the other hand, if the oil is too viscous, droplets will not enter the oil to any significant extent. Once in the oil, the droplets slowly gravitate to the bottom of the oil layer. The formation of emulsions is an important event in an oil spill. First, and most importantly, it substantially increases the actual volume of the spill. Emulsions of all types contain about 70% water and thus, when emulsions are formed, the volume of the oil spill more than triples. Even more significantly, the viscosity of the oil increases by as much as 1000 times, depending on the type of emulsion formed. Emulsion formation also changes the fate of the oil. It has been noted that when oil forms stable or meso-stable emulsions, evaporation slows considerably. Biodegradation also appears to slow down. The dissolution of soluble components from oil may also cease once emulsification has occurred (Fingas, 2000).

A crude spill can become a 40% water emulsion in a single day due to open sea action. In 5 days, this can increase to 80%. Increased shearing rates and action decreases water droplet size and increases emulsion stability. Pumping emulsions with free water may result in up to 98% water in the oil emulsions, which are so formed (Liu, 1999).

2.1.3.3 Dispersion

The lifetime of an oil slick on an ocean surface is often controlled by the dispersion or vertical transport of small particles of oil or oil-in-water emulsions into the water column (NRC, 1985).

Natural dispersion occurs when fine droplets of oil are transferred into the water column by wave action or turbulence. Small oil droplets (less than 20 µm or 0.020 mm) are relatively stable in water and will remain so for long periods. Large droplets tend to rise and larger droplets (more than 100 µm) will not stay in the water column for more than a few seconds. Depending on oil conditions and the amount of sea energy available, natural dispersion can be insignificant or it can remove the bulk of the oil (Fingas, 2000).

2.1.3.4 Spreading

After an oil spill on water, the oil tends to spread into a slick over the water surface. This is especially true of the lighter products such as gasoline, diesel fuel, and light crude oils, which form very thin slicks. Heavier crudes and Bunker C spread to slicks several millimeters thick. Heavy oils may also form tar balls and tar mats and thus may not go through progressive stages of thinning (Fingas, 2000).

Oil spreads horizontally over the water surface even in the complete absence of wind and water currents. The force of gravity and the interfacial tension between oil and water cause this spreading. The viscosity of the oil opposes these forces. As time passes, the effect of gravity on the oil diminishes, but the force of the interfacial tension continues to spread the oil. The transition between these forces takes place in the first few hours after the spill occurs. Winds and currents also spread the oil out and speed up the process (Fingas, 2000). Wind adds a component of about 3–4% of the wind velocity, and natural spreading acts concentrically to disperse the slick. The oil's hydrostatic head balanced by the oil's inertia initially cause this. Variations in spreading rate depend on the oil's specific gravity, surface tension, characteristic evaporation, solubility in water, emulsification of water into the oil, and pour point (Liu, 1999).

2.1.3.5 Dissolution

Dissolved hydrocarbon concentrations in water are particularly important because of their potentiality for exerting a toxic effect on biological systems. They are less important from the viewpoint of the mass lost by the spill, for dissolution of even a few percent of the spill is unlikely (NRC, 1985).

The significance of dissolution is that the soluble aromatic compounds are particularly toxic to fish and other aquatic life. Gasoline, diesel fuel, and light crude oils are the most likely to cause aquatic toxicity. Dissolution is considerably less important than evaporation in determining the fate of spilled oil because of the low aqueous solubility of most components (Fingas, 2000).

2.1.3.6 Oxidation

Oxidation occurs when oil contacts the water and oxygen combines with the oil hydrocarbons to produce water-soluble compounds. This process affects oil slicks mostly around their edges. Thick slicks may only partially oxidize, forming tar balls. These dense, sticky black spheres may linger in the environment, washing up on shorelines long after a spill (USEPA, 1999a).

Photooxidation can change the composition of an oil. It occurs when the sun's action on an oil slick causes oxygen and carbons to combine and form new products that may be resins. The resins may be somewhat soluble and dissolve into the water or they may cause water-in-oil emulsions to form. It is not well understood how photooxidation specifically affects oils, although certain oils are susceptible to the process while others are not. For most oils, photooxidation is not an important process in terms of changing their fate or mass balance after a spill (Fingas, 2000).

2.1.3.7 Sedimentation

Sedimentation is the process by which oil is deposited on the bottom of the sea. Once oil is on the bottom, it is usually covered by other sediment and degrades very slowly (Fingas, 2000).

The various forms of oil in seawater can be sorbed onto settling particles and delivered to the bottom sediments. Sedimentation of spilled oil takes place primarily through sorption on particulates or by incorporation into fecal matter. Weathering processes increase the density of floating of oil and, when this occurs, incorporation into the particles will eventually cause an increase in density above that of seawater so that the oil then sinks below the surface into the water column and, in some cases, eventually to the sediments (NRC, 1985).

2.1.3.8 Biodegradation

The biodegradation of petroleum is one of the principal mechanisms for removal of petroleum from the marine environment. This applies particularly to the nonvolatile components of crude oil or refines products. The various compounds differ widely in terms of their biodegradability. Thus, alkanes, alkenes, and the simpler monoaromatics are biodegraded quite readily, but the tars and resins are virtually impervious to biological attack (NRC, 1985).

A large number of microorganisms are capable of degrading petroleum hydrocarbons. Many species of bacteria, fungi, and yeasts metabolize petroleum hydrocarbons as a food energy source. As each species can utilize only a few related compounds at most, however, broad-spectrum degradation does not occur. Hydrocarbons metabolized by microorganisms are generally converted to an oxidized compound, which may be further degraded, may be soluble, or may accumulate in the remaining oil. The aquatic toxicity of the biodegradation products is sometimes greater than that of the parent compounds (Fingas, 2000).

The biodegradable portion of various crude oils ranges from 11 to 90%. A low percentage of biodegradation may result from a high amount of volatile components, for these ordinarily evaporate before significant biodegradation can take place. Low percentages of biodegradation can result also from high proportions of condensed polyaromatic, condensed cycloparaffinic, and asphaltic petroleum components, because these compounds are biodegraded at extremely slow rates if at all. Toxicity of certain petroleum components can delay or prevent the biodegradation of susceptible ones. The nature of the marine environment restricts petroleum biodegradation to the mesophilic and psychrophilic organisms. Hydrocarbon biodegradation has been reported at temperatures below 0°C (NRC, 1985).

2.2 Oil Spills

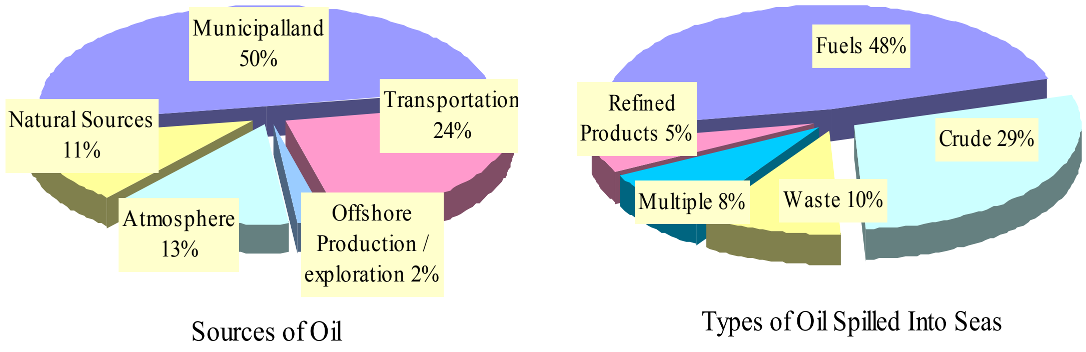
2.2.1 Oil spill statistics

The production and consumption of oil and petroleum products are increasing worldwide and the threat of oil pollution is increasing accordingly. The movement of petroleum from the oil fields to the consumer involves as many as 10-15 transfers between many different modes of transportations making the surrounding environments vulnerable to any accidental or sabotaged oil spills. The extent of vulnerability can be judged from the huge numbers of oil tankers involved in the transportation of crude oil and oil products; and amount of oil and petroleum products consumed around the world estimated to be approximately 8,000 and 10 million tonnes each day respectively (Huijer, 2005; Fingas, 2000).

The sources of oil spills, the types of oil spilled into the sea, and the causes of spills from any type of ship or vessel worldwide are shown in Figure 2.4. Half of the oil spilled in the seas is the runoff of oil and fuel from land-based sources, usually from wastewater. Much lubricating oil finds its way into wastewater, which is often discharged directly into the sea. About 24% of oil spilled into the sea comes from the transportation sector, which includes tankers, freighters, barges, and other vessels. Natural sources of oil constitute about 11% of the input. Natural sources include the many natural “seeps” or discharges from oil-bearing strata on the ocean floor that reach the surface. Atmospheric sources constitute 13% of oil pollution in the sea. This pollution is the result of hydrocarbons in the air from a variety of sources and causes such as inefficient combustion. Much of the material is re-precipitated onto land and subsequently ends up in the sea.

As shown in Figure 2.4, most oils spilled into the sea worldwide are fuels (48%) and then crude oils (29%). Fuels consist primarily of Bunker oils and intermediate fuel oils (IFO) which consist of Bunker oils mixed with fuels such as diesel. Figure 3 also shows that grounding is the leading cause of oil spills from vessels (26%), followed by collision at 22%. Some other accidental causes of oil spills are explosion / fire (9%), ramming (9%), and sinking (7%), with human error (5%) and mechanical failure (2%) causing the least number of spills (Fingas, 2000).

The Table 2.2 gives a brief summary of 20 major oil spills since 1967. The Exxon Valdez is included because it is so well known although it is not the twentieth largest spill but rather the 35th (ITOPF, 2005).



Sources of Oil

Types of Oil Spilled Into Seas

Figure 2.4: Sources of oil and types of oil spilled into seas

Table 2.2: Major Oil Spills since 1967 (ITOPF, 2005)

Position	**Shipname**	**Year**	**Location**	**Spill Size (tonnes)**
1	Atlantic Empress	1979	Off Tobago, West Indies	287,000
2	ABT Summer	1991	700 nautical miles off Angola	260,000
3	Castillo de Bellver	1983	Off Saldanha Bay, South Africa	252,000
4	Amoco Cadiz	1978	Off Brittany, France	223,000
5	Haven	1991	Genoa, Italy	144,000
6	Odyssey	1988	700 nautical miles off Nova Scotia, Canada	132,000
7	Torrey Canyon	1967	Scilly Isles, UK	119,000
8	Sea Star	1972	Gulf of Oman	115,000
9	Irenes Serenade	1980	Navarino Bay, Greece	100,000
10	Urquiola	1976	La Coruna, Spain	100,000
11	Hawaiian Patriot	1977	300 nautical miles off Honolulu	95,000
12	Independenta	1979	Bosphorus, Turkey	95,000
13	Jakob Maersk	1975	Oporto, Portugal	88,000
14	Braer	1993	Shetland Islands, UK	85,000
15	Khark 5	1989	120 nautical miles off Atlantic coast of Morocco	80,000
16	Aegean Sea	1992	La Coruna, Spain	74,000
17	Sea Empress	1996	Milford Haven, UK	72,000
18	Katina P	1992	Off Maputo, Mozambique	72,000
19	Nova	1985	Off Kharg Island, Gulf of Iran	70,000
20	Prestige	2002	Off the Spanish coast	63,000
35	Exxon Valdez	1989	Prince William Sound, Alaska, USA	37,000

Most incidents are the result of a combination of actions and circumstances, all of which contribute in varying degrees to the final outcome. It is apparent from the Table 2.3 that:

- most spills from tankers result from routine operations such as loading, discharging and bunkering which normally occur in ports or at oil terminals;
- the majority of these operational spills are small, with some 91% involving quantities of less than 7 tonnes;
- accidental causes such as collisions and groundings generally give rise to much larger spills, with at least 84% of incidents involving quantities in excess of 700 tonnes being attributed to such factors.

Table 2.3: Incidence of Spills by Cause, 1974-2005 (Adapted from ITOPF, 2005)

	> 700 tonnes	**Percentage of Spills, %**	
OPERATIONS			
Loading/discharging	30	8,7	**9,1**
Bunkering	0	0,1	
Other operations	1	0,3	
ACCIDENTS			
Groundings	118	34,4	**83,9**
Collisions	97	28,3	
Hull failures	43	12,5	
Fires & explosions	30	8,7	
Other/Unknown	24		**7**
TOTAL	**343**		**100**

Most oil tankers accidents mostly occur in narrow water passages, in rough seas and while navigating along coastlines with busy sea traffic. Tankers from oil exporting countries surrounding the Black Sea have only one exit to the Mediterranean Sea: via the Bosphorus Strait, the Sea of Marmara and the Dardanelle Strait. The Bosphorus and the Dardanelle's are typical narrow water channels and navigation route through the Sea of Marmara. This route therefore increases the risk of collisions and thus major tanker accidents (Otay, 2000).

The 19 mile long, Bosphorus is the dividing line between Asia and Europe. At its widest, the strait is 2.3 miles; but at its narrowest, it is only half a mile wide. Over 50,000 ships pass through the Bosphorus yearly, ten percent of which are oil tankers.

The Bosphorus is by far the world's most crowded waterway, three times as busy as the Suez Canal. Historically one of the most dangerous and catastrophic waterways, the strait is narrow, winding, and has a very rapid current. Due to the high traffic and dangerous passage, nearly ten ships a year fall victim to the strait and either ground themselves or collide.

Oğuzülgen (1995) identifies the reasons of these accidents due to collision, grounding and stranding and fire as follows:

- Insufficient pilotage skills
- Natural structure of the Strait
- Surface currents
- Restricted visibility
- Local conditions
- Breakdowns and technical insufficiencies

Few of the recent accidents that occurred in the Bosphorus are briefly explained as under (Turkish Maritime Pilots' Association, 2006):

M/T Independenta, Romanian flag and freighter *M/V Evriyali***,** Greek flag, collided on 15 November 1979. Almost all of the crew of the Romanian tanker, 43 crew member lost their lives. Collision caused fire and agrounded tanker's wreck affected the area for some years.

Ammonia loaded tanker *M/T Blue Star*, Panama flag, collided with a Turkish Crude Oil Carrier *M/T Gaziantep***,** which was on anchor, on 28 October 1988. Huge quantities of ammonia cargo polluted the environment.

M/T Jambur, Iraqi flag and *M/V Datton Shang*, Chinese flag bulk carrier, collided on 29 March 1990. Thousands of tons of petroleum severely polluted the whole Strait and cleaning operations were carried out for weeks.

M/V Madonna Lily, Philippines flag bulk carrier and *M/V Rabunion 18*, Lebanese flag live stock carrier, collided on 14 November 1991. Rabunion 18 sank with her cargo of 21,000 sheep.

M/T Nassia, and bulk carrier *M/V Shipbroker*, both South Cyprus flag, collided on 13 March 1994. Apart from causing a huge loss of lives, it also affected the Strait and its environment. Approximately 20,000 MIT crude oil (a considerable part of Nassia's cargo) caused severe pollution and fire that lasted 4 days and consequently traffic was suspended in the Strait for several days.

The latest major accident is the grounding and consequently breaking of Russian river tanker *Volgoneft-248* in 1999, which resulted in a major oil spill in an environmentally and historically sensitive area.

2.2.2 Compensation for pollution damage

Following the Torrey Canyon incident off the English coast in March 1967, the maritime world become aware of the need for international regimes of liability and compensation for pollution damage caused by spills of oil from tankers. At the time, there was no internationally accepted comprehensive liability and compensation regime covering spills of oil from tankers (IOPC, 2003).

The Civil Liability Convention, 1969 (CLC) applies to oil pollution damage resulting from spills from laden tankers and suffered in the territory (including the territorial sea) of a Contracting State. The only criterion for its applicability is, therefore, where the damage occurred. The flag State of the tanker and the nationality of the ship owner are irrelevant for determining the scope of application of the CLC.

Damage caused by non-persistent oil (gasoline, light diesel oil, kerosene, etc…) is not covered by the CLC.

Only spills from a tanker, which is actually carrying oil in bulk as cargo, are covered by the CLC. Spills from a tanker during a ballast voyage and spills of bunker oil from ships other than tankers are not covered.

The CLC applies only to damage caused or measures taken after incident has occurred in which oil has escaped or been discharged.

The owner of a tanker has strict liability (that is, is liable also in the absence of fault) for pollution damage caused by oil spilled from the tanker as a result of an accident. He may be exempted from liability only in a few particular cases namely when the damage results from:

- An act of war or a great natural disaster;
- Sabotage by third party;
- The failure of authorities to maintain navigational aids.

Claims for pollution damage under the CLC can be made only against the registered owner of the tanker concerned. The owner of tanker carrying more than 2,000 tonnes of persistent oil as cargo is obliged to maintain insurance to cover its liability under the CLC. Tankers must carry on board a certificate attesting the insurance coverage of the ship. When entering or leaving a port or terminal installation of a Contracting State of the CLC, such a certificate is required for ships flying the flag of a State, which is not a Contracting State of this Convention (IMO/UNEP, 1995).

The Fund Convention (FC) was elaborated in 1971 as a supplementary Convention to the CLC and the International Oil Pollution Compensation Fund (IOPC) was set up in 1978 to administer the FC. Only those States, which have become Parties to the CLC, can become members of the IOPC Fund. Persons who receive crude oil and heavy fuel oil in Fund Member States after sea transport finance the IOPC Fund.

The main functions of the FC are to provide supplementary compensation to those who cannot obtain fuel and adequate compensation for oil pollution damage under the CLC (and to indemnify the owner for a portion of his liability under that Convention) for one of following reasons:

a) No liability for pollution damage areas under the CLC (for example, because the owner can invoke one of the exemption under that Convention).

b) The owner is financially incapable of meeting his obligations under the CLC and his insurance is insufficient to satisfy the claim for composition for pollution damage.

c) The damage exceeds the owner’s liability under the CLC.

The experience of the IOPC Fund has shown that most incident fall within category c. So far, there has been no incident within category b (IOPC, 2003).

The IOPC Fund is relieved of its obligations to pay compensation if it proves that the pollution damage resulted from an act of war or if it was caused by a spill from a warship. In addition, the IOPC Fund has no obligation to pay compensation if the claimant cannot prove that the damage resulted from an incident involving one more ship. This latter case refers to spills of oil from an identified source. The IOPC Fund is also relieved of its obligation to pay indemnification if it proves that the damage resulted from the willful misconduct off the owner himself. The same applies if it proves that, as a result of the personal fault of the owner, the ship did not comply with the requirements laid down in certain International Conventions, and that the damage arose as a consequence of such non-compliance.

Spills of persistent oil from tankers are covered by two-tier compensation system. The first tier under 1992 CLC holds individual tanker owner / oil pollution liability insurer (P&I Club) legally liable to maintain oil pollution insurance and to carry certificate enabling direct action against insurer. It ensures approximately US$ 4.2 million for tanker of less than 5,000 gross tonnes and up to approximately US$ 84 million for tankers of more than 140,000 gross tonnes. Supplementary compensation (second tier) paid by 1992 Fund, financed by oil receivers in Member States may provide up to approximately US$ 189 million (including amount paid by tanker owner / insurer). These funds are provided by levies on oil companies and other entities in Fund-Member States receiving more than 150,000 tonnes per annum of crude and / or heavy fuel oil (contributing oil) after sea transport (IMO/UNEP, 1995).

The 1992 CLC and 1992 Fund Convention provide a straightforward mechanism whereby the costs of cleanup and pollution damage can be recovered on strict liability basis from the individual tanker owner and P&I Club involved in the incident and from the 1992 Fund so long as the cleanup measures taken in response to an incident and the associated costs are reasonable and the claims for compensation are well presented. Turkey is member of both the 1992 CLC and 1992 Fund Convention but is not a signee to the supplementary fund protocol (IOPC, 2003).

However, certain factors are incorporated in the assessment of claims for compensation for oil spills within the above-mentioned funds / agreements. These factors help determine the cost of oil spills. They are briefly explained as under:

- Type of oil
- Physical, biological and economic characteristics of the spill location
- Weather and sea conditions
- Amount spilled and rate of spillage
- Time of the year
- Effectiveness of cleanup

Of the various individual factors that determine the seriousness and therefore the ultimate cost of an oil spill is the type of oil.

The heavy crudes and heavy fuel oils are highly persistent when spilled due to their greater proportion of non-volatile components and high viscosity. Such oils have the potential, therefore, to travel great distances from the original spill location. Consequently, the cleanup of heavy oil spills can be extremely difficult, extend over large areas and be costly. This is illustrated by two of the most expensive tanker spills of all time- the *Erika* and *Nakhodka* off France and Japan, respectively. Both involved relatively small amounts of oil (some 17,500 tonnes in the case of the *Nakhodka* and about 20,000 tonnes in the *Erika*) spilled some distance from the coast. Severe weather impeded offshore recovery operations, allowing the highly persistent oil to spread over a large area of sea, leading eventually to extensive coastal contamination (White and Molloy, 2003).

Heavy crude, emulsified crude and heavy fuel oils, whilst generally of lower toxicity, will constitute a threat to seabirds and other wildlife (for example on shorelines) that become physically coated or smothered. Amenity areas, fishing gear, mariculture facilities and other structures can also be contaminated, sometimes over very extensive lengths of coastline due to the highly persistent nature of the oil. Further problems can arise if the already high density of the heavy oil increases further (for example due to the incorporation of sediment in coastal water) to the extent that residues sink. This can result in the prolonged contamination of the seabed, forming a reservoir for the fouling of bottom fishing gear and repeated re-oiling of cleaned amenity areas as the sunken oil is remobilized after storms. All these problems can result in extended cleanup cost and large third party damage claims for economic loss, as illustrated by the spills of heavy fuel oil cargo from the *Nakhodka* and *Erika*.

The location of a spill can have considerable bearing on the cost of an incident since it will determine the requirement for and extent of the cleanup response, as well as the degree of damage to the environment and economic resources. All oils, if they remain at sea long enough, will dissipate through natural processes. When a tanker spills oil far from the coast, the response will therefore often be confined to aerial surveillance of the slick to monitor its movement and dissipation in order to check that predictions of its probable fate are correct. The cost of responding to oil spills under these circumstances can therefore be low. This is illustrated by the fact that the three largest tanker spills of all time – *Atlantic Empress* off Tobago, West Indies in 1979 (287,000 tonnes), *Castillo De Bellver* off South Africa in 1983 (252,000 tonnes) and *Abt Summer* off Angola in 1991 (260,990 tonnes) – resulted in very low cleanup and damage costs because no significant quantities of oil reached coastlines. Had a similar volume and type of oil been spilled near a sensitive coastline (as, for example, occurred in the *Amoco Cadiz* in France in 1978), the requirement for cleanup would have been entirely different, as would have been the impact on fisheries, tourism and other sensitive economic and environmental resources. The costs would have therefore been much greater (White and Molloy, 2003).

The physical characteristics of the spill site (e.g. prevailing winds, tidal range, currents, water depth) as well as its distance from the coast are important since they have a considerable bearing on the feasibility of mounting a cleanup response at sea and a successful salvage operation. They will also in part determine the extent of shoreline contamination, which is one of the most important factors in determining costs.

Socio-economic factors and resources at risk vary both within and between countries. Some areas will be of high national or even international importance for fishing, mariculture, tourism, other industries or conservation, whereas other will only rank as locally important. Seasonal differences will also occur in the sensitivity of these resources to oil pollution and therefore the economic impact of a spill. This in turn will help determine the requirement for and extent of the cleanup (White and Molloy, 2003).

The amount of oil spilled is clearly an important factor in determining cost. Thus, given no variation in other factors, a 100,000 tonnes spill will result in far wider contamination, will require a far more extensive cleanup response, cause greater damage and result in substantially higher costs than, say, 10,000 tonnes spill. However, the relationship is not linear. Etkin (1999), who showed that the cleanup costs on a per tonne basis decreased significantly with increasing amounts of oil spilled, explored this. Thus, the relative cost of cleaning up small spills is much greater than for large spills (White and Molloy, 2003).

The existence of such a trend makes it tempting to conclude that is legitimate to calculate average costs of spills of different sizes. However, such a simplistic approach ignores the underlying complexity and inter-relation between the factors that give rise to the considerable variation in the cost of similar sized incidents, which can be several orders of magnitude. This illustrates why simple comparisons between the costs of individual spills based on the single parameter of the cost per unit of spill volume can be highly misleading. This does not necessarily prevent some people making such comparisons and using spurious extrapolations in an attempt to justify the level of claims per cleanup costs or alleged damage in a new incident.

It is often stated that shore cleanup is much more costly than offshore cleanup. This may indeed appear to be the case if costs of the two operations in a single spill are compared directly. However, such comparisons frequently take no account of the fact that offshore cleanup is almost invariably incomplete leaving the bulk of the oil to be dealt with on the shore. Thus, a fairer comparison of costs should take into account the success rate of the operations by relating the costs to the amount of oil removed. When considered on this basis it is apparent that shoreline cleanup can frequently be highly cost-effective.

Various technical factors in combination determine the actual costs of any particular incident. Simplistic comparisons between different events based on a single parameter such as quantity of oil spilled can be highly misleading. Type of oil, location of spill and the characteristics of the affected area are generally the most important technical factors influencing the cost of both cleanup and damage. However, the quality of the contingency plan and of the management and control of the actual response operations will also be crucial (White and Molloy, 2003).

Talınlı et al. (2003) calculated the compensation for heavy fuel oil spillage from the Volgoneft-248 as 20 million US$ by assuming 2000 US$ compensation charges per barrel of spilled heavy fuel considering general factors such as the type of oil, location of spill and the characteristics of the affected area. Furthermore, the calculation incorporated 31 % of total spilled oil as residual left in the environment.

For estimation of oil spill costs and damages, taking into account spill specific factors for cost benefit analysis and resource planning cost estimation models have been developed. Among these models, United States Environmental Protection

Agency’s Basic Oil Spill Cost Estimation Model (BOSCEM) is well known and has been used for analysis and estimation of oil spills (Etkin, 2004).

2.2.3 Oil spill cleanup

The economic and environmental impact of oil spills on coastal areas can be immense. Recovery of the environment from an oil spill can take many years, so there is considerable incentive to quickly cleanup these areas after a spill, but the efforts can be expensive and themselves destructive. According to the US News and World Report (May 17, 1999), the Exxon Valdez oil spill in Alaska has cost Exxon over 8 billion dollars in cleanup and litigation expenses (Page et al., 2002).

Factors that affect the type of cleanup method used include the type of oil spilled, the geology of the shoreline and rate of water flow, and the type and sensitivity of biological communities in the area. Natural processes, such as evaporation, oxidation, and biodegradation, help to clean the shoreline.

Because natural removal processes are often too slow to prevent an oil slick from reaching the shoreline, active measures to remove the slick from the water may be required. These processes include mechanically removing the oil from the open water to prevent oil from reaching shorelines and adding materials to the slick to enhance natural removal processes (Reis, 1996).

Physical methods, such as wiping with sorbent materials, pressure washing, and raking and bulldozing, can be used to assist these natural processes. Oil collected during cleanup activities must be reused or disposed off properly, using such methods as incineration or landfilling. Choosing the most effective yet potentially least damaging cleaning methods helps to ensure that the natural systems of shorelines and the recreational benefits they offer will be preserved and protected for future generations.

Damage to spill-contaminated shorelines and dangers to other threatened areas can be reduced by timely and proper use of containment and recovery equipment. Different individual methods or a combination of them may be applied for cleanup purposes depending upon the factors discussed above. Methods applied may include (USEPA, 1999b):

- Mechanical Containment
  - Booms
  - Skimmers
  - Sorbents
- Chemical and Biological Treatment
  - Dispersing agents
  - Biological agents
- In-situ Burning

Chemical and biological methods can be used in conjunction with mechanical means for containing and cleaning up oil spills. Dispersants are most useful in helping to keep oil from reaching shorelines and other sensitive habitats. Biological agents have the potential to assist recovery in sensitive areas such as shorelines, marshes, and wetlands. In-situ burning has shown the potential to be an effective cleanup method under certain circumstances. Research into these technologies continues in the hope that future oil spills can be contained and cleaned up more efficiently and effectively (USEPA, 1999b).

2.2.4 Effects of oil spills

When an oil spill occurs, many factors determine whether that spill will cause heavy, long lasting biological damage; comparatively little or no damage; or some intermediate degree of damage. Factors affecting impact of oil (NRC, 1985):

- Geographic location
- Oil dosage and impact area
- Oceanographic conditions
- Meteorological conditions
- Season
- Oil type

2.2.4.1 Effects on physical environment

A film of oil spread on the water surface, prevents air/sea exchanges necessary for marine biological cycles. Thus (IMO/UNEP, 1995);

- it diminishes the renewal of oxygen,
- it gets in the way of sunbeams, thus curbing the photosynthesis,
- it entails a rise in temperature and favours the proliferation of oxygen consuming microorganisms.

2.2.4.2 Effects on biological environment

The effects of oil on the environment are varied and complex. Some appear immediately, others over a longer period. These affect to different degrees both the animal and vegetable kingdom on and in the sea. For the biological environment, toxicity caused by oil spills may be termed as the most important factor in the cause and effect relationship. In the case of crude oils, the most volatile fractions and the aromatic compounds are the most toxic. For refined products the most harmful effects generally result from products with a low boiling point, the petrol containing tetraethyl lead is considered as the most toxic, followed by kerosene, gas-oil and fuel no.6 (or Bunker C) (IMO/UNEP, 1995). The effects on different biological species are briefly explained as under (IPIECA, 2000):

Mammals: It has been rare for whales, dolphins, seals and sea lions to be affected following a spill. Sea otters are more vulnerable because of both their way of life, and their fur structure.

Birds: Birds using the water-air interface are at risk, particularly auks and divers. Badly oiled birds usually die. Treatment requires specialist expertise and the right facilities—amateur attempts can distress the birds even more.

Recovery of populations depends either on the existence of a reservoir of young non-breeding adults from which breeding colonies can be replenished (e.g., guillemots) or a high reproductive rate (e.g., ducks). There is no evidence so far that any oil spill has permanently damaged a seabird population, but the populations of species with local distributions could be at risk in exceptional circumstances.

Fish: Eggs and larvae in shallow bays may suffer heavy mortalities under slicks, particularly if dispersants are used. Adult fish tend to swim away from oil. There is no evidence so far that any oil spill has significantly affected adult fish populations in the open sea.

Even when many larvae have been killed, this has not been subsequently detected in adult populations, possibly because the survivors had a competitive advantage (more food, and less vulnerable to predators). Adult fish in fish farm pens may be killed, or at least made unmarketable because of tainting.

There was a commonly held belief that fish are able to swim away from the oil contaminated field sites.

Invertebrates: Invertebrates include shellfish (both mollusks and crustaceans), worms of various kinds, sea urchins and corals. All these groups may suffer heavy casualties if coated with fresh crude oil. In contrast, it is quite common to see barnacles, winkles and limpets living on rocks in the presence of residual weathered oil.

Planktonic: Serious effects on plankton have not been observed in the open sea. This is probably because high reproductive rates and immigration from outside the affected area counteract short-term reductions in numbers caused by the oil.

Larger algae: Oil does not always stick to the larger algae because of their mucilaginous coating. When oil does stick to dry fronds on the shore, they can become overweight and subject to breakage by the waves. Intertidal areas denuded of algae are usually re-populated once the oil has been substantially removed. Many algae are of economic importance either directly as food, or for products such as agar. Algae cultured for this purpose lose their commercial value if tainted.

Marsh plants: Some species of plant are more susceptible to oil than others. Perennials with robust underground stems and rootstocks tend to be more resistant than annuals and shallow rooted plants. If, however, perennials such as the grass Spartina are killed, the first plants to recolonize the area are likely to be annuals such as the glasswort (Salicornia). This is because such annuals produce large numbers of tidally dispersed seeds.

Mangroves: The term ‘mangrove’ applies to several species of tree and bush. They have a variety of forms of aerial ‘breathing root’, which adapts them for living in fine, poorly oxygenated mud. They are very sensitive to oil, partly because oil films on the breathing roots inhibit the supply of oxygen to the underground root systems.

2.2.4.3. Effects on human health

Besides direct intoxication through inhaling or massive ingestion of petroleum products, the consumption of certain marine animals (fish, crustaceans, and shellfish) which have been in contact with oil can be dangerous for human health through cumulative effects.

However, most of the time, the harmful effects of pollution are felt indirectly through the economic and ecological impact (IMO/UNEP, 1995):

- Damage to biological resources: marine flora and fauna, consequently hindering certain maritime activities,
- Defacement of amenities and a blow to tourism,
- Lowering of the quality of sea water affecting its multiple beneficial usages.

Given the complexity of the marine environment, it follows that there are significant limits to the extent to which damage can be repaired by artificial means. It also follows that attempts to meticulously reinstate a damaged site will, in many cases, both be impossible and unreasonable, specially if natural recovery is likely to be rapid (Dicks, 1998).

3. TOXICOLOGY

3.1 General Information

Early scientific knowledge recognized two basic types of substances: beneficial ones (such as foods and medicines) and harmful ones (those that cause sickness or death). The latter were defined as poisons. Modern science acknowledges that such a strict division is not justified. Many chemical substances or mixtures exert a whole spectrum of activities, ranging from beneficial to neutral to lethal. Their effect depends not only on the quantity of the substance to which an organism is exposed, but also on the species and size of the organism, its nutritional status, the method of exposure, and a number of other related factors (Zakrzewski, 1991).

Toxicity is a relative property reflecting a chemical’s potential to have a harmful effect on a living organism. It is a function of the concentration and composition/properties of the chemical to which the organism is exposed and the duration of exposure. Traditionally, toxicity data have been used in comparing chemical substances or the sensitivities of different species to the same substance. Information about the biological mechanism affected and the conditions under which the toxicant is harmful are also important for this comparison. Toxicity tests are therefore used to evaluate the adverse effects of a chemical on living organisms under standardized, reproducible conditions that permit comparison with other chemicals or species tested and comparison of similar data from different laboratories (Rand, 1995).

Toxicity of a substance can be affected by many different factors, such as the pathway of exposure (is the toxin applied to the skin, ingested, inhaled, injected), the time of exposure (a brief encounter or long term), the number of exposures (a single dose or multiple doses over time), the physical form of the toxin (solid, liquid, gas), the genetic makeup of an individual, an individual's overall health, and many others (Philp, 2000).

3.1.1 Subdisciplines of toxicology

Toxicology has a broad scope. It deals with toxicity studies of chemicals used (1) in medicine for diagnostic, preventive, and therapeutic purposes, (2) in the food industry as direct and indirect additives, (3) in agriculture as pesticides, growth regulators, artificial pollinators, and animal feed additives, and (4) in the chemical industry as solvents, components, and intermediates of plastics and many other types of chemicals. It is also concerned with the health effects of metals, petroleum products, paper and pulp, toxic plants, and animal toxins (Lu and Kacew, 2002).

Because of its broad scope as well as the need to accomplish different goals, toxicology has a number of subdisciplines. If the identity of the exposed toxicant is not known, *analytical toxicology* will be called upon to identify the toxicant through analysis of body fluids, stomach contents, etc. Those engaged in *clinical toxicology* will administer antidotes, if available, to counter the specific toxicity, and take other measures to ameliorate the symptoms and hasten the elimination of the toxicant from the body. There may also be legal implications, and that will be the task of *forensic toxicology*. Intoxication may occur as a result of occupational exposure to toxicants, which is in the domain of *occupational toxicology*. The public is exposed to a variety of toxicants. The sources of these substances, their transport, degradation, and bioconcentration in the environment, and their effects on humans are dealt with in *environmental toxicology*. *Regulatory toxicology* attempts to protect the public by setting laws, regulations, and standards to limit or suspend the use of very toxic chemicals (Lu and Kacew, 2002).

Environmental toxicology is defined as the study of the fate and effects of chemicals in the environment. Although this definition would encompass toxic chemicals naturally found in the environment (i.e., animal venom, microbial and plant toxins), environmental toxicology is typically associated with the study of environmental chemicals of anthropogenic origin. Environmental toxicology can be divided into two subcategories: environmental health toxicology and ecotoxicology. Environmental health toxicology is the study of the adverse effects of environmental chemicals on human health, while ecotoxicology focuses upon the effects of environmental contaminants upon ecosystems and constituents thereof (fish, wildlife, etc.). Assessing the toxic effects of chemicals on humans involves the use of standard animal models (i.e., mouse and rat) as well as epidemiological evaluations of exposed human populations (i.e., farmers and factory workers). In contrast, ecotoxicology involves the study of the adverse effects of toxicants on numerous of organisms that compose ecosystems ranging from microorganisms to top predators. Further, comprehensive insight into the effects of chemicals in the environment requires assessments auxiliary to toxicology such as the fate of the chemical in the environment, and toxicant interactions with abiotic (nonliving) components of ecosystems (Hodgson, 2004).

Ecotoxicology and aquatic toxicology

Truhaut first coined the term ecotoxicology in 1969 as a natural extension from toxicology, the science of the effects of poisons on individual organisms, to the ecological effects of pollutants. In the broadest sense, ecotoxicology has been described as toxicity testing on one or more components of any ecosystem. This definition of ecotoxicology can be further expanded as the science of predicting effects of potentially toxic agents on natural ecosystems and non-target species (Hoffman et al., 2003).

Ecotoxicology employs ecological parameters to assess toxicity. In a more restrictive but useful sense, it can be defined as the science of assessing the effects of toxic substances on ecosystems with the goal of protecting entire ecosystems and not merely isolated components (Hoffman et al., 2003).

Aquatic toxicology is the study of the effects of toxic agents on aquatic organisms. This broad definition includes the study of the toxic effects at the cellular, individual, population, and community levels. The field of aquatic toxicology has grown out of the disciplines of water pollution biology and limnology. Aquatic toxicology studies evolved from simple tests conducted over intervals as short as a few hours to standard acute lethality tests lasting 48 or 96 hours, depending on the species. Acute toxicity tests were followed by the development of various short sublethal tests and tests with prolonged exposures such as partial life-cycle studies and full life cycle studies (Hoffman et al., 2003).

The vulnerability of the aquatic environment to chemical insult depends on several factors, including (1) physical and chemical properties of the chemical and its transformation products; (2) concentrations and total loading of the chemical entering the ecosystem; (3) duration and type of inputs (acute or chronic, intermittent spill or continuous discharge); (4) properties of the ecosystem that enable it to resist changes that could result from the presence of the chemical (e.g., pH buffering capacity of seawater dissolved organic matter concentrations) or return to its original state after the chemical is removed from the system (e.g., flushing of water from estuaries by tidal action); and (5) location of the ecosystem in relation to the release site of the chemical (Rand, 1995).

Because aquatic ecosystems involve complex interactions of physical, chemical, and biological factors, it is difficult to understand the response of a system to a chemical unless the relationships among components of the system are well defined (Rand, 1995).

3.2 Toxic Effects

Toxic effects are greatly variable in nature, potency, target organ, and mechanism of action. A better understanding of their characteristics can improve assessment of the associated health hazards. It can also facilitate the development of rational preventive and therapeutic measures. All toxic effects result from biochemical interactions between the toxicants (and/or their metabolites) and certain structures of the organism. The structure may be non-specific, such as any tissue in direct contact with corrosive chemicals. More often, it is specific, involving a particular subcellular structure. A variety of structures may be affected (Lu and Kacew, 2002).

Toxicity can be divided into the broad categories; direct and indirect. Direct toxicity results from the toxic agent acting more or less directly at sites of action and/or on organisms; indirect toxicity occurs because of the influence of changes in the chemical, physical and/or biological environment (e.g. changes in the quality and/or biological environment organisms or habitat changes and/or losses). Although most indirect toxicity on a population or community may be tracked back to direct toxicity in a particular group and species, this is not always the case. Most experimental toxicology studies have been concerned with direct toxicity to individual species. The direct toxicity information gained is then used to estimate indirect effects or interpret site-specific situations (Rand, 1995).

Certain chemicals can cause injuries at the site of first contact with an organism. These local effects can be induced by caustic substances on the gastrointestinal tract, by corrosive materials on the skin, and by irritant gases and vapors on the respiratory tract. Systemic effects result only after the toxicant has been absorbed and distributed to other parts of the body. Most toxicant exerts their main effects on one or a few organs. These organs are referred as the “target organs” of these toxicants (Lu and Kacew, 2002).

Some toxic effects are reversible and the others are irreversible. Effects may be reversible by normal repair mechanisms, such as by regeneration of damaged or lost tissue and recovery from narcosis. In many cases, effects are reversible only if the organism can escape the toxic medium and find a toxicant-free environment. Serious damage or injury to an organism may be irreversible and may eventually result in death (Rand, 1995).

Morphologic effects refer to gross and microscopic changes in the morphology of the tissues. Many of these effects, such as necrosis and neoplasia, are irreversible and serious. Functional effects usually represent reversible changes in the functions of target organs. Functions of the liver and kidney (e.g. rate of excretion of dyes) are commonly tested in toxicologic studies. Functional effects are in general reversible, whereas morphologic effects are not, and functional changes are generally detected earlier or in animals exposed to lower doses than those with morphologic changes. In addition, functional tests are valuable in following the progress of effects on target organs in long-term studies in animals and humans. However, the results are often more variable (Lu and Kacew, 2002).

Adverse or toxic effects can be produced in the laboratory or in the natural environment by acute or chronic exposure to chemicals or other potentially toxic agents. In acute exposure, organisms come in contact with the chemical delivered either in a single event or in multiple events that occur within a short period of time, generally hours to days. Acute exposures to chemicals that are rapidly absorbed generally produce immediate effects, but they may also produce delayed effects similar to those caused by chronic exposure. During chronic exposure, organisms are exposed to low concentrations of a chemical delivered either continuously or at some other periodic frequency over a long period of time (weeks, months, or years), measured in relation to the organism’s life cycle. Chronic exposure to chemicals may induce rapid, immediate effects similar to acute effects, in addition to effects that develop slowly (Rand, 1995).

3.3 Dose – Response Relationship

The graphic representation describing the response of an enzyme, organism, population, or biological community to a range of concentrations of a xenobiotic is the dose response curve. Enzyme inhibition, DNA damage, death, behavioral changes, and other responses can be described using this relationship (Landis and Yu, 1998).

Two parameters of this curve are used to describe it: (1) the concentration or dose that results in 50% of the measured effect and (2) the slope of the linear part of the curve that passes through the midpoint. Both parameters are necessary to describe accurately the relationship between chemical concentration and effect. The midpoint is commonly referred to as a LD_{50}, LC_{50}, EC_{50}, and IC_{50}. The definitions are relatively straightforward (Landis and Yu, 1998):

- **LD_{50}:** The dose that causes mortality in 50% of the organisms tested estimated by graphical or computational means.
- **LC_{50}:** The concentration that causes mortality in 50% of the organisms tested estimated by graphical or computational means.
- **EC_{50}:** The concentration that has an effect on 50% of the organisms tested estimated by graphical or computational means. Often this parameter is used for effects that are not death.
- **IC_{50}:** Inhibitory concentration that reduces the normal response of an organism by 50% estimated by graphical or computational means. Growth rates of algae, bacteria, and other organisms are often measured as an IC_{50}.

A typical dose-response curve is shown in Figure 3.1, in which the percentage of organisms or systems responding to a chemical is plotted against the dose. For many chemicals and effects there will be a dose below which no effect or response is observed. This is known as the *threshold dose*. This concept is of significance because it implies that a *no observed effect level* (NOEL) can be determined and that this value can be used to determine the safe intake for food additives and contaminants such as pesticides. Although this is generally accepted for most types of chemicals and toxic effects, for chemical carcinogens acting by a genotoxic mechanism the shape of the curve is controversial and for regulatory purposes, their effect is assumed to be a no-threshold phenomenon (Hodgson, 2004).

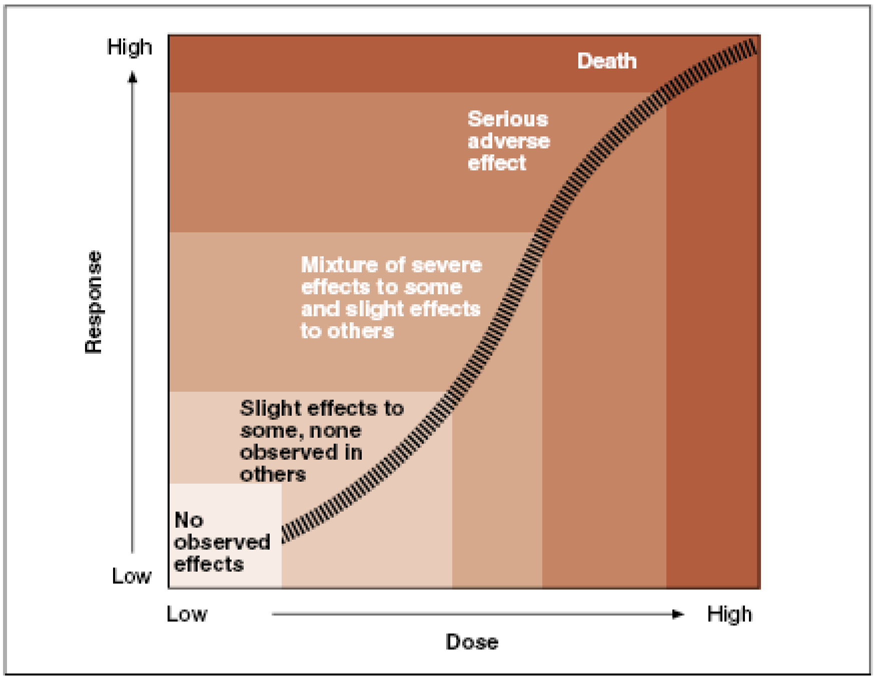


Figure 3.1: The dose response curve (Moore, 1999)

The various segments (Figure 3.1) of the curve are represented as follows (Hodgson, 2004):

Segment I. This portion of the line has no slope and is represented by those doses of the toxicant that elicited no mortality to the treated population of organisms.

Segment II. This segment represents those dosages of the toxicant that affected only the most susceptible members of the exposed population. Accordingly, these effects are elicited at low doses and only a small percentage of the dosed organisms are affected.

Segment III. This portion of the line encompasses those dosages at which most of the groups of organisms elicit some response to the toxicant. Because most of the groups of exposed organisms respond to the toxicant within this range of dosages, segment III exhibits the steepest slope among the segments.

Segment IV. This portion of the line encompasses those dosages of the toxicant that are toxic to even the most tolerant organisms in the populations. Accordingly, high dosages of the toxicant are required to affect these organisms.

Segment V. Segment V has no slope and represents those dosages at which 100% of the organisms exposed to the toxicant have been affected. A well-defined dose-response curve can then be used to calculate the LD_{50} for the toxicant.

3.4 Toxicity Tests

Microbial tests have been widely used in environmental toxicity screening procedures due to the similarity of complex biochemical functions in bacteria and higher organisms, ease of handling, short testing time and reproducibility among laboratories. In addition, the use of bioassays to evaluate toxic effects of complex mixtures of chemicals has the advantage that the influence of multiple factors such as pH, solubility, synergism/antagonism, and bioavailability are taken into account (Mowat, 2000).

An aquatic toxicity test is frequently called as a bioassay. A bioassay is performed to measure the degree of response produced by a specific level of chemical concentration. A biological assay (bioassay) is an experiment for estimating the nature, constitution, or potency of a material (or of a process), by means of the reaction that follows its application to living matter (Rand, 1995). Bioassays used in aquatic toxicology have taken a prominent position among analytical test for identifying and measuring environmental hazards. In particular, chronic toxicity tests have been developed for testing effluents, surface water, and sediment samples to estimate the safe or no effect sample concentration (Ostrander, 1996).

Almost all ecosystems are contaminated by a more or less complex mixture of chemicals from anthropogenic source; many of these are synthetic chemicals. This does not necessarily mean that all of them will trigger a biological response or possibly harmful effects. The risk of ecotoxicity increases for compounds used in large amounts that are persistent, concentrate in the abiotic and biotic matter of ecosystems, are lipophilic, and are highly active (Rand, 1995).

During the last decade, significant effort has been expended in developing rapid toxicity assays. There has been an increasing need to assess toxicity of various sample types in minutes to hours instead of days. The use of assays (such as BioTox™ assay) can speed up the toxicity identification evaluation (TIE) process considerably (Hoffman et al., 2003).

To determine the toxicity of a compound for a biological system, an observable and well-defined end effect must be identified. Turbidity or acid production, reflecting the growth or growth inhibition of a culture, may be used as an end point in bacterial systems. In some cases, such as in the study of mutagenesis, colony count may be used. Similarly, measures of viable cells, cell protein, or colony count are useful end points in cell cultures. The most readily observable end point with in vivo experiments is the death of an animal, and this is frequently used as a first step in evaluating the toxicity of a chemical. Inhibition of a cell growth or death of animals are not the only concerns of toxicology. Many other end points may be chosen, depending on the goal of the experiment. Examples of such choices are inhibition of a specific enzyme, sleeping time, occurrence of tumors, and time to the onset of an effect (Zakrzewski, 1991).

Bioassays using luminescent bacteria are routinely used to assess the acute toxicity of environmental samples. Luminescent bacteria posses several attributes that support their practical use for toxicity testing. Their small cell size provides a high surface-to-volume ratio, which maximizes exposure potential. This structural characteristic plus (1) lack of membrane-aided compartmentalization; (2) location of most respiratory pathways (including enzymes required for bioluminescence) on or near the cell membrane; and (3) a metabolic rate 10 to 100 times mammalian cells, provide a dynamic metabolic system which can be easily quantities by measuring the rate of light output. The close association of the light production pathway with the bacteria’s respiratory system provides a convenient and sensitive biological system for quantization a metabolic inhibition due to the presence of toxic chemicals (Ostrander,1996; Ren and Frymier, 2003).

Acute Toxicity Tests: These are tests designed to evaluate the relative toxicity of a chemical to selected aquatic organisms upon short-term exposure to various concentrations of test chemical. Common effect criteria for fish are mortality; for invertebrates, immobility and loss of equilibrium; and for algae, growth. These tests may be conducted for a predetermined length of (time-dependent test) to estimate the 24- or 96-h LC_{50} or the 48- or 96-h EC_{50}. An acute toxicity test may also have a duration that is not predetermined, in which case it is referred to as a *time-independent* (TI) test. In a TI test, exposure of the test organisms continues until the toxic response manifested has ceased or economic or other practical considerations dictate that the test be terminated. For example the acute T1 test should be allowed to continue until acute toxicity (mortality or a defined sublethal effect) has ceased or nearly ceased and the toxicity curve indicates that a threshold or incipient effect concentration can be estimated (Rand, 1995).

In the early development of acute toxicity tests, data were expressed as the *median tolerance limit* (TL_m or TL_{50}) the test material concentration at which 50% of the test organisms survive for a specified exposure time (usually 24-96 h). This term has been replaced by median lethal concentration (LC_{50}) and median effective concentration (EC_{50}) (Rand, 1995).

Chronic Toxicity Tests: The fact that a chemical does not have adverse effects on aquatic organisms in acute toxicity tests does not necessarily indicate that it is not toxic to these species. Chronic toxicity tests permit evaluation of the possible adverse effects of the chemical under conditions of long-term exposure at sublethal concentrations. In a full chronic toxicity test, the test organism is exposed for an entire reproductive life cycle (e.g., egg to egg) to at least five concentrations of the test material. Partial life cycle (or partial chronic) toxicity tests involve only several sensitive life stages; these include reproduction and growth during the first year but do not include exposure of very early juvenile stages. In full chronic toxicity tests, exposure is generally initiated with an egg or zygote and continues through development and hatching of the embryo, growth and development of the young organism, attainment of sexual maturity, and reproduction to produce a second-generation organism. Tests may also begin with the exposed adult and continue through egg, fry, juvenile, and adult to fertilized eggs and criteria for effect include growth, reproduction, development of gametes, maturation, spawning, success, hatching success, survival of larvae or fry, growth and survival of different life stages, and behavior. The duration of a chronic toxicity test varies with the species tested; for instance, it is approximately 21 d for the water flea *Daphina magna* and can be 275-300 d for the fathead minnow, *Pimephales promels* (Rand, 1995).

From the data obtained in partial life cycle and complete life cycles test the *maximum acceptable toxicant concentration* (MATC) can be estimated. This is the estimated threshold concentration of a chemical within a range defined by highest concentration tested at which no significant deleterious effect was observed (NOEC) and the lowest concentration tested at which some significant deleterious effect was observed (LOEC). Because it is not possible to test an unlimited number of intermediate concentrations, an MATC is generally reported as being greater than the NOEC and less then the LOEC (NOEC < MATC < LOEC; e.g., 0.5 ppm < MATC < 1.0 ppm). For regulatory purposes, the MATC is sometimes calculated as the geometric mean of the LOEC and NOEC, so it can be used as a point estimate (Rand, 1995).

Toxicity assessment is the determination of the potential of any substance to act as a poison, the conditions under which this potential will be realized, and the characterization of its action. Risk assessment, however, is a quantitative assessment of the probability of deleterious effects under given exposure conditions. Both are involved in the regulation of toxic chemicals. Regulation is the control, by statute, of the manufacture, transportation, sale, or disposal of chemicals deemed to be toxic after testing procedures or according to criteria laid down in applicable laws.

Although for a variety of reasons extrapolation from experimental animals to humans presents problems, including differences in metabolic pathways, dermal penetration, mode of action, and others, experimental animals present numerous advantages in testing procedures. These advantages include the possibility of clearly defined genetic constitution and their amenity to controlled exposure, controlled duration of exposure, and the possibility of detailed examination of all tissues following necropsy (Hodgson, 2004).

4. CASE STUDY

4.1 Technical Properties of Volgoneft-248

Volgoneft-248 was built in 1975 as a river tanker and classified by the Russian River Register. The technical properties of the vessel are given in Table 4.1 (ITOPF, 2000).

Table 4.1: Technical Properties of Volgoneft-248 (ITOPF, 2000)

Type	River Vessel
Length over all	132.6 m
Length on the waterline	128.6 m
Breadth	16.5 m
Draught	3.5 m
Depth	5.5 m
Gross tonnage	3463
Net tonnage	1039
Deadweight tonnage	4300 tonnes
Built in	1975

4.2 Details of Accident

On 29th December 1999, a severe storm with southwestern winds broke Volgoneft-248 (4,039 DWT) into two off the port of Ambarli. The storm forced the anchor to break free and the ship broke into two approximately one kilometer off the coast. The bow section of the ship sank immediately and the stern was driven aground at 100 meters off the shore. The vessel was reportedly carrying 4,365 tonnes of heavy fuel oil loaded in Bourgas, Bulgaria. The break occurred across tanks 5 and 6, and all the oil contained (1,279 tonnes) therein was spilled. The stern section with two intact tanks (7 & 8) containing 1,013 tonnes was driven aground by storm-force winds, but after re-floating in early January the oil was discharged ashore without further spillage. The bow section with four full tanks containing the balance of 2,073 tonnes sank in shallow water and settled upright on the seabed. For several weeks, small but continuous oil seepage surfaced above the sunken bow until divers were able to plug various leaks from the submerged tank vents and damaged pipe-work. Most of the oil in the bow tanks was recovered in February 2000 and transferred to the small shuttle tanker *Beste S* for delivery to the original loading port in Bulgaria. The out-turn figure for the discharge of the transferred cargo at Bourgas was 1,773 tonnes. The entire bow section was lifted from the seabed in May 2000. In light of these events, the best estimation of the total spill quantity is 1,578 tonnes (ITOPF, 2000; Otay, 2000; Moller, 2002).

Buildings, roads, fishing ports and coastal structures located in the area were heavily affected from the oil pollution. The spilled oil was carried ashore by the strong winds and waves within several hours of the accident. In the morning, at first sight, the scene of the accident exhibited an oil cover of about five kilometers of beaches, rocks and concrete platforms. The oil layer was 2-10 meters wide and five centimeters thick. Oil slicks on the sea surface could be observed (Otay, 2000).

At the low temperatures during the winter months, the oil was thick and viscous, but soon penetrated to fill the spaces between sand grains and forming sheets of stiff oil-saturated sand. Much of the oil stranded on beaches also quickly became buried underneath fresh deposits of sand, creating a layered effect. At many locations along the beach a distinct 1-3 cm layer of buried oil was found running at a depth of 3-30 centimeters under the surface (ITOPF, 2000).

The heavy fuel oil cargo had a specific gravity of 0.9914 g/cm^3 (15°C), close to that of sea water. Considerable quantities of the spilled oil became mixed with sand, mussel shells and other debris, and sank in shallow water at or near the shoreline. The largest accumulations of sunken oil were located between Güverte Restaurant and Marmara Motelleri. At Güverte, the deposit of sunken oil was found to be up to 20 centimeters thick. During subsequent episodes of strong southern winds in January, February and March, large amounts of sunken oil and oily mussel shells were cast ashore or brought to the waters edge by wave action. The most significant of these events occurred on 25-27 January. The original distribution of stranded and sunken oil is shown in Figure 4.1 (Moller, 2002).

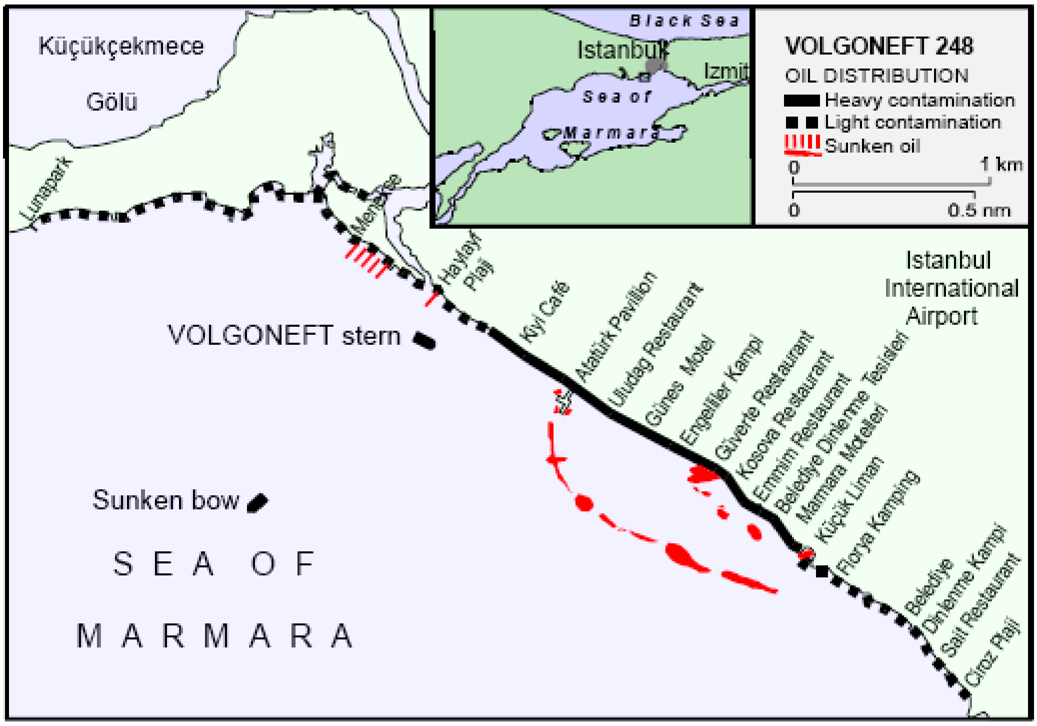


Figure 4.1: Heavy fuel oil pollution profile along the shoreline (Moller, 2002)

The environmental pollution due to an oil spill can be observed in four areas: at the sea surface, within the water column, at the sea floor, and swashed to the coast. Depending on the environmental conditions, most affected living creatures are the fish, marine mammals, planktons, and sea birds. If the oil reaches the coast, aquaculture, beaches, coastal parks and marinas are the most sensitive facilities (Otay, 2000). The oil-affected area in the Florya district is used for recreation and is backed by numerous resorts operated mainly by the Municipality of Istanbul. Several restaurants and shore side cafés were affected by the spill, as well as the Atatürk Pavilion, which is used as a summer residence for senior government officials. Many seabirds were present in the area, mainly sea gulls, ducks and cormorants. Contaminated birds encountered during the cleanup operation were generally taken for treatment at a bird cleaning station established at Istanbul University (ITOPF, 2000).

The Ministry of Environment has overall responsibility for dealing with oil pollution. Local responsibility is assigned to managers of individual ports or, in the case of spills at sea, to the Turkish Navy. Oil on shorelines would normally be dealt with by the municipalities or oil-handling installation concerned. A National Marine Pollution Contingency Plan has been developed by the Ministry of Environment, the

Under-secretariat for Maritime Affairs, the Turkish Coast Guard and the city governors. A National Contingency Plan Executive Committee has been established to co-ordinate preparedness and response. Plans for some cities, including Istanbul, have been formulated. As in previous major oil spills in Turkey, the Governor of Istanbul established a Crisis Committee to oversee the response to the Volgoneft-248 spill. The Committee included representatives of Istanbul Municipality, Ministry of Environment, Istanbul Port Authority and Istanbul University (ITOPF, 2000).

4.3 Cleanup Response

All collected oil waste was transported by trucks to Izmit Waste and Residue Treatment, Incineration and Recycling Co. Inc. (İZAYDAŞ), where the oil-rich waste was incinerated, whilst the lightly contaminated waste was deposited at a landfill site. By analyzing the calorific value of the collected waste and comparing the results with the known calorific value of the loaded cargo, it was possible to calculate the amount of fuel oil recovered which was found to be 69% of the spilled amount (Moller, 2002).

4.3.1 Shoreline cleanup response

Cleanup operations at the shore continued for more than four months. Field surveys were carried out right after the accident and at later stages of the cleanup operations to document the initial and later stages of the environmental damage on the coast and fishing ports in the area. Significant progress was observed from the initially catastrophically oil contamination at the coast. Approximately three months after the accident, a larger field program was initiated to document the contamination in the area within the scope of legal investigations related to the accident and the following oil pollution. In April and May 2000, the southern coast of Istanbul was surveyed between Yenikapı and Silivri. Site visits were concentrated on a five kilometer-long coastal strip located West of Çiroz Beach and East of Menekşe Coast where heavy contamination was found earlier (Otay, 2000).

The first priority was to remove the major accumulations of oil on beaches and concrete platforms. The work was performed manually using simple hand tools. Shovels were used to lift oil off concrete surfaces and to dig oil from beaches. The waste was stored temporarily in plastic bags (10–15 kg/bag), awaiting transportation to the disposal site. On concrete walkways, the oil was of a pasty, non-sticky consistency and easy to collect with shovels, and generally leaving remarkably little residue. Hot water washing machines were used for final cleaning of man-made surfaces.

Comparison of field observations at the day of accident and approximately three months later have shown that most of the oil contamination at the surface of beach sediments was recovered during the cleanup operations along the coastline (ITOPF, 2000).

4.3.2 Recovery of sunken oil

Considerable effort was spent recovering sunken oil from the shallows. The main areas worked were Güverte, Atatürk Pavilion and Menekşe. Workers would wade to the patches of sunken oil and remove it piece by piece spades. The oil was extremely viscous and progress was slow (ITOPF, 2000). The presence of sunken oil in shallow water and within reach of wave motion in rough weather created serious problems. Some of the observed contamination in April 2000 had signs of fresh oily marks, suggesting that oil might be still leaking from the sunken bow of the tanker. A boat trip off the Menekşe Coast on April 7th, 2000 showed oil slick concentrating on the water surface approximately one kilometer offshore. At the exact location of the sunken ship bow indicated with surface markers, oil has been observed to be rising from 30 m water depth up to the surface. After reporting the evidence to the court, the sunken half of the tanker was recovered and the oil leakage was stopped further polluting the sea (Otay, 2000).

5. MATERIALS AND METHODS

5.1 Experimental Approach

Grab samples were collected to represent sea water (SW), sediment (S) and beach sand (BS) in May 2005. The certain amount of oil was superimposed on the composite samples in order to represent the accident moment 1999. These synthetic samples (SW_s, S_s and BS_s) were incubated in 1-day, 7-day and 14-day periods to assess short-term effects in 1999 with similar conditions and to compare the differences between accident moment and performance of the cleanup operations till today. Effective Concentrations (EC_{50}) are measured and Toxicity Units (TUs) are calculated for each sample. The experimental approach of this study is shown in Figure 5.1.

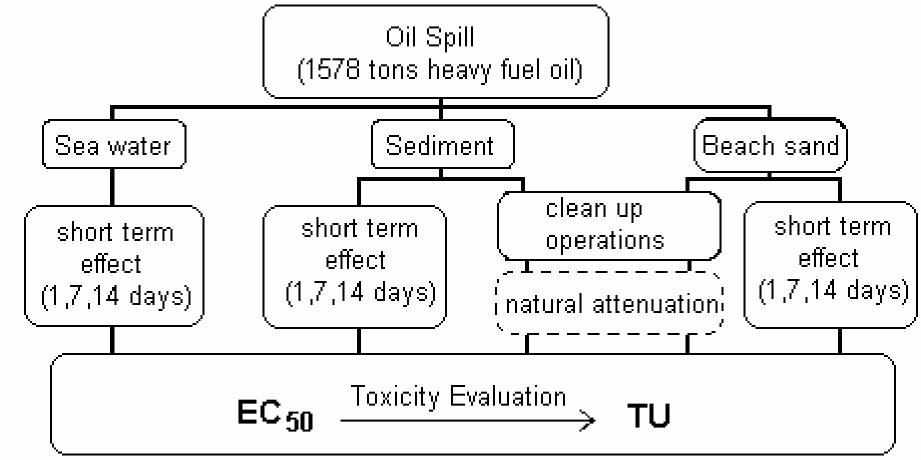


Figure 5.1: Experimental approach for designation of toxicity

5.1.1 Sample preparation

In May 2005, representative samples were taken from 3 sites for sea water (SW), sediment (S) and beach sand (BS). A diver collected sediment samples from Sites 1b, 2b and 3b. Each collected sample from sea (a), sediment (b) and beach (c) through the shoreline were transported immediately to laboratory and homogenized to prepare a composite sample for toxicity studies by BioTox^{TM}.

Shoreline pollution profile and sampling sites are given in Figure 5.2. Heavy contamination and accumulation were located between Site 1 and Site 3, which is almost 2100m long including 1000m of concrete and 1100m of beach pollution.

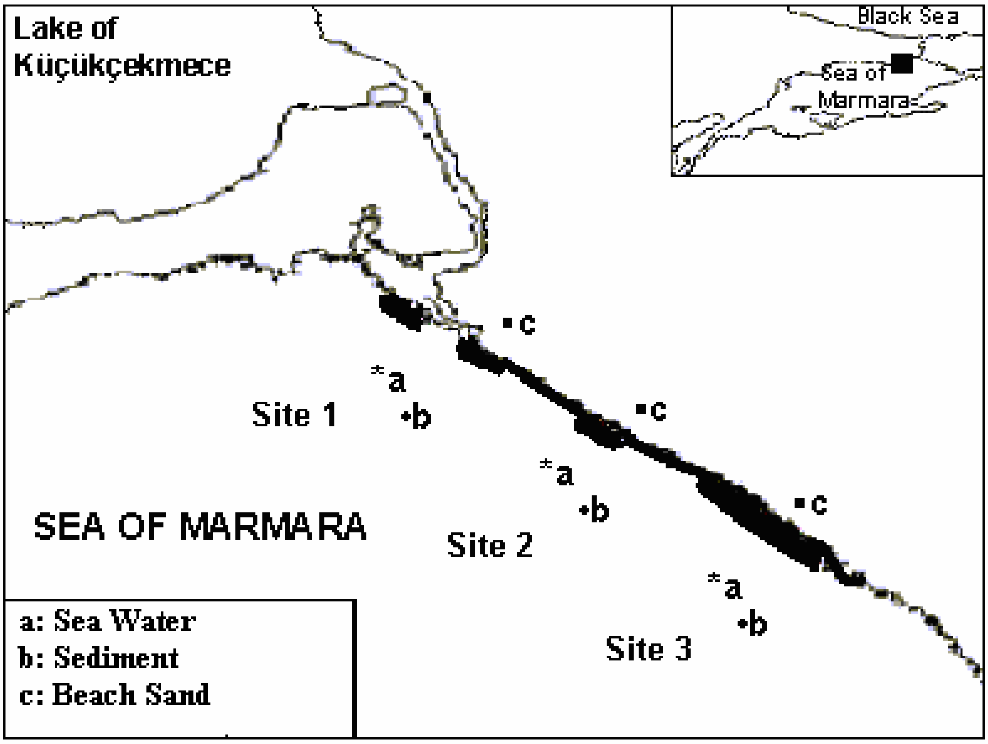


Figure 5.2: Heavy fuel oil pollution profile of the shoreline and sampling sites

For preparation of synthetic samples representative of the accident moment and conditions after that certain assumptions were made based on literature survey regarding the accident (Talınlı et al., 2005). It was assumed that:

- 1578 tonnes of heavy fuel oil spilled and 300 tonnes immediately leaked to the seabed
- 1 ton fuel oil spread in an area of 50m in diameter with film thickness of 0.1-10mm in 10 minutes on the surface of the water

- 50% fuel was emulsified in water in 1 to14 days according to a stable emulsification rate
- Oil recovery was impossible from the surface of the water due to rough weather conditions
- 1100m length, 10m width and 0.25m thickness of beach sand was contaminated with 1200 tonnes of heavy fuel oil.

All sample preparations according to assumptions given above simulating the accident moment and conditions later on are summarized in Table 5.1.

Synthetic Sample of Sea Water (SW_s) was prepared with the aim of representing the first moment of the spill on the sea surface. Assuming the formation of a 10mm film in an area of 50m in diameter by 1 ton of heavy fuel oil (d>0.95), it was calculated that 1 m^3 of heavy fuel oil forms a 5% emulsion with 20m^3 of water in first 10 minutes. Therefore, an emulsion of 5% is prepared in a constant temperature shaker by shaking it vigorously considering rough winter weather conditions. In order to represent the heavy pollution on the beach sand, Synthetic Sample of Beach Sand (BS_s) was prepared. According to the assumptions mentioned above, it is calculated that 2750m^3 of sand was contaminated by 1200m^3 of heavy fuel oil. Hence accordingly a solid mixture of 0,44L oil/kg sand proportion was incubated and the corresponding toxicities were measured. By considering 1200 m^3 of heavy fuel oil contamination to beach sand and leaching of 300 tonnes of heavy fuel oil to seabed the magnitude of superimposed oil for Synthetic Sample of the Sediment (S_s) was calculated as 0,11L oil/kg which is a ratio of 1/4 of the BS_s. Cleanup procedures applied from accident moment to 2002 were simulated at lab scale. During the cleanup operations high amount of beach sand and sediment had been collected and incinerated in a hazardous waste site until 2002 and 69% of the spilled oil had been removed. In the lab scale cleanup simulations, upper level of 10cm oiled beach sand (B_s) and oily part of dewatered sediment (S_s) were skimmed at the end of 14-day incubation period. It was attempted to simulate 69% of total oil removal from sand and sediment.

Table 5.1: Sample Preparation for Experimental Framework

Sample code	Sampling point	Incubation period	Magnitude of superimposed oil	Experimental procedure
SW	1a,2a,3a	No incubation (2005 May)	-	BioTox^{TM}
S	1b,2b,3b	No incubation (2005 May)	-	TCLP with ZHE, BSPT and then BioTox^{TM}
BS	1c,2c,3c	No incubation (2005 May)	-	TCLP with ZHE, BSPT and then BioTox^{TM}
SW$_s$	SW composite	1 day 7 days 14 days	5% of oil emulsification	Filtration and then BioTox^{TM}
S$_s$	S composite	1 day 7 days 14 days	0.1L oil/kg sediment	BSPT and then BioTox^{TM}
BS$_s$	BS composite	1 day 7 days 14 days	0.44L oil/kg sand	BSPT and then BioTox^{TM}

TCLP: Toxicity Characteristic Leaching Procedure
ZHE : Zero Headspace Extractor
BSPT: Basic Solid Phase Test

5.1.2 Toxicity analysis

BioTox^{TM} toxicity bioassay is based on the measurement of light output of the bioluminescent marine bacterium *Vibrio fischeri*. Light production is the result of a chemical reaction involving the oxidation of a substrate, generally called luciferin, mediated by a protein called luciferase in the presence of an ionic cofactor; the intensity of produced light is proportional to the amount of reagents involved in the chemical reaction. A decrease in the intensity of the light produced therefore indicates alteration of one of the events leading to light production: either the chemical reaction (e.g., configurational inactivity of reagents), the expression of genes coding for the reagents, and/or any physiological control associated with the process (Deheyn et al., 2004). Bacteria bioluminescence is intimately associated with cell respiration and any inhibition of cellular activity results in a changed rate of respiration and a corresponding change in the rate of bioluminescence. The more toxic the sample, the greater the percent light loss from the test suspension of luminescent bacteria. The inhibition of natural luminescence of bioluminescent bacteria is regarded as the toxicity endpoint. Bacterial bioluminescence has proved to be a convenient measure of cellular metabolism and consequently, a reliable sensor for measuring the presence of toxic chemicals in aquatic samples (AZUR Environmental, 1998).

EC_{50} values, defined as the concentration, which provokes a 50% light reduction on *V. fischeri* measured in the analyzer of $BioTox^{TM}$ basic test protocol, are calculated by regression analysis between toxic material concentration and light intensity ratio (ISO, 1999; Fulladosa et al., 2005). Although EC_{50} value represent a concentration of toxicity for an individual material, the obtained values based on a concentration of percent from mixtures or wastes such as oil, hazardous waste, may indicate the type of toxic interaction such as antagonistic (implying that the observed toxicity of the mixture is lower than the sum of toxicities), synergistic (implying that the observed toxicity of the mixture is higher than the sum of toxicities) or additive.

The extent of deviation from a simple additive effect generally depends on (Fulladosa et al., 2005):

1. The measured parameter,
2. The chemical nature of toxicants, and
3. The relative contribution of each toxicant to the toxicity of the mixture.

In this case, it is assumed that each material act independently to provoke the toxic effect by a specific way. For this reason and for a clearer presentation, the computed mixture toxicities must be expressed as toxicity units (TU), defined as $TU=100/EC_{50}$ (Fulladosa et al., 2005). Greater toxicity is reflected by higher TU values.

The inhibition of the luminescence was determined by combining different dilutions of the test sample with luminescent bacteria. The decrease of light intensity was measured with Aboatox 1253 luminometer after a contact time of 15 minutes. Filtered seawater was used as emulsification water for only synthetic samples and the salinity of the samples was adjusted within 2% sodium chloride by adding standard diluent solutions of the Aboatox. The pH was adjusted to 7±0.2. All samples were tested in duplicates. The inhibitory effect of dilutions was compared to a toxin free control to give the percentage inhibition. The value was plotted against the dilution factor and the resultant curve was used to calculate the EC_{50} of the sample. The standard dose-response curve method was used to determine a 50 percent loss of light in the test bacteria. The luminometer and supporting computer software with a standard log-linear model were used to calculate EC_{50} values.

The Basic Solid Phase Test (BSPT) procedure allows the test organisms to come in direct contact with the solid sample in an aqueous suspension of the test sample.

Thus, it is possible to detect toxicity, which is due to the insoluble solids that are not in solution. The BSPT was performed according to standard operating procedure (AZUR Environmental, 1998).

The BioTox^{TM} Software performs automatically all needed calculations according to the equations below.

$$KF = \frac{IC_t}{IC_0} \tag{5.1}$$

$$INH\% = 100 - \frac{IT_t}{KF \times IT_0} \times 100 \tag{5.2}$$

Where

INH % = Inhibition percentage
KF = Correction factor
IC_t = Luminescence intensity of control after control time
IC_0 = Initial luminescence intensity of control sample
IT_t = Luminescence intensity of test sample after control time
IT_0 = Initial luminescence intensity of the test sample

5.1.3 Extraction of sand and sediment samples

Oiled sand and sediment samples in solid form were extracted by both Millipore Zero Headspace Extractor (ZHE) according to Toxicity Characteristic Leaching Procedure (TCLP) given by USEPA and “Protocol for the Basic Test Using Organic Solvent Sample Solubilization” (USEPA, 1992; Azur Environmental, 1998; Johnson and Long, 1998; Lee et al., 2003).

The ZHE allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels should have an internal volume of 500 ml, and be equipped to accommodate a 90 mm diameter 0.6 µm pore sized filter.

Following the Protocol for the Basic Test Using Organic Solvent Sample Solubilization, sediment and beach sand samples were solvent extracted using dichloromethane (DCM) and acetone-dimethylsulfoxide mixture.

5.2 Theoretical Background for Compensation Analysis

An approach for the estimation of compensation costs is developed based on Toxicity Units (TUs). TUs are determined by toxicity measurements incorporating the short and long term effects of the spill. In this study, the differences of toxicity caused by spilled heavy oil and toxicity reduced by cleanup performance is postulated in terms of Toxicity Units. The acute toxicity of sea water caused due to heavy oil spill could not be measured hence the total spilled amount of heavy oil is assumed to be equivalent to the amount dispersed and recovered by cleanup from the beach sand and the sediment. The amount of heavy oil recovered and detoxified also incorporates detoxification by the natural attenuation processes.

Assumptions

For this study the compensation costs analysis is performed by making the following assumptions:

The cost of a spill is broken down under three separate cost headings namely cost of cleanup operations, the cost incurred due to natural attenuation and the cost of residual toxicity for the parameters BS_S and S_S defined earlier.

Specific parameters for such an assessment are the corresponding toxicity units (TUs) detoxified by cleanup operations TU_c, natural attenuation TU_n and the residual TU_r withheld in the system.

The compensation charges (P) is taken as monetary amount in USD for a barrel of spilled heavy oil.

It is assumed that the percentage of toxicity reduction (f) by cleanup operations is equivalent the percentage of the amount of oil removed. The cleanup efficiency is defined as the amount of heavy oil removed or recovered.

(Q) is defined as the amount of spilled oil onto the beach sand and the seabed in barrels.

The difference between the initial TU_i and final TU_f for each synthetic sample gives us the toxicity reduction (ΔTU) by the cleanup operations and the natural attenuation processes. The corresponding percentage of the toxicity reduction by cleanup is assumed as described above whereas the rest of toxicity reduction is assumed to be by natural attenuation processes. The corresponding proportion of toxicities TU_c and TU_n for cleanup and natural attenuation respectively are calculated based upon the above mentioned assumption. TU_f corresponds to the residual toxicity (TU_r) withheld in the system. The corresponding TUs contributed by each are added and total toxicity units (TU_t) is given by equation number 5.7.

Hence the toxicity fractions for cleanup operations (F_C) and natural attenuation (F_N) are defined as the ratio of toxicity units removed by the respective processes and the total amount of toxicity units. Where as (F_R) is defined as fraction of total toxicity units remaining in the environment as residue.

Furthermore a hypothetical scale between 0-1 is defined with three classes to assign a toxicity fraction coefficient (TFC) used for quantification and magnification of environmental effects in the final costs estimation. TFC is defined as a multiplicative cost factor quantifying environmental effects caused due to loss of natural assimilation capacity of the system by natural attenuation and residual toxicity into compensation costs as a consequence of an oil spillage. It is assumed:

TFC = 1 if F is between 1 and 0.5

TFC = 5 if F is between 0.5 and 0.1

TFC = 10 if F is between 0.1 and 0

It is obligatory that a minimum cleanup efficiency of 50 % is achieved and in a case where no cleanup operations are performed the toxicity fractions removed by natural attenuation and that remaining in the environment shall contribute TFC values of 5 and 10 respectively.

Justifications

The selection of TFC values of 5 and 10 for F values below 0.5 reflect the magnified effects of natural attenuation and residual toxicity in the system respectively. It is assumed that higher costs incurred upon the polluters for toxicity reduced by natural attenuation and residual in the system will dissuade them from taking for granted the assimilative capacity of environment and will encourage them to keep F value for cleanup as higher as possible to maintain a TFC value of 1 meaning higher cleanup efficiency.

Formulation

Compensation = C + N + R **(5.3)**

Where

C = Cost incurred upon by cleanup efforts (USD)
N = Cost incurred upon by natural attenuation (USD)
R = Cost incurred upon by residual damage (USD)

$C = TFC \times F_c \times Q \times P$ **(5.4)**

$N = TFC \times F_n \times Q \times P$ **(5.5)**

$R = TFC \times F_r \times Q \times P$ **(5.6)**

Where

TFC = Toxicity Fraction Coefficient corresponding to F
F_c = Cleanup fraction within Total Toxicity (TU_c / TU_t)
F_n = Natural Attenuation fraction within Total Toxicity (TU_n / TU_t)
F_r = Residual fraction within Total Toxicity (TU_r / TU_t)
Q = The amount of spilled oil as barrel
P = Compensation Charge (USD per barrel)

$TU_t = TU_c + TU_n + TU_r$ **(5.7)**

$TU_c = \Delta TU \times f$ **(5.8)**

$TU_n = \Delta TU - TU_c$ **(5.9)**

Where

TU_t = Total Toxicity
TU_c = Detoxification by Cleanup Operations in terms of TU
TU_n = Detoxification by Natural Attenuation in terms of TU
TU_r = Residual Environmental Damage in terms of TU
ΔTU = Toxicity reduction ($TU_{initial} - TU_{final}$)
f = Percentage of toxicity reduction by cleanup operations

6. RESULTS AND DISCUSSION

Toxicity data obtained from sea water, beach sand, sediment samples, and their synthetic samples are summarized in Table 6.1.

Table 6.1: BioTox^{TM} Test Results as EC_{50}

Samples	**Toxicity Unit ($100/EC_{50}$)**					
	t_{2005}[a]	$t_{1\text{-day}}$	$t_{7\text{-day}}$	$t_{14\text{-day}}$	t_{2002}[b]	Toxicity reduction (%)
SW_s	Nt[c]	Na[d]	Na	Na	-	-
BS_s	Nt	60	62	72	1.5	98
S_s	Nt	51	54	58	2.1	96

[a] TU values for t_{2005} are obtained from SW, BS, S
[b] TU values for t_{2002} are obtained from cleanup simulations of synthetic samples
[c] Non toxic
[d] Not available

6.1 Sea Water Sample

There was no detectable toxicity to the luminescent marine bacteria, *Vibrio fischeri,* on exposure to composite samples of sea water, collected in 2005 due to EC_{50} values being all bigger than 100% in the 100% test.

Application of the bioassay to sea water samples is limited due to the very low concentrations of the potential inhibitors that have to be concentrated before exposing the organisms. Similarly, the EC_{50} values from the assay for SW_s samples were not detected and most of them exhibited an enhancement of the bioluminescent intensity of *V. fischeri* possibly due to soluble nutrients naturally present in sea water. These negative toxic responses from the BioTox^{TM} test procedure showed that simple filtrations or natural emulsifications are not appropriate for insoluble materials in water such as heavy fuel oil.

An accurate determination of EC_{50} toxicity index for a particular toxicant is possible if responses of a test organism to several toxicant concentrations include values from

0% to 50% and above. When such responses are not observed, the EC_{50} is reported as a value, which is greater than the maximal tested concentration. Such expression of EC_{50} is very uncertain and limits its suitability for comparisons with toxicity values for other toxicants. This problem can be overcome by using more sensitive test organisms. The response of the given test organism can also be increased by facilitating transfer of a toxicant into water-soluble fraction (WSF). In case of petroleum products with lower solubility in water, for which a standard agitation time is not sufficient for attaining the equilibrium concentration, extending that time beyond 24h could satisfy requirements for test solutions with higher concentrations (Tsvetnenko and Evans, 2002).

6.2 Beach Sand and Sediment Samples

As with the composite samples of sea water, there was no detectable toxicity to the luminescent marine bacteria, *Vibrio fischeri,* on exposure to sediment and beach sand collected in 2005 due to EC_{50} values being all bigger than 100% in the 100% test.

BS_s and S_s samples in solid form were initially extracted by ZHE according to TCLP and then the BioTox^{TM} 100% test that quantifies the adverse effects of a serial dilution of samples on the luminescent bacteria was conducted. As none of the samples inhibited the light emission of *V. fischeri* below the 100% of reference solution and some of them stimulated the activity of bacteria, thus EC_{50} could not be calculated. As elutriates were not toxic, no more detailed tests were carried out by BioTox^{TM} basic test protocol and toxic responses were obtained by BSPT for synthetic samples for the corresponding incubation periods of 1-day, 7-days and 14-days.

Some recent studies have demonstrated that when used with fine-grained sediments, solid phase tests give results that are grain-size dependent, as a result of bacteria becoming adsorbed onto sediment particles (Campisi et.al., 2005). Assessment of the toxicity of beach sand and sediment bound contaminants therefore focused on dichloromethane (DCM) extracts of sediments.

In spite of stimulated light output on BS_s and S_s, toxicity of DCM extracts of these synthetic samples was high. Toxicity of DCM extracts of beach sand and sediments cannot necessarily be interpreted as indicating that they will have significant ecological impacts. Some contaminants that are extracted by DCM may not be bioavailable, particularly those with a high octanol-water partition coefficient K_{ow} which is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature and is used to help determine the fate of chemicals in the environment. However, the solvent extraction methods allow the processing of large numbers of samples and the use of the $\text{BioTox}^{\text{TM}}$ acute test allows rapid toxicity determination of EC_{50} values. Contaminants from a relatively large volume of solid samples can be extracted and concentrated into a small volume of dimethylsulfoxide (DMSO) by solvent exchange, as the presence of DMSO in the $\text{BioTox}^{\text{TM}}$ test has negligible effect on the measured toxicity (Johnson et.al., 2004).

Toxicity units for BS_s and S_s obtained from EC_{50} values given in Figure 6.1 and Figure 6.2 increased gradually in a weekly incubation period (Figure 6.3). The increasing toxicities may be justified from the fact that first day impacts of the oil spill may not be acutely toxic to reduce the light emission due to either it cannot be exactly emulsified or cannot be sufficiently extracted for $\text{BioTox}^{\text{TM}}$ test.

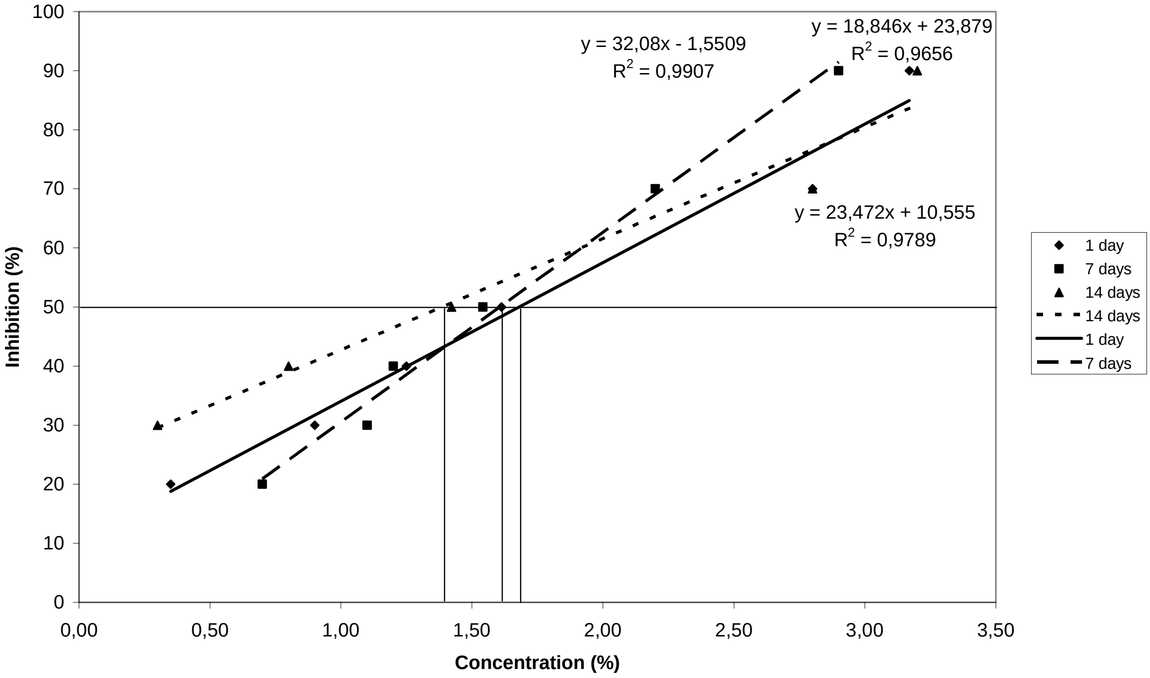


Figure 6.1: EC_{50} values for BS_s

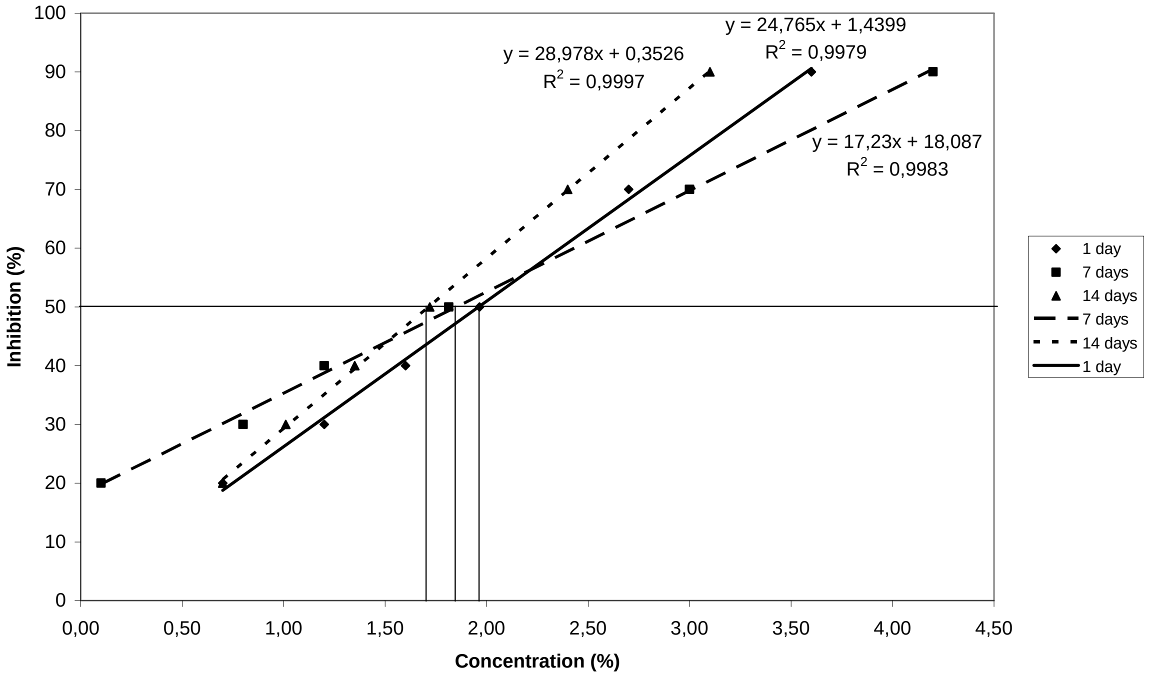


Figure 6.2: EC_{50} values for S_s

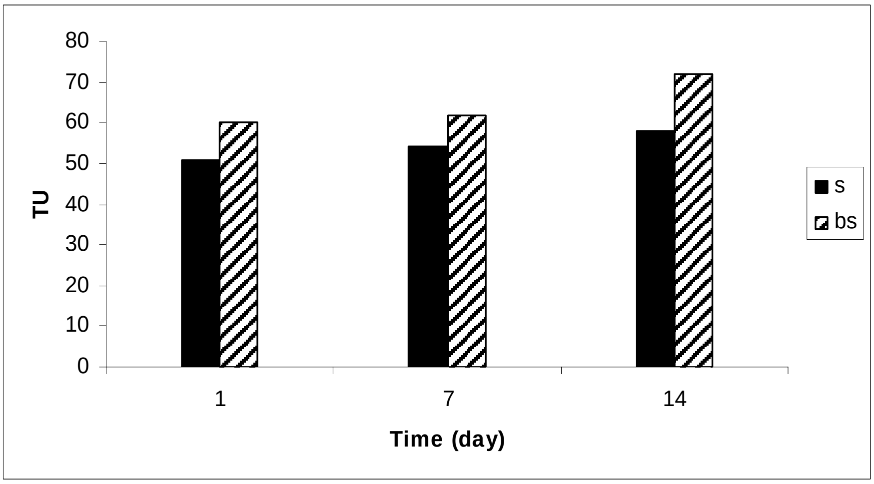


Figure 6.3: Comparison of the toxicity units for incubation periods of 1-day, 7-days and 14-days

6.3 Toxicity of Synthetic Samples after Cleanup Simulations

According to applied cleanup procedures evaluation of the toxicity was performed by BSPT for beach sand and sediment samples. Toxic units for the samples from lab scale cleanup simulations of BS_s and S_s were calculated as 1.5 and 2.1 (Figure 6.4) and for 14 days samples of BS_s and S_s decreased from 70 to 1.5 and 58 to 2.1 respectively. These significant differences represent an efficiency of the detoxification on the shoreline by applying of cleanup operations with simultaneous natural attenuation. 97% of average toxicity reduction was obtained from experimental simulations considering cleanup works in 2000-2002. In this period, excavation and incineration processes had been applied to the huge amount of oiled sand and sediment. The amount of removed oil was calculated as 69% of the total spilled oil. Natural weathering processes undoubtedly reduced the toxicity of the residual oil. Figure 6.5 shows the comparison of the toxicity units for a period of five years from the accident moment till today.

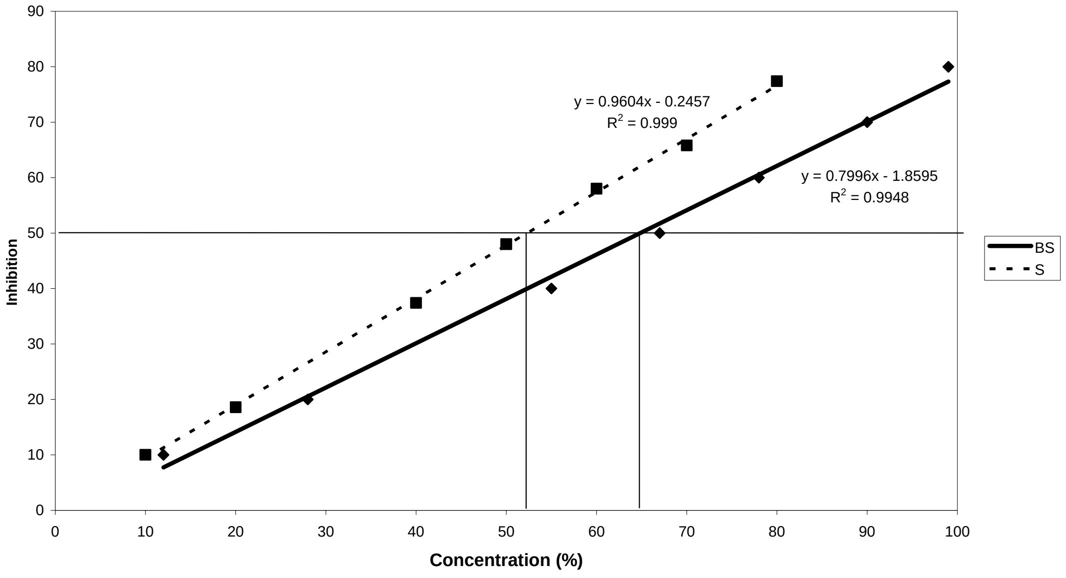


Figure 6.4: EC$_{50}$ values for BS$_s$ and S$_s$ in 2002

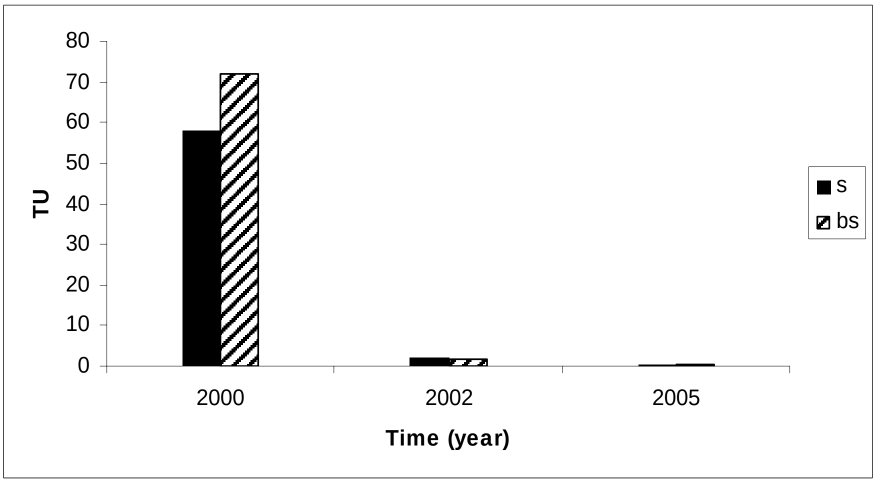


Figure 6.5: Comparison of the toxicity units for five years period

6.4 Compensation Calculations

Considering general factors such as the type of oil, location of spill and the characteristics of the affected area the compensation charges per barrel of spilled heavy fuel oil (P) is taken as 2000 USD.

The cleanup efficiency as defined in the assumptions is found to be 69% and is equivalent to the percentage of the amount of oil removed.

The amounts of spilled oil (Q) onto the beach sand and the seabed are calculated to be 7378 and 1860 barrels respectively based on assumptions defined earlier.

The toxicity units determined from experimental work corresponding to cleanup operations, natural attenuation and residue are given in Table 6.2 and Table 6.3 consists of formulation steps for the calculation of compensation costs.

Table 6.2: Calculation of Toxicity Units

	TU_i	TU_f	TU_c	TU_n	TU_r
BS	72	1.5	48.6	21.9	1.5
S	58	2.1	38.6	17.3	2.1

TU_i : Initial Toxicity Unit
TU_f : Final Toxicity Unit
TU_c : Detoxification by Cleanup Operations in terms of TU
TU_n : Detoxification by Natural Attenuation in terms of TU
TU_r : Residual Environmental Damage in terms of TU

Table 6.3: Calculation of Compensation Cost Components

	Beach Sand			Sediment		
Detoxificants	Cleanup	Natural Attenuation	Residual	Cleanup	Natural Attenuation	Residual
TU	48.6	21.9	1.5	38.6	17.3	2.1
F	0.676	0.304	0.020	0.665	0.299	0.036
TFC	1	5	10	1	5	10
Q (barrel)	7378			1860		
Cost (USD)	9,975,056	22,355,340	3,098,760	2,473,800	5,561,400	1,339,200

The TU fractions and corresponding toxicity fraction coefficients are determined for each fraction. Table 6.4 shows the summary of the total cost calculated based upon the methodology developed.

Table 6.4: Total Compensation

	C (USD)	N (USD)	R (USD)	TOTAL (USD)	
BS	9,975,056	22,355,340	3,098,760	35,429,156	**44,803,556**
S	2,473,800	5,561,400	1,339,200	9,374,400	

The total compensation amount for the accident is calculated as approximately **44.8 million USD.** From the Figure 6.6 and Figure 6.7 it can be seen that though the fractions of TUs detoxified by cleanup operations for beach sand and sediment are 0.675 and 0.665 respectively the cost incurred due to natural attenuation are much higher with TU fractions of 0.304 and 0.299 respectively. It shows a double fold increase in the amount of compensation for natural attenuation though its detoxification contribution is half of that of cleanup operations. This signifies the multiplicative effect of the coefficient TFC. The high cost equivalent of natural attenuation encourages polluters to maximize cleanup TU detoxification than to leave it for natural attenuation or as residual. Similarly, for residual TUs in the environment the comparative costs with respect to cleanup operations are higher per unit TU left in the environment as residue.

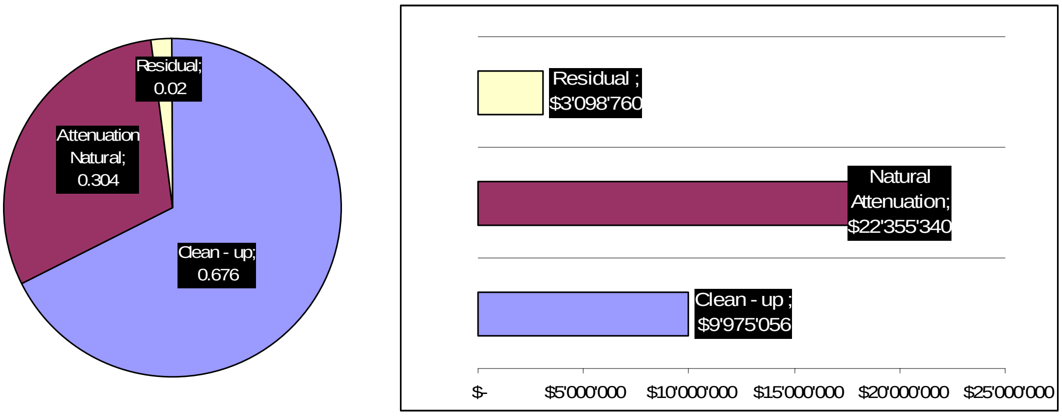


Figure 6.6: (a) Toxicity unit fractions for beach sand (b) Cost calculations for beach sand

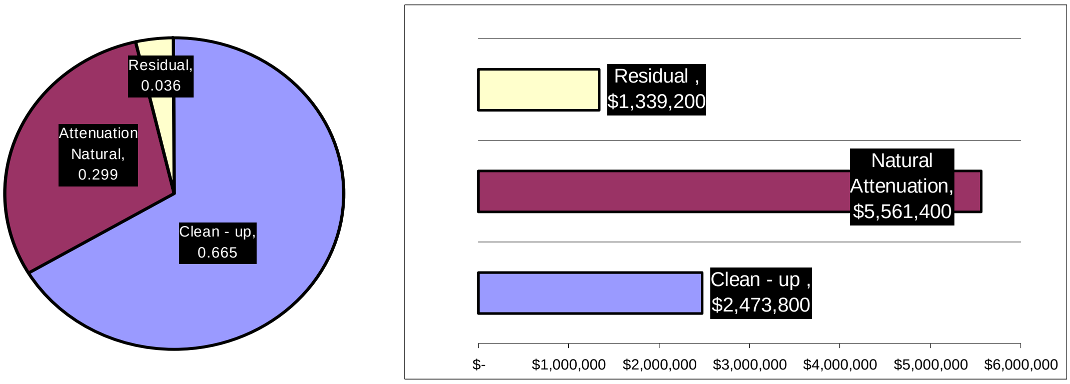


Figure 6.7: (a) Toxicity unit fractions for sediment (b) Cost calculations for sediment

7. CONCLUSIONS

Vibrio fischeri is a marine bacteria hence the bioluminescence test (BioTox™ assay) can be applied as a rapid pre-screening test for toxicity evaluation of spilled oil in the beach sand and the sediment. A picture of pollution caused by the spill can be obtained.

Heavy fuel oil cannot conjugate to toxicity in the BioTox^{TM} bioassay because of its low soluble fraction in the sea. Therefore, it can be measured by using tests based on organic extraction of sediment and beach sand. Dimethylsulfoxide (DMSO) is a solvent compatible with the BioTox^{TM} system because of its low test toxicity and its ability to solubilize a broad spectrum of non-polar organic compounds. Hence, it is concluded that BioTox^{TM} system using DMSO is a suitable method for toxicity assessment just after accident moment and during the cleanup and natural attenuation processes.

The presumption that everything has a price and that money can always compensate for the damage may not always be true. In truth, the effects to the natural environment may not be estimated in terms of amount of money specially so in an environmentally sensitive area. General compensation assessments do not include the damage costs to environment because of natural attenuation during the cleanup and heavy oil residual remaining in the environment long after the cleanup work is finished. However a methodology based upon such an evaluation needed to be developed accounting for the components of damage described above.

It has been concluded that toxicity evaluation should be used in assessment of the environmental residual damage for sensitive areas on the shoreline. In addition to estimation of the compensation based on amount of spilled oil and/or cost of cleanup operations, the detoxification fractions by cleanup operations, natural attenuation and toxic units residual in the environment may also be considered as quantitative criterion for damage cost estimations.

It is recommended to use a multiplicative compensation factor defined as Toxicity Fraction Coefficient (TFC) for natural attenuation and residual environmental damage instead of using only a subjective calculation such as $ per barrel of spilled oil. The TFC based on assumptions described in the theoretical background for compensation analysis encourages higher cleanup efficiency, which in turn will result in lower damage to environment in terms of natural attenuation and residual heavy oil thus decreasing the overall compensation amount. In the case of high contributions from natural attenuation processes in the recovery and high residual amounts in the environment will enormously increase the compensation to be paid by the polluter.

The compensation calculated from this method gives an amount equivalent to 44.8 million USD for the Volgoneft-248 accident. This amount includes the environmental cost of natural attenuation and residue remaining in the environment. Of the total amount only approximately 12.5 million USD account for the cost of cleanup operations while rest of it is compensation for the damage due to natural attenuation and residue in the environment. The cost incurred upon the polluter due to more efficient cleanup operations would have been much lesser than the magnified costs of natural attenuation and residue in the environment calculated using the Toxicity Fraction Coefficient (TFC). Therefore, to keep the costs as low as possible the polluter must increase the efficiency of the cleanup operations that in turn will reduce the stress over the environment due to natural attenuation and residue.

The use of toxicity tests for assessment of performance of cleanup operations with respect to time can be concluded from this study. Similarly, the damage to the environment in terms of natural attenuation and residue can also be effectively quantified for compensation assessment.

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